Magnetoresistance in Germanium in the Impurity Conduction Range*

G. SADASIV
Department of Physics, Purdue University, Lafayette, Indiana
(Received June 25, 1962)

In germanium samples with impurity concentrations between 5×10^{16} and 3×10^{17} per cm^3, when impurity conduction sets in, there is a temperature range in which the resistivity is characterized by an activation energy ϵ_2. The magnetoresistance in this region has been studied. It is found that the effect of a magnetic field is to change the activation energy ϵ_2 to $\epsilon_2+\alpha H^2$. The value of α depends on the nature and concentration of the impurity. The experimental results for Sb-, As-, and Ga-doped samples are presented.

1. INTRODUCTION

WHEN the temperature of a semiconductor is lowered, carriers freeze out from the conduction or valence band to localized states around impurities; the resistivity increases, and is characterized by an activation energy ϵ_1 corresponding to the ionization energy of the impurity. At still lower temperatures, when practically all the carriers are frozen out, there is still a finite conductivity through the mechanism of "impurity conduction." Impurity conduction in germanium has been extensively studied[1]; reference 1 gives a list of papers on this subject.

In what follows, terminology applicable to n-type germanium is used, with N_D as the number of majority impurities per cm^3, and N_A as the number of minority impurities per cm^3. We shall be concerned only with the case when the degree of compensation is small, of the order of 10% or less.

Impurity conduction is greatly dependent on the impurity concentration.[2-4] In distinguishing between the various regions of impurity concentration the useful parameter is d/a^*, where d is an average distance between impurities defined by the relation $\frac{4}{3}\pi d^3 N_D=1$, and a^* is the effective Bohr radius of the localized ground state of an electron. When $d>5a^*$ we have the "pure region"; when $2a^*<d<5a^*$ we have the "transition region"; and $d<2a^*$ gives the "degenerate region." The behavior of the resistivity in different regions of impurity concentration is illustrated in Fig. 1.

In the pure region impurity conduction is characterized by a single activation energy ϵ_3. The basic mechanism of conduction in this region is as follows. At low temperatures there are N_A ionized acceptors, N_A ionized donors, and N_D-N_A neutral donors. The conduction process consists of the phonon-aided tunneling of an electron from a neutral to an ionized donor. Mott[5] pointed out that an activation energy is needed for conduction because the donors are at different electrostatic potentials due to the Coulomb fields of the ionized acceptors. Theoretical treatments[6,7] based on the Mott model have proved successful in explaining the experimental results, though a few discrepancies still remain.[1]

The transition region is not well understood. After the initial freeze out of carriers there is a temperature range in which the resistivity is characterized by an activation energy ϵ_2. On going to still lower temperatures the resistivity exhibits a smaller activation energy ϵ_4. The temperature at which the transition from the ϵ_2 to the ϵ_4 region occurs decreases as the impurity concentration increases; in the case of Sb-doped samples, for instance, only the ϵ_2 region is seen down to temperatures of 1.2°K when $N_D>8\times10^{16}$ cm^{-3}. In the previous literature on this subject the smaller activation energy seen in these samples has been termed ϵ_3; since the conduction mechanism here may not be the same as in the pure region we have introduced the name ϵ_4 in place of ϵ_3.

The distinguishing feature of ϵ_2 as opposed to ϵ_3 is its strong concentration dependence. For Sb-doped germanium[2] ϵ_2 decreases from 3.6×10^{-3} eV to zero when N_D increases from 3.5×10^{16} cm^{-3} to 2×10^{17} cm^{-3}. We have measured the magnetoresistance in the ϵ_2 region for several n- and p-type samples and find that the effect of a magnetic field H is to change the activation energy ϵ_2 by an amount proportional to H^2, that is,

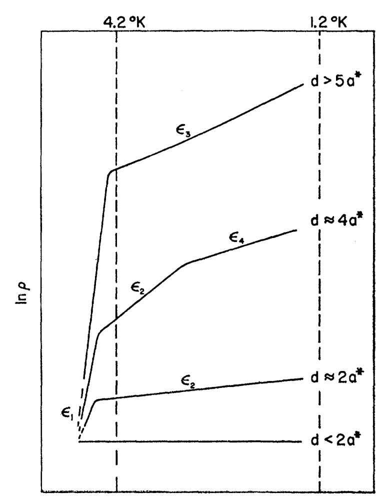

FIG. 1. The temperature dependence of the resistivity of germanium in different regions of impurity concentration, illustrating the activation energies involved.

