Electrical Properties of Germanium Semiconductors at Low Temperatures*

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Low-temperature anomalies in the Hall coefficient and electrical resistivity—a steep maximum and a change of the slope of the log resistivity *versus* $1/T$ curve in germanium semiconductors—which were first observed by Hung and Gliessman, have been reinvestigated at temperatures between 1.5°K and 300°K using single crystals of *n*- and *p*-type germanium of various impurity concentrations. The influence of contacts and of various surface treatments has been studied. It was found that the effects observed cannot be explained by surface conduction. To exclude electrical field effects at low temperatures, fields well below the breakdown field have been used. The Hall coefficient was measured with magnetic fields ranging from 100 to 3500 gauss. Measurements on crystals cut in different crystal orientations show that the anomalies cannot be due to directional effects. In the same temperature region where the Hall effect and resistivity become anomalous, the magnetoresistive ratio also shows a drastic change. Throughout the whole temperature range the sample type, *n* or *p*, is retained. The results indicate that in order to describe the observations it seems necessary to assume conduction in at least two bands, the regular conduction band (valence band in the case of *p*-type material) and one band with a very small mobility. Hung's model of impurity band conduction has to be refined considerably or altered to account for the complicated behavior of germanium samples with impurity contents between 2×10^{16} and 7×10^{16} acceptors/cc or between 3×10^{16} and 1×10^{17} donors/cc.

INTRODUCTION

SINCE the discovery of low-temperature anomalies in the Hall effect and electrical resistivity of germanium semiconductors by Hung in 1950,[1] the question of the accuracy of the experimental results and of alternate explanations to the one given by Hung[2] has been discussed.

The observations of Hung[1,3,4] can be summarized: with decreasing temperature the resistivity and Hall coefficient first increase exponentially, as expected from the usual theory of semiconductors, but at a certain temperature the Hall coefficient reaches a maximum value and then decreases sharply by orders of magnitude. In the temperature range of the Hall maximum the resistivity seems to reach a saturation value. With increasing concentration of impurity atoms in the germanium, the onset of the anomalies shifts to higher temperatures and the Hall maximum as well as the low-temperature resistivity decrease rapidly.

For the explanation of these results Hung[2] postulated that conduction in an impurity band is the dominating process at the low temperatures.

By assuming that at low temperatures the number of carriers in the impurity band is equal to the number of carriers in the conduction band observed at higher temperatures, in the exhaustion range, and that the mobility in the impurity band is extremely small compared to the ordinary mobility in the conduction band, Hung obtained reasonable agreement with the experiments.

Although the conduction properties of an impurity band have been discussed by several authors,[5] a detailed theory has not been worked out so far.

The probability of a charge exchange from occupied to unoccupied impurity atoms decreases very rapidly with increasing distance between the impurity atoms. It, therefore, is very difficult to explain the formation of a band with impurity concentrations of the order of 10^{15}/cc, which corresponds to an average impurity separation of about 500 atomic distances.

Before developing such a theory, one should first investigate whether the irregular behavior of the Hall coefficient and the resistivity of germanium at these low temperatures might be caused by some other effects which have been overlooked in previous measurements.

For this reason, Lark-Horovitz suggested a reinvestigation of germanium using the most recent methods of purification and extending the range of observation to about 1.5°K by use of more sensitive detecting devices.

This paper reports experiments which were performed to study the effects of surface treatment, of different kinds of contacts and of the electric and magnetic field strength on the low temperature anomalies. The germanium samples were cut in different crystallographic orientations to investigate whether the anisotropy of the constant energy surfaces might give rise to the observed anomalies.

Measurements of resistivity, Hall coefficient, and magnetoresistive ratio on a large number of germanium samples containing various amounts of impurities are reported. The extent of agreement with the proposed models of impurity band conduction is discussed.

EXPERIMENTAL PROCEDURE

Preparation of Samples

The germanium crystals were grown by Miss L. Roth of this laboratory. The germanium was first purified

* Work supported by U. S. Signal Corps Contract. Based partly on Ph.D. thesis at Purdue University.
[1] C. S. Hung and J. R. Gliessman, Phys. Rev. **79**, 726 (1950).
[2] C. S. Hung, Phys. Rev. **79**, 727 (1950).
[3] C. S. Hung and J. R. Gliessman, Phys. Rev. **96**, 1226 (1954).
[4] H. Fritzsche and K. Lark-Horovitz, Physica **20**, 834 (1954).
[5] B. Gudden and W. Schottky, Z. tech. Phys. **16**, 323 (1935); W. Schottky, Z. Elektrochem. **45**, 33 (1939); G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946); H. M. James and A. S. Ginzbarg, J. Phys. Chem. **57**, 840 (1953); C. Erginsoy, Phys. Rev. **80**, 1104 (1950), also Phys. Rev. **88**, 893 (1952); X. Baltensperger, Phil. Mag. **44**, 1355 (1953); P. Aigrain, Physica **20**, 978 (1954).

either by repeated pulling of single crystals or by the method of zone refining until it contained less than 10^{13} impurity atoms per cc. This starting material was n-type and had a resistivity of about 40 ohm-cm at room temperature. P-type germanium with the desired concentration of impurity atoms was obtained by doping this starting material with an appropriate amount of indium or gallium and drawing a new single crystal. For n-type germanium the doping material was antimony which was zone-refined until spectroscopically pure.

The crystal orientation was determined in the Purdue x-ray laboratory by I. G. Geib and J. Radavich. Some indium-doped samples used originate from older melts and were found to consist of several crystals.