* Work supported by a U. S. Signal Corps contract.

[1] N. F. Mott and W. D. Twose, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1961), Vol. 10, p. 107.

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

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

[4] H. Fritzsche, Phys. Rev. **125**, 1552 (1962).

[5] N. F. Mott, Can. J. Phys. **34**, 1356 (1956).

[6] T. Kasuya and S. Koide, J. Phys. Soc. Japan **13**, 1287 (1958).

[7] A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1960).

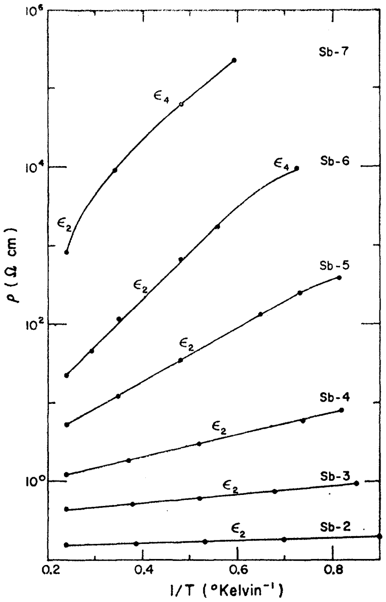

FIG. 2. Resistivity of Sb-doped samples at low temperatures.

TABLE I. Sample characteristics.

Sample	300°K $\lvert R\rvert$ ($cm^3\ C^{-1}$)	300°K ρ (Ω cm)	78°K $\lvert R\rvert$ ($cm^3\ C^{-1}$)	78°K ρ (Ω cm)	N_{maj} (cm^{-3})
Sb-1	10.48	0.00848	13.13	0.0108	5.9×10^{17}
Sb-2	44.3	0.0254	70.8	0.0247	1.4×10^{17}
Sb-3	57.4	0.0296	92.1	0.0251	1.1×10^{17}
Sb-4	76.9	0.0382	119.7	0.0293	8.1×10^{16}
Sb-5	90.9	0.0410	137.5	0.0292	6.9×10^{16}
Sb-6	106.8	0.0480	168.2	0.0305	5.9×10^{16}
Sb-7		0.0687		0.0367	3.8×10^{16}
As-1	18.9	0.0144	29.3	0.0204	3.3×10^{17}
As-2	25.8	0.0167	41.4	0.0219	2.4×10^{17}
As-3	31.1	0.0203	51.0	0.0251	2.0×10^{17}
Ga-1	8.57	0.0141	8.36	0.0133	7.3×10^{17}
Ga-2	78.0	0.0632	105.7	0.0389	8.0×10^{16}
Ga-3	90.4	0.0720	122.4	0.0403	6.9×10^{16}
Ga-4	111.0	0.0908	148.5	0.0458	5.6×10^{16}

$\Delta\epsilon_2=\alpha H^2$. The experimental results which lead to this conclusion, and the dependence of α on the concentration and nature of the impurity, are given in Sec. 3. A brief discussion of these results is presented in Sec. 4. In Sec. 5 we describe experiments performed at very low temperatures to see the transition to an ϵ_4 region for samples which have $d\approx 2a^*$.

2. SAMPLES

The characteristics of the samples at room temperature and at 78°K are given in Table I. In the case of the Ga-doped samples the values of the Hall coefficient given are those obtained with a magnetic field of about

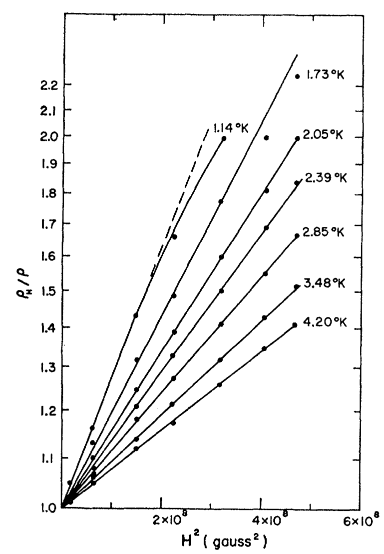

FIG. 4. Semilogarithmic plot of ρ_H/ρ vs H^2 for sample As-3.

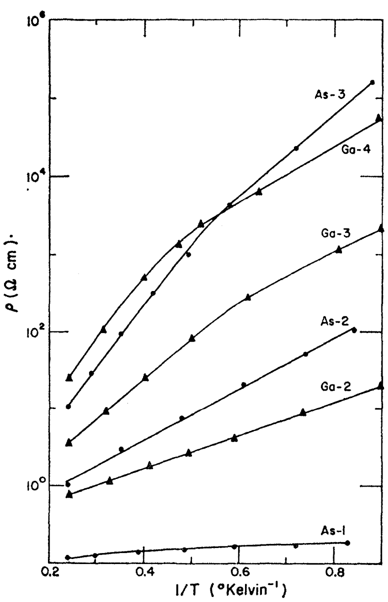

FIG. 3. Resistivity of As-doped and Ga-doped samples at low temperatures.

23 kG. The degree of compensation in the samples is estimated to be of the order of 5%. The number of majority impurities given in Table I has been calculated by setting $r=1$ in the relation $N_{maj}=r/(e|R|)$, where R is the Hall coefficient at room temperature. The absolute values of N_{maj} may have considerable error, as r may not be equal to unity; however, since we are working in a narrow region of impurity concentration r should not vary greatly, and we expect the relative values of N_{maj} for the different samples to be correct to within a few percent.

The resistivity of the Sb-doped samples at temperatures between 4.2° and 1.2°K is shown in Fig. 2. The transition from an ϵ_2 to an ϵ_4 region is seen in Sb-7, the ϵ_2 region and the beginning of an ϵ_4 region are seen in Sb-6 and Sb-5, and the other samples show only the ϵ_2 region down to 1.2°K. In Fig. 3 the resistivities of the As-doped and Ga-doped samples are shown.

Samples Sb-1 and Ga-1 are in the degenerate region. The resistivity of Sb-1 decreased from 0.0106 to 0.0102

TABLE II. The directions of current and field used in measuring magnetoresistance; the values of ρ_0, ϵ_2, and α of Eq. (2); and the average impurity separation d for the samples.

Sample	$\langle i \rangle$	$\langle H \rangle$	ρ_0 (Ω cm)	ϵ_2 (10^{-3} eV)	α (10^{-13} eV G^{-2})	d (Å)
Sb-1	001	110				74
Sb-2	001	110	0.14	0.03	0.40	119
Sb-3	011	100	0.30	0.11	1.29	129
Sb-4	001	110	0.53	0.28	2.34	143
Sb-5	001	110	0.75	0.69	3.48	151
Sb-6	001	110	0.70	1.25	4.01	160
Sb-7	001	110				184
As-2	011	$0\bar{1}1$	0.22	0.64	1.84	99
As-3	011	$0\bar{1}1$	0.12	1.52	2.64	106
Ga-1	001	110				69
Ga-2	001	110	0.23	0.43	0.87	144
Ga-3	001	110	0.21	0.58	1.17	151
Ga-4	001	110				162

Ω cm on going from 4.2 to 1.2°K; the resistivity of Ga-1 remained constant at 0.0134 Ω cm. Sample As-1 was not quite degenerate, showing a slight increase in resistivity as the temperature was lowered, but there was no clear activation energy seen in this range of temperature.

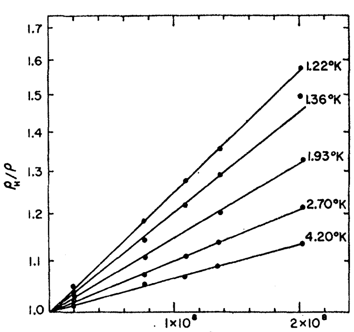

FIG. 5. Semilogarithmic plot of ρ_H/ρ vs H^2 for sample Sb-4

3. EXPERIMENTAL RESULTS

The transverse magnetoresistance of the samples was measured as a function of magnetic field at different temperatures between 4.2 and 1.2°K. The field and current directions are given in Table II. During the course of these experiments different magnets were used, and the range of fields over which the measurements were made is not the same for different samples. In the case of samples Sb-1, 2, 3, and 4 the maximum field was 14.2 kG; for samples Sb-5, 6, 7, As-1, and 2 it was 11.4 kG; and for the rest of the samples it was about 23 kG.