The samples cut from the crystals normal to the gradient of the impurity concentration were of about 1.5 cm in length, 0.3 cm in width, and 0.08 cm in thickness. The sample surfaces were either ground with No. 600 carborundum or etched with CP4 etching solution. For some experiments the surface was electro-polished by using the germanium as cathode and platinum wire as anode. The electrolyte was diluted chemically pure HCl.

Teflon-insulated 0.003-in copper wires were attached to the sides of the sample with Cerroseal-35 solder to serve as current and potential leads in the usual arrangement as described before.[3]

All samples were found to be electrically homogeneous at room temperature by measuring the potential distri-

TABLE I. R and ρ at 298°K and at 78°K and the crystal orientation of the samples.

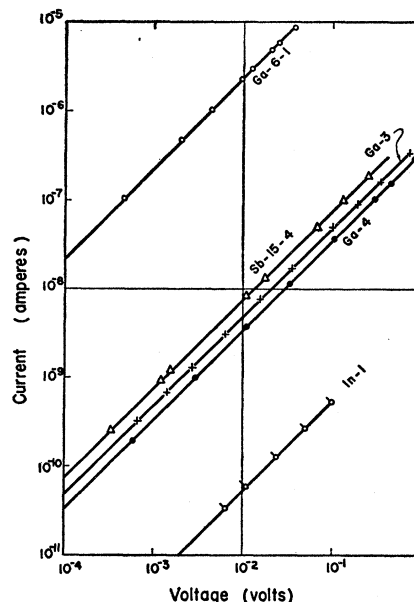| Sample code number	298°K R cm³ coul⁻¹	ρ ohm cm	78°K R cm³ coul⁻¹	ρ ohm cm	Crystal orientation of Current flow I	Mag. field H
In-1	15 300	4.40	11 600	0.48	a	a
In-2	4900	1.69	4590	0.306	(110)	(100)
In-3	281	0.171	320	0.070	polycrystalline	
In-4	165	0.0932	225	0.0488	polycrystalline	
In-5	79.2	0.0785	130	0.054	polycrystalline	
Ga-1	3180	1.055	2570	0.140	(100)	(110)
Ga-2	2360	0.809	1900	0.115	(100)	(110)
Ga-3	1850	0.620	1640	0.098	(100)	(110)
Ga-4	1350	0.494	1220	0.0883	(100)	(110)
Ga-5	940	0.375	850	0.0754	(100)	(110)
Ga-6	450	0.190	420	0.0568	(100)	(110)
Ga-7	230	0.090	300	0.044	(100)	(110)
Ga-4-1	380	0.174	420	0.0545	(211)	b
Ga-4-2	240	0.1186	282	0.0494	(211)	b
Ga-4-3	176	0.0965	224	0.0439	(211)	b
Ga-4-4	120	0.0755	160	0.0423	(211)	b
Ga-6-1	215	0.1106	270	0.0459	(101)	(100)
Ga-7-1	170	0.0938	223	0.0445	(100)	(110)
Sb-15-1	−985	0.281	−1130	0.0746	(100)	(010)
Sb-15-2	−1000	0.290	−1150	0.0755	(110)	(010)
Sb-15-3	−770	0.245	−935	0.066	(110)	(010)
Sb-15-4	−860	0.252	−955	0.070	(110)	(101)
Sb-19-1	−205	0.0695	−295	0.0356	(110)	(100)
Sb-19-2	−128	0.0508	−191	0.0350	(110)	(100)
Sb-19-3	−66	0.0284	−110	0.0251	(110)	(100)

a No prominent orientation.
b 26° off (111).

FIG. 1. Current as a function of applied voltage at $T=4.2$°K. A voltage of 1 volt corresponds to a field of about 2 volts/cm.

bution along the surface with the aid of a movable point contact probe.

Apparatus

The cryostat and the electrical measuring circuit used have been described before.[3] Few alterations assured a more stable temperature control and a higher insulation resistance for the electrical leads.

For sample resistances larger than 10^5 ohms a vibrating reed electrometer made by the Applied Physics Corporation is used as zero indicating instrument, in order to increase the input impedance of the voltage reading circuit. The voltages to be measured are applied directly to the vibrating condenser and the compensating voltage from a type K-2 potentiometer is used as bias for the amplifying circuit. The current flowing into the electrometer from the sample circuit is smaller than 10^{-16} ampere.

EXPERIMENTAL RESULTS

The samples which were investigated are listed in Table I. The sample code number indicates the doping element, Ga, In, or Sb.

The Hall coefficient and resistivity at 298°K and 78°K of the samples investigated are listed in columns 2, 3 and in columns 4, 5, respectively. The last two columns give the crystallographic orientations of the current flow I and the directions of the magnetic field H.

Ohmic Behavior and Surface Effects

If the applied electric field is high enough, the charge carriers may gain enough energy between two collisions
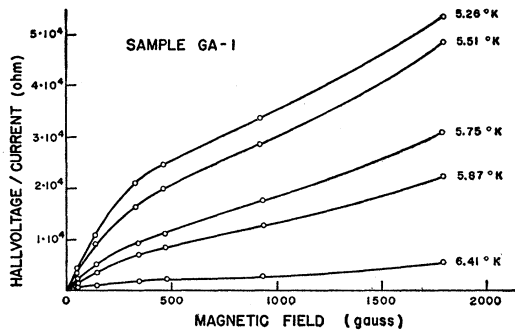
FIG. 2. Hall voltage/current as a function of magnetic field strength at temperatures above that of the maximum in the Hall curve.

to ionize neutral impurities and thus produce an avalanche excitation of carriers. This increase in carrier concentration would cause the Hall coefficient to drop sharply, as is observed and thus might explain[6] the anomalous phenomena. In this case, one would expect the resistivity to depend strongly on electric field strength.