In the ϵ_2 region the resistivity is given by

$$\rho = \rho_0 \exp(\epsilon_2/kT). \quad (1)$$

We denote the resistivity in a magnetic field H by ρ_H. The experimental data for samples As-3 and Sb-4 are given in Figs. 4 and 5, respectively. Here we have shown ρ_H/ρ as a function of H^2 on a semilogarithmic plot, the temperature being the parameter for the family of curves. It can be seen from the figures that $\ln(\rho_H/\rho)$ is

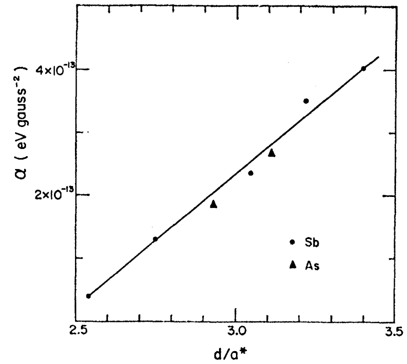

FIG. 6. α vs d/a^* for Sb-doped and As-doped samples. The value of $a_{Sb}^* = 47$ Å, and of $a_{As}^* = 34$ Å.

proportional to H^2; and further, that the constant of proportionality varies inversely as the temperature. Thus, the experimental results show that ρ_H obeys the relation

$$\rho_H = \rho_0 \exp[(\epsilon_2 + \alpha H^2)/kT], \quad (2)$$

that is, the effect of a magnetic field is to change the activation energy ϵ_2 to $\epsilon_2 + \alpha H^2$. All the samples show similar behavior in the ϵ_2 region; the values of ρ_0, ϵ_2, and α for the different samples are given in Table II. It should be mentioned that Sb-2 showed a small negative magnetoresistance, about a half-percent change in resistivity, in a field of 4500 G; in higher fields the behavior was approximately given by Eq. (2). This sample has N_D equal to 1.4×10^{17}, and is almost in the degenerate region.

The value of α increases as d increases. Figure 6 shows the dependence of α on d/a^* for the n-type samples. The values of a^* for Sb and As impurities have been taken as 47 and 34 Å, respectively, these being calculated from the observed optical ionization energies 0.0098 and 0.0135 eV.[8] From the figure it seems that the behavior of Sb and As impurities can be normalized by using the parameter a^*. For n-type impurities the use of a

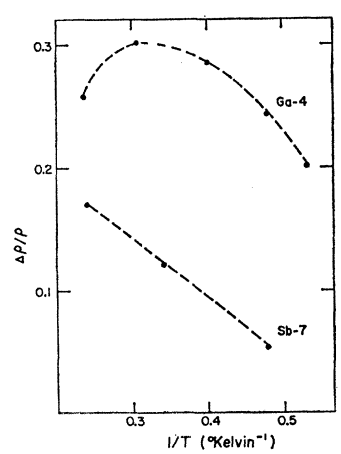

FIG. 7. $\Delta\rho/\rho$ at 23.4 kG for sample Ga-4, and $\Delta\rho/\rho$ at 11.4 kG for sample Sb-7. The ratio decreases when the transition to an ϵ_4 region occurs.

[8] P. Fisher (private communication).

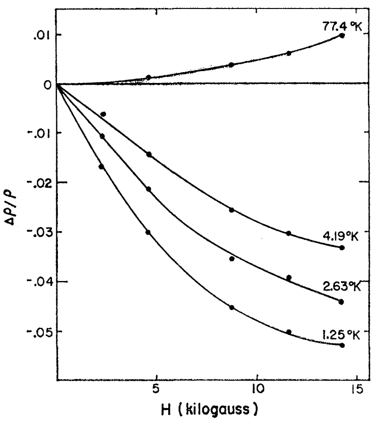

FIG. 8. $\Delta\rho/\rho$ vs H for the degenerate sample Sb-1.

single parameter to describe the ground-state wave function of a localized carrier is not a bad approximation. In the case of p-type impurities like Ga, the radial wave function for the ground state is not hydrogen-like,[9] and comparison with n-type impurities is not possible.

Samples Sb-7 and Ga-4 show a transition from the ϵ_2 to the ϵ_4 region; their mangetoresistance behavior is complicated. Figure 7 shows the values of $\Delta\rho/\rho$ at 23.4 kG as a function of $1/T$ for sample Ga-4, and the values of $\Delta\rho/\rho$ at 11.4 kG for Sb-7. The magnetoresistance ratio decreases when the transition to an ϵ_4 region occurs. The field dependence varied at different temperatures, in general, $\Delta\rho/\rho$ increased more rapidly than H^2. Similar behavior has been seen in purer samples by Sladek and Keyes.[10]

Only two degenerate samples have been studied, one Sb doped and the other Ga doped. Sample Sb-1 showed a positive magnetoresistance at 78°K, and the value of $\Delta\rho/\rho$ was proportional to H^2. At low temperatures the magnetoresistance was negative. The results are shown in Fig. 8. Similar behavior in Sb-doped samples has been reported previously.[11] Sample Ga-1, at 78°K, also showed a positive magnetoresistance ratio which was proportional to H^2. At low temperatures, however, the behavior was different from that of Sb-1, $\Delta\rho/\rho$ was positive and varied approximately linearly with H. The results are shown in Fig. 9.

4. DISCUSSION OF ϵ_2 AND α

Since the value of ϵ_2 is strongly dependent on d/a^*, any change in a^* might be expected to produce a change in ϵ_2. The effect of a magnetic field on the hydrogen-like ground-state wave function has been discussed by Csavinszky[12] and by Miller.[13] The dominant term in the interaction is the one quadratic in H. For this term Miller finds that

$$a_H^* = a^*[1-\tfrac{1}{2}(\kappa a^{*3}/m^*c^2)H^2] \qquad (3)$$

where a_H^* is the effective Bohr radius in a magnetic field H, and κ is the dielectric constant. If we assume that ϵ_2 depends only on the value of d/a^* the dependence of ϵ_2 on the magnetic field can be calculated. The results of such an analysis show that ϵ_2 should increase with magnetic field, and the change should be proportional to H^2. The calculated values of α, however, are smaller than the observed values. An order of magnitude calculation made by setting $a^*=47$ Å, $m^*=0.2\,m$, $\kappa=16$, and using the experimental values of ϵ_2 for Sb-4, 5, and 6 to get the variation of ϵ_2 with d/a^*, gives a value of α in this region of the order of 5×10^{-14} eV G^{-2}. The observed values of α, which are given in Table II, are of the order of 3×10^{-13} eV G^{-2}. The results indicate that Eq. (3) underestimates the effect of a magnetic field. This might be due to the fact that the expression has been derived for the case of isolated donors, and in the transition region of impurity concentration the interaction between neighboring donors cannot be neglected.

That the hydrogenic model of isolated donors underestimates the effect of a magnetic field is also suggested by the experimental data on the magnetic susceptibility of the extrinsic electrons. Damon and Gerritsen[14] have measured the susceptibility χ_e for Sb and As impurities in germanium. They find that between 4.2 and 1.2°K χ_e is negative and temperature independent. For Sb-doped samples with impurity concentration between 8×10^{16} and 1.8×10^{17} cm^{-3} the susceptibility per impurity increases slightly as N_D increases, and is about -1.8×10^{-13} eV G^{-2}. The calculated value using the hydrogenic model is -0.9×10^{-13} eV G^{-2}. They also find that the behavior of Sb and As impurities can be normalized by plotting χ_e as a function of d/a^*. The value of a_{Sb}^*/a_{As}^* which they use is 1.32; the value of a_{Sb}^*/a_{As}^* which normalizes the behavior of α is nearly the same, being 1.38. A better understanding of the mechanism which gives rise to ϵ_2 is necessary before we can make a quantitative comparison between the results of the susceptibility and magnetoresistance measurements.