Figure 1 shows the current-voltage relation of several samples (n-type and p-type) at 4.2°K. The resistivity is ohmic in the voltage range used. Special care was taken in the lower temperature range, which was extended down to about 1.5°K and for some samples down to 1.2°K.

No field dependence of the resistivity was observed at any temperature between fields of 10^{-3} volt/cm and 0.5 volt/cm which have been used. One, therefore, has to discard this explanation.

It has been reported before[4] that no errors seem to be introduced by soldering voltage probes directly to the germanium sample. This technique of attaching probes was used throughout all measurements.

To study the effect of surface treatment, ground, etched, and electropolished samples with various ratios of volume to surface area and different recombination rates have been compared. The results[4] show that measurements on etched germanium samples yield the
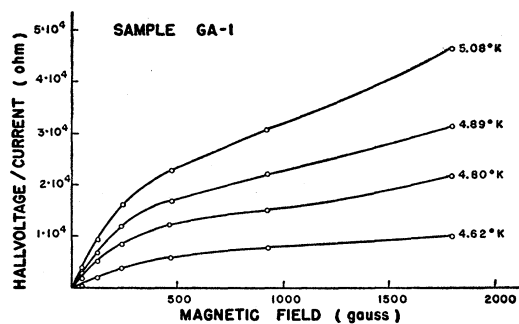

FIG. 3. Hall voltage/current as a function of magnetic field strength at temperatures below that of the maximum in the Hall curve.

[6] Dresselhaus, Kip, and Kittel, Phys. Rev. 92, 827 (1953).

resistivity and the Hall coefficient of the bulk material. All measurements reported below were performed on etched samples.

Hall Coefficient as a Function of Magnetic Field

Figures 2 and 3 show the ratio of the Hall voltage to the sample current as a function of the magnetic field for sample Ga-1 at various temperatures above and below the Hall maximum, respectively.

Already at fields as small as 250 gauss deviations from the linear relationship become noticeable. The large field dependence of the Hall coefficient of p-type material at higher temperatures has been explained successfully by taking into account the double-band structure of the valence band which gives rise to the existence of a small percentage of high-mobility holes.[7] These fast holes having a very small effective mass are strongly influenced already by weak magnetic fields.
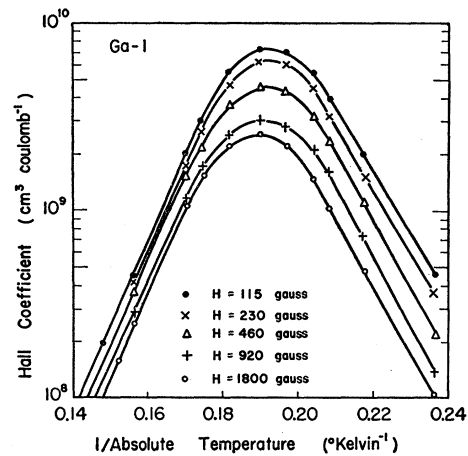

FIG. 4. The maximum of the Hall coefficient at various magnetic fields.

Since the same arguments hold also for low temperatures, the strong field dependence of the Hall coefficient can be understood.

The low-temperature Hall maximum does not disappear in the limit of zero-field slopes in Fig 2 at decreasing temperature (6.41°K to 5.26°K); the slope and therefore the Hall coefficient increases as the temperature is lowered. However, in going from 5.08°K to 4.62°K (Fig. 3) the slope decreases, indicating a maximum at about 5.15°K.

Throughout the temperature range investigated, the condition that the transverse Hall electric field be small compared to the applied electric field was fulfilled. Although the Hall coefficient depends on the magnetic field used, the shape of the Hall curve is not significantly altered by the magnetic field strength. This behavior is illustrated in detail in Fig. 4. The Hall coefficient has an even greater anomaly at larger mag-

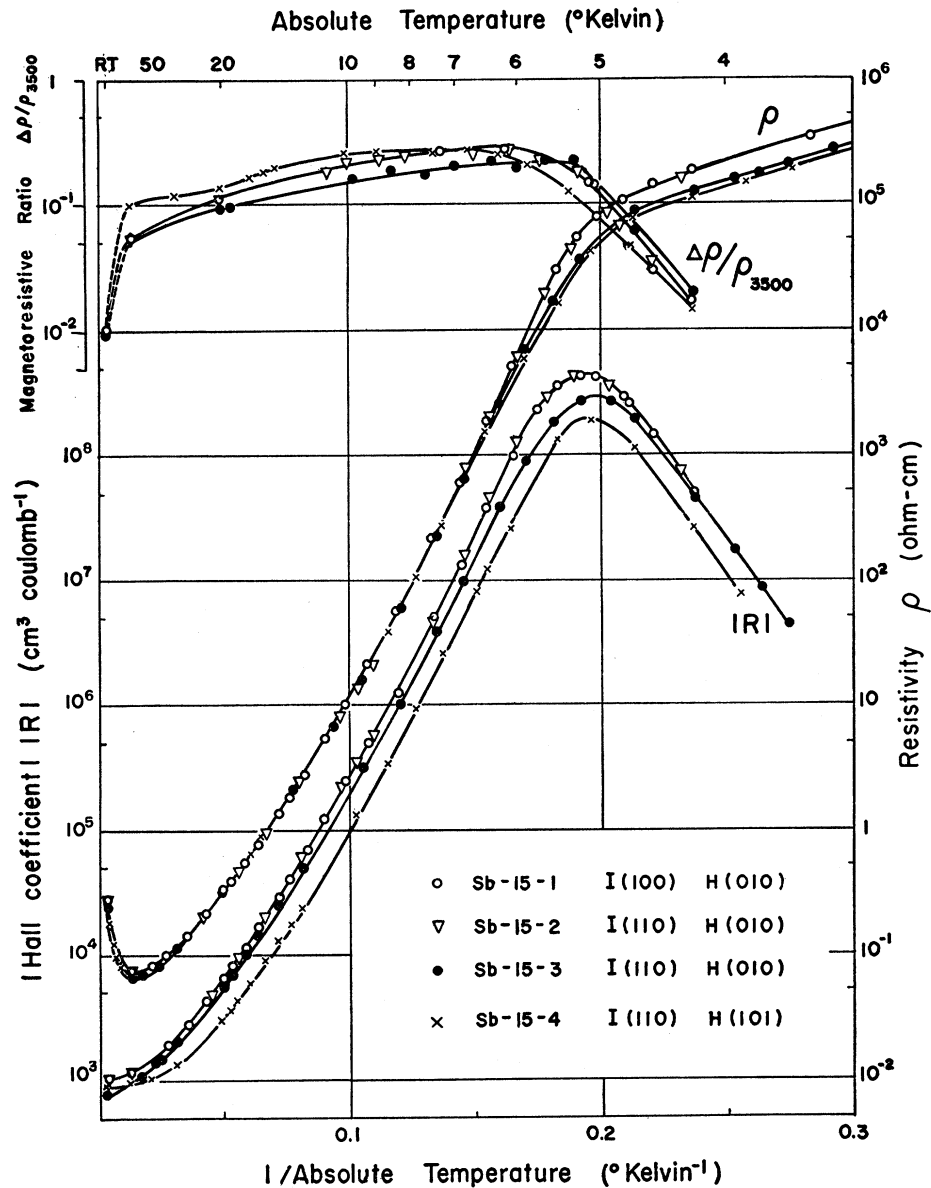[7] Willardson, Harman, and Beer, Phys. Rev. 96, 1512 (1954).

FIG. 5. R, ρ, and $\Delta\rho/\rho_H$ of n-type samples with different crystallographic orientations of I and H.

netic fields, since at low temperatures the Hall coefficient decreases with increasing field strength.

The measurements of the Hall coefficient were performed with a magnetic field of between 115 gauss and 230 gauss. Higher fields up to 4600 gauss were used only at very low temperatures where the Hall angle, which is proportional to R/ρ, becomes very small.

Directional Effects

The work on the directional properties of the magnetoresistive ratio[8] and on the cyclotron resonance[9] in germanium shows a structure of the conduction band

in which the surfaces of constant energy consist of ellipsoids of revolution lying along the (111) axis. The warped energy surfaces of the valence band on the other hand are anisotropic to a much smaller degree.

In order to investigate the anisotropy effect of the Hall coefficient and the resistivity and to see whether the low temperature anomalies depend significantly on the choice of crystal orientation, four n-type samples of almost equal impurity content have been measured. These are Sb-15-1, Sb-15-2, Sb-15-3, and Sb-15-4 listed in Table I.

The resistivity of these samples is measured between 1.5°K and 300°K, the Hall coefficient and magnetoresistive ratio between 4.2°K and 300°K. The results are plotted in Fig. 5. The measurements on sample

[8] G. L. Pearson and H. Suhl, Phys. Rev. **83**, 768 (1951).
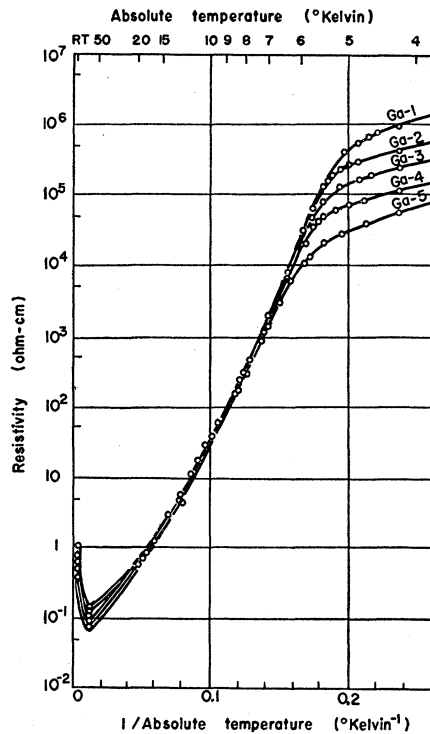[9] Lax, Zeiger, Dexter, and Rosenblum, Phys. Rev. **93**, 1418 (1954).

FIG. 6. Resistivity of p-type germanium (gallium-doped) as a function of $1/T$.

Sb-15-1 and sample Sb-15-2 agree in the whole temperature range within the limits of accuracy. The Hall coefficient of Sb-15-4 is found to be smaller than that of Sb-15-3 by a factor of about two at temperatures below 20°K, whereas the magnetoresistive ratio of Sb-15-4 is larger by a factor between 1.5 and 2 at temperatures between 20°K and 7°K. The resistivities of Sb-15-3 and Sb-15-4 again agree in the whole temperature range. The accuracy of the magnetoresistive ratios, however, is rather poor, since they have been measured at a constant field of 3500 gauss, a field at which there already occur strong deviations from the quadratic relation between magnetoresistive ratio and field. Smaller fields will have to be used to check this point.

Although the samples originate from the same region of the ingot and those samples which are being compared differ in resistivity at room temperature only by about 5 percent, one cannot be certain that they contain the same amounts of n-type and p-type impurities. The quantitative comparison of the results is, therefore, uncertain to that degree.

However, since the small difference which has been found in the Hall coefficient of two of the oriented samples (Fig. 5) is the same before and after the onset of the anomaly and since the Hall curves of all four samples go through a maximum at 5.2°K, one can conclude that the low-temperature anomalies cannot be due to anisotropy effects.

Transverse Magnetoresistive Effect

The magnetoresistive ratio has been measured on p-type[4] and n-type samples. The results obtained on n-type samples are shown in Fig. 5. In the temperature range above the Hall maximum the magnetoresistive ratio changes only slowly with temperature, but it starts to decrease sharply near the temperature where the Hall coefficient approaches the maximum and where the resistivity curve changes slope.

Since a magnetic field of 3500 gauss is used, which is, for these samples, larger than the critical field below which the expected quadratic field dependence is observed, a quantitative comparison with the low field approximation cannot be made. However, one can conclude from the sudden change of the magnetoresistive ratio in the same temperature region where Hall coefficient and resistivity become anomalous, that also the magnetoresistive ratio shows a behavior which cannot be accounted for by the usual semiconductor theory.

R and ρ of P-Type Germanium as a Function of of Impurity Concentration

Figures 6 and 7 show how the resistivity and the Hall coefficient of germanium containing various amounts of gallium impurities depend on temperature between 1.5°K and 300°K. These samples originate from the same crystal, the impurity concentration of which
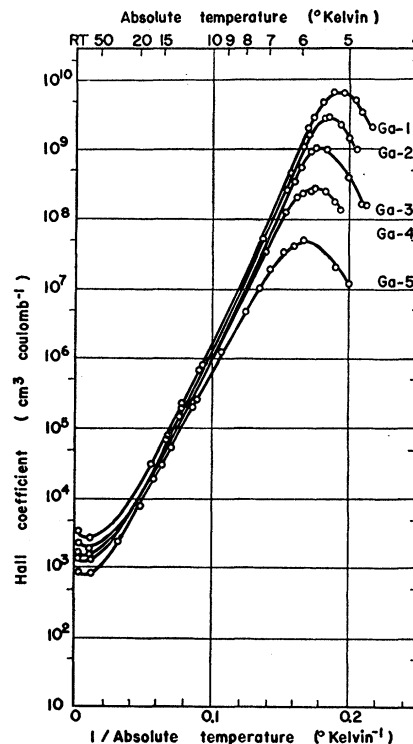

FIG. 7. Hall coefficient of p-type germanium (gallium-doped) as a function of $1/T$.
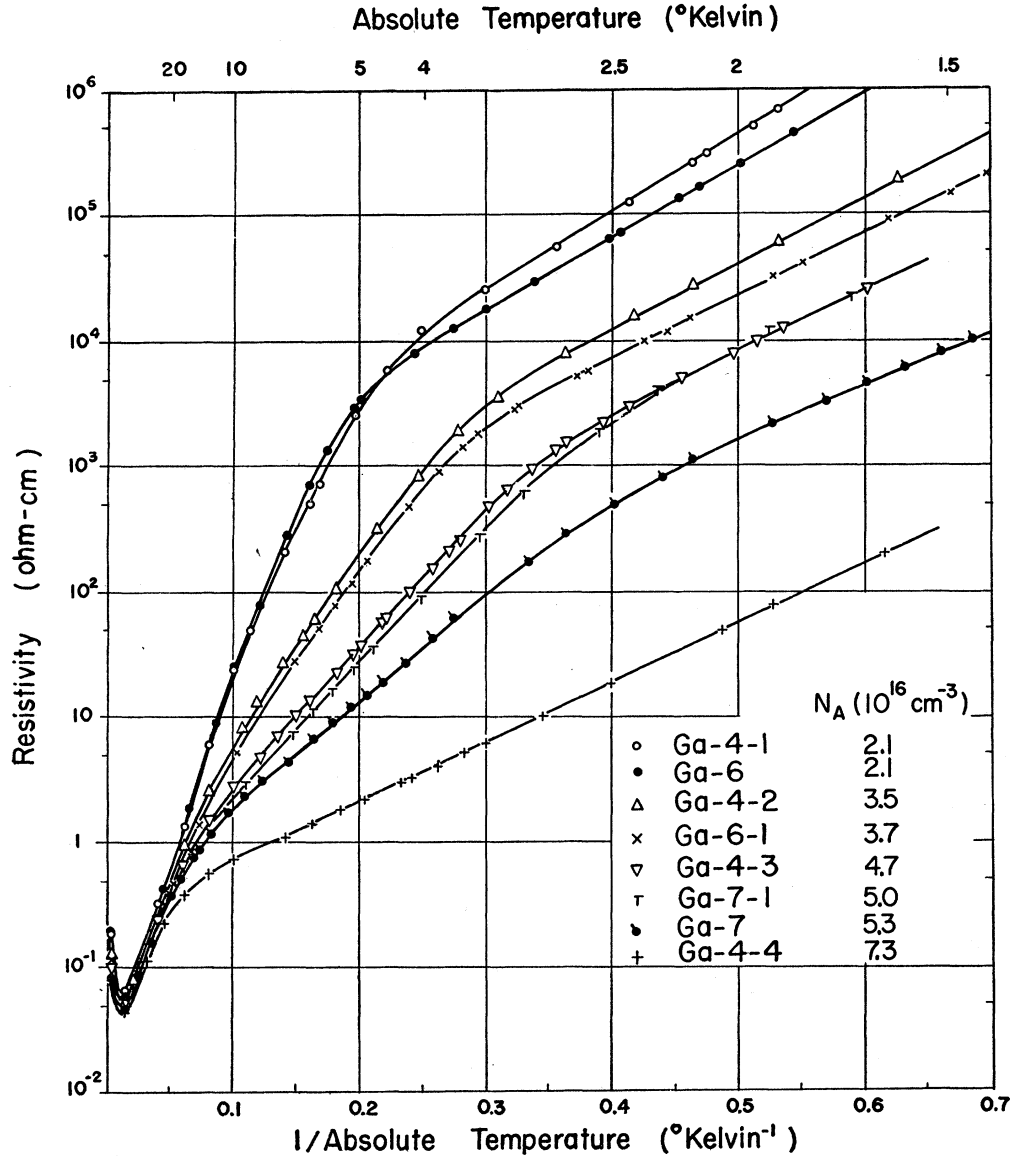
FIG. 8. Resistivity measurements of p-type germanium with large concentrations of gallium.

extends from 3×10^{15}/cc to 10^{16}/cc. The low-temperature behavior observed by Hung is essentially confirmed. The main features will be summarized here.

(a) The Hall coefficient reaches a maximum value with decreasing temperature and decreases thereafter by orders of magnitude. (b) The log resistivity *versus* $1/T$ curves have a large slope at temperatures above the maximum and a much smaller slope at temperatures below the maximum in the Hall curve. The resistivity can be described approximately by the equation[10]
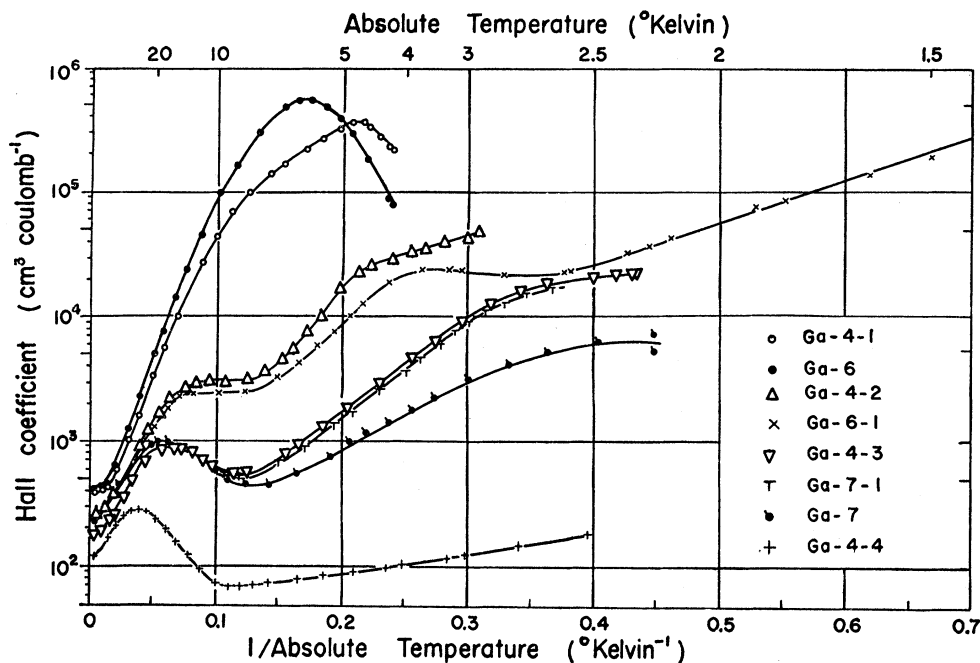
$$1/\rho = C_1 e^{-\epsilon_1/kT} + C_3 e^{-\epsilon_3/kT}, \qquad (1)$$

[10] Where the C_i may be temperature dependent. C_1, C_2, C_3 will be used later, but in this concentration range only C_1 and C_3 are measurable.

with $\epsilon_1 \approx 1\times10^{-2}$ ev and $\epsilon_3 \approx 2\times10^{-3}$ ev. (c) The Hall maximum shifts to higher temperatures and decreases in magnitude with increasing impurity content.

The Hall coefficient could not be measured at still lower temperatures because the Hall angle becomes too small. The lowest temperature region was investigated to find out whether the Hall voltage again becomes large enough to be measured but with no success.

It is difficult to interpret the temperature dependence of the resistivity in the lowest temperature region without knowing the concentration and sign of the charge carriers. For this reason samples with impurity contents larger than 2×10^{16} atoms/cc were measured. The Hall coefficient of these samples could be followed down to much lower temperatures.

FIG. 9. Hall coefficient of p-type germanium with large concentrations of gallium.

Resistivity and Hall coefficient of these samples with gallium contents larger than 2×10^{16} atoms/cc and smaller than 7×10^{16} atoms/cc are shown in Figs. 8 and 9 as a function of the reciprocal temperature. These curves exhibit a much more complicated behavior than those previously discussed. The log resistivity *versus* $1/T$ curves consist of three straight lines, instead of two as the resistivity curves of samples with smaller impurity content do. The temperature dependence of the resistivity can thus be described approximately by the equation

$$1/\rho = C_1 e^{-\epsilon_1/kT} + C_2 e^{-\epsilon_2/kT} + C_3 e^{-\epsilon_3/kT}. \qquad (2)$$

The values for C_2, C_3, ϵ_2, and ϵ_3 determined from the experimental curves are listed in Table II. It is particularly remarkable that C_2 does not depend on the concentration of p-type and n-type impurities at all. C_3, which is proportional to Hung's "mobility" in the impurity band, decreases rapidly with decreasing impurity content.

ϵ_3—of the dimension of an energy—which is determined from the slope of the resistivity curve in the lowest temperature region, depends only slightly on the impurity content, whereas ϵ_2 increases rather strongly with decreasing impurity concentration. The latter increases from 9.2×10^{-4} ev for sample Ga-4-4 to 4×10^{-3} ev for sample Ga-4-1, and it would become larger than ϵ_1, which is about 8×10^{-3} ev, in the case of samples with impurity concentrations smaller than 10^{16}/cc if it continues to increase at the same rate. An ϵ_2 equal to or larger than ϵ_1 would make the second term in the Eq. (2) negligible compared to the first term and, therefore, unnoticeable in the resistivity curve. This might be the reason why an intermediate slope in the resistivity curve, and with it the complicated behavior of the Hall coefficient, were never observed on samples with impurity concentrations smaller than about 10^{16}/cc.

In contrast to the behavior of samples with smaller impurity content (Fig. 7), the Hall curve of these samples do not have one sharp maximum, but a very

TABLE II. Resistance temperature parameter for Ge.
[See Eq. (2) of text.]

	N_A cm^{-3}	N_D cm^{-3}	C_2 ohm^{-1} cm^{-1}	ϵ_2 ev	C_3 ohm^{-1} cm^{-1}	ϵ_3 ev
In-1	9.3×10^{14}	3.1×10^{14}			4.0×10^{-7a}	5.3×10^{-4a}
In-2	3.0×10^{15}	1.4×10^{15}			1.8×10^{-4}	5.9×10^{-4}
In-3	3.6×10^{16}	1.1×10^{16}				
In-4	5.2×10^{16}	7.5×10^{15}			1.54×10^{-1}	7.0×10^{-4}
In-5	1.3×10^{17}	3.3×10^{16}			1.43	5.0×10^{-4}
Ga-1	2.9×10^{15}	1.1×10^{14}				
Ga-2	3.9×10^{15}	1.3×10^{14}				
Ga-3	4.4×10^{15}	1.0×10^{14}			2.5×10^{-4a}	1.4×10^{-3a}
Ga-4	6.1×10^{15}	1.7×10^{14}				
Ga-5	9.0×10^{15}	5.1×10^{14}			7.7×10^{-4}	1.3×10^{-3}
Ga-6	2.1×10^{16}	2.1×10^{15}			3.03×10^{-3}	1.1×10^{-3}
Ga-4-1	2.1×10^{16}	1.5×10^{15}	4.30	4.04×10^{-3}	2.78×10^{-3}	1.2×10^{-3}
Ga-4-2	3.5×10^{16}	3.9×10^{15}	4.30	2.87×10^{-3}	1.00×10^{-2}	1.0×10^{-3}
Ga-6-1	3.7×10^{16}	2.9×10^{15}	4.00	2.75×10^{-3}	1.17×10^{-2}	0.95×10^{-3}
Ga-4-3	4.7×10^{16}	4.5×10^{15}	4.25	2.44×10^{-3}	3.90×10^{-2}	1.0×10^{-3}
Ga-7-1	5.0×10^{16}	6.7×10^{15}	4.16	2.1×10^{-3}	3.90×10^{-2}	1.0×10^{-3}
Ga-7	5.3×10^{16}	2.0×10^{16}	4.09	1.74×10^{-3}	6.66×10^{-2}	0.8×10^{-3}
Ga-4-4	7.3×10^{16}	7.0×10^{15}	4.09	0.93×10^{-3}	4.09	0.9×10^{-3}
Sb-15-1	4.7×10^{14}	6.9×10^{15}			10^{-3}	1.6×10^{-3}
Sb-15-2	4.0×10^{14}	6.7×10^{15}			10^{-3}	1.6×10^{-3}
Sb-15-3	5.0×10^{14}	8.7×10^{15}			10^{-3}	1.6×10^{-3}
Sb-15-4	9.0×10^{14}	8.3×10^{15}			10^{-3}	1.6×10^{-3}
Sb-19-1	2.8×10^{15}	3.4×10^{16}			2.33×10^{-2}	1.06×10^{-3}
Sb-19-2	1.5×10^{16}	6.5×10^{16}			2.5×10^{-1}	8.6×10^{-4}
Sb-19-3	2.6×10^{16}	1.2×10^{17}			4.45	4.7×10^{-5}

a The logρ vs $1/T$ curves of these samples have a continuously increasing slope at the lowest temperatures. The values listed here for comparison have been determined at 2.5°K.

irregular shape which is different for different impurity contents.

The only exception is sample Ga-4-4, the Hall coefficient of which reaches a maximum value at 27°K and decreases then with decreasing temperature to a minimum value which is lower than that at room temperature. After this, the Hall coefficient rises exponentially with $1/T$ with an $\epsilon = 3.4_5 \times 10^{-4}$ ev, which is smaller than $\epsilon_3 = 9.3 \times 10^{-4}$ ev of the corresponding resistivity curve in the same temperature region.

No Hall curve approaches its exhaustion range value at low temperatures, as was predicted and also observed by Hung on three neutron-bombarded samples. The Hall coefficient of sample Ga-6-1 in particular is 10^3 times larger at 1.5°K than at room temperature and continues to increase at still lower temperatures.

A reversal of the sign of the Hall coefficient was looked for, particularly in measurements of these impure samples, which could be carried out at very low temperatures. In all cases thus far, the sign of the Hall coefficient is the same throughout the whole temperature range in which observations were made.

It is very unlikely that the complicated behavior of the samples with gallium concentrations higher than 2×10^{16}/cc and lower than 7×10^{16}/cc is only accidental and caused by spurious impurities which are not present in the other samples. If this were the case one could not understand the remarkable agreement of the results obtained on Ga-4-3 and Ga-7-1, which were cut from different crystals.

The fact that the samples Ga-6 and Ga-7 (Figs. 8 and 9) show a quite different temperature dependence of the Hall coefficient and resistivity than the samples Ga-1, Ga-2 to Ga-5 (Figs. 6 and 7), although they are
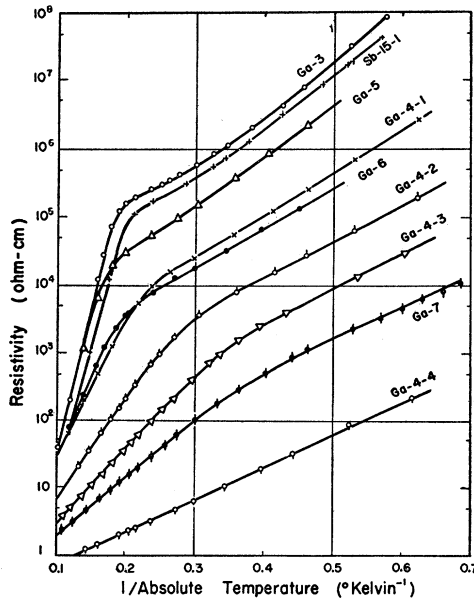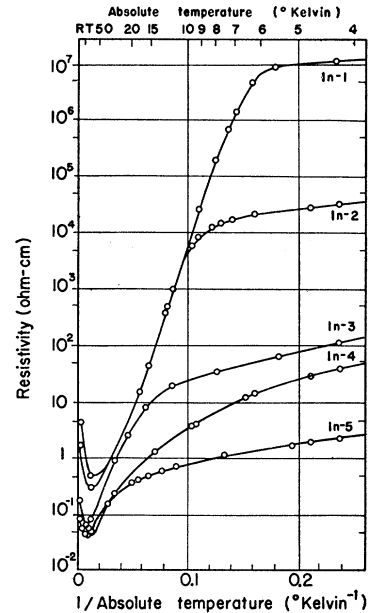

FIG. 11. Resistivity of indium-doped germanium (p-type) as a function of $1/T$.

cut from the same crystal, also indicates that the more complicated behavior is a general property of samples with higher gallium concentrations. Measurements on n-type samples with large antimony concentrations will be reported below. They also show a complicated behavior of Hall coefficient and resistivity as the p-type samples do which contain corresponding concentrations of gallium.

The temperature dependence of the resistivity of the germanium samples, which have been doped with gallium, is shown in Fig. 10 for temperatures between 1.5°K and 10°K. With the exception of the highest resistivity curves, the slopes of which continue to increase with decreasing temperature, the curves have a constant slope at the lowest temperatures which increases slowly as the impurity content of the samples is decreased.

The results of measurements on germanium containing various amounts of indium impurities are shown in Figs. 11, 12, and 13. The Hall and resistivity curves of these samples also exhibit the anomalies at low temperatures. One again finds that the Hall maximum shifts to higher temperatures and decreases in magnitude if the impurity content is increased (Fig. 12). The behavior of indium-doped samples, however, differs from that of gallium-doped samples in some respects.

(a) The slopes of the log resistivity *versus* $1/T$ curves as determined in the lowest temperature range vary between 4×10^{-4} ev and 7×10^{-4} ev in the case of indium-doped samples and between 1×10^{-3} ev and 1.8×10^{-3} ev in the case of gallium-doped samples.

(b) The Hall curves of the samples In-4 and In-5 are

FIG. 10. Resistivity as a function of $1/T$ between 1.5°K and 10°K. Note the similar resistivity curves of Ga-3 and Sb-15-1.
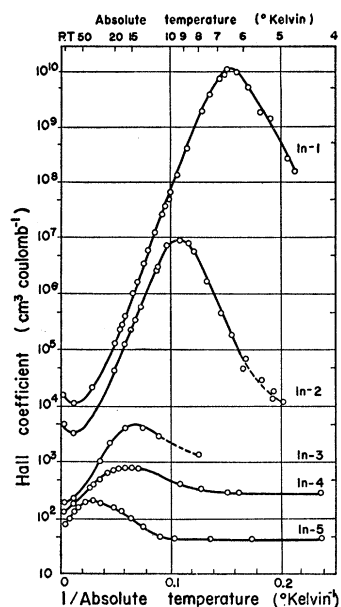
FIG. 12. Hall coefficient of indium-doped germanium
(p-type) as a function of $1/T$.

flat in the lowest temperature region. There is no indication of a slope.

Upon comparing the gallium-doped samples with the indium-doped samples one has to keep in mind, however, that several of the samples doped with indium are polycrystalline.

Electrical Properties of N-Type Germanium

Four n-type samples containing about 7.5×10^{15} antimony atoms/cc have been discussed above and the results are plotted in Figs. 5 and 10. These samples show the same behavior at low temperatures as the p-type samples which contain corresponding amounts of gallium or indium impurities. The resistivity curves have a large slope at temperatures above the Hall maximum, and in the lowest temperature range a much smaller slope, which is the same as the slopes of the resistivity curves of the p-type samples which are doped with gallium. This can be seen from Fig. 10, where sample Sb-15-1 is included for comparison.

Three samples with antimony concentrations between 3 and 12×10^{16} atoms/cc have been investigated to find out whether also highly doped n-type samples exhibit the more complicated behavior which is shown in Figs. 8 and 9 for highly doped p-type samples. The results are shown in Figs. 14 and 15. It is uncertain whether the conductivity of these samples can be described by a sum of three exponential terms as in Eq. (2).

The Hall curves of the samples Sb-19-1 and Sb-19-2 show a behavior similar to that of highly doped p-type samples. They do not approach their exhaustion range value at very low temperatures but after reaching a maximum they decrease only slightly with decreasing

temperature and then continue to increase down to the lowest temperatures at which measurements could be performed. The slopes of the Hall curves of these two samples are considerably smaller than the slopes of their corresponding resistivity curves in the lowest temperature range. The Hall coefficient and the resistivity of sample Sb-19-3 are almost independent of temperature below 10°K. This behavior has to be compared with that of other samples of this impurity range before one can discuss it.

Concentration of Impurities

The problem of calculating the concentration of majority impurities and of minority impurities to a reasonable degree of accuracy has become very complicated, since the discovery of high-mobility holes in the valence