Fritzsche has made piezoresistance measurements in the ϵ_2 region, and analyzed his results in terms of the effect of stress on the ground-state wave function.[4,15]

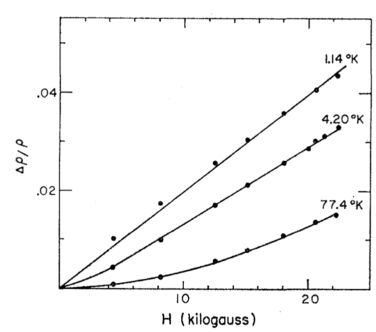

FIG. 9. $\Delta\rho/\rho$ vs H for the degenerate sample Ga-1.

[9] K. S. Mendelson (private communication).
[10] R. J. Sladek and R. W. Keyes, Phys. Rev. 122, 437 (1961).
[11] W. Sasaki and R. de Bruyn Ouboter, Physica 27, 877 (1961).
[12] P. Csavinszky, Phys. Rev. 119, 1605 (1960).
[13] A. Miller, thesis, Rutgers University, 1960 (unpublished).
[14] D. H. Damon and A. N. Gerritsen, Phys. Rev. 127, 405 (1962).
[15] H. Fritzsche, Phys. Rev. 125, 1560 (1962).

The experiments show that the effect of a compression along the [111] direction is to increase ϵ_2 for Sb-doped samples, and to decrease ϵ_2 for As-doped samples. From this he concludes that the effect of stress is to decrease the overlap between the wave functions of electrons localized on neighboring donors in the case of Sb impurities, whereas it increases the overlap in the case of As impurities. The mechanism by which this might come about is discussed in reference 15.

5. MEASUREMENTS AT VERY LOW TEMPERATURES

In the purer samples, when the temperature is lowered there is a transition from an ϵ_2 region to one in which the resistivity exhibits a smaller activation energy ϵ_4. The magnetoresistance in the more impure samples indicates that the single activation energy seen down to 1.2°K is to be identified with ϵ_2. It would therefore be of interest to measure the resistivity at still lower temperatures for these samples to see if there was a transition to an ϵ_4 region. These measurements were made with an adiabatic demagnetization cryostat. Powdered potassium chrome alum, or chromium methylammonium alum, mixed with glycerine was used as the coolant. The electrical connections to the sample were made through copper strips imbedded in the salt pill, and these served also as thermal contacts between salt and sample. The glycerine was used to give thermal contact between the salt and the copper strips. The mutual inductance between coils wound around the salt pill was measured and the temperature calculated from the relation $M=A+B/(T-\Theta-b)$. Here M is the mutual inductance; Θ is the Curie-Weiss constant of the salt, the values of Θ used being those suggested by Durieux[16]; b is the demagnetization correction for the shape of the salt pill; and A and B are constants determined from measurements between 4.2 and 1.2°K.

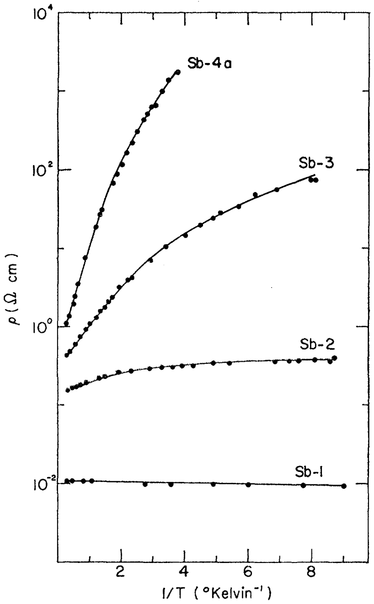

FIG. 10. Resistivity at very low temperatures for Sb-doped samples.

Resistance measurements were made with different currents flowing through the sample to check that there was adequate thermal contact between it and the salt. The measurements were made on Sb-1, 2, 3, and Sb-4a, a sample which had room temperature characteristics close to those of Sb-4. The results are shown in Fig. 10. We see that there is indeed a transition to an ϵ_4 region in the nondegenerate samples.

At the moment we have no idea about the mechanism of conduction in the ϵ_4 region; a clearer understanding of the ϵ_2 region might throw some light on this problem.

ACKNOWLEDGMENT

The author is grateful to Miss Louise Roth for growing the crystals used in these experiments.

[16] M. Durieux, thesis, University of Leiden, Leiden, The Netherlands, 1960 (unpublished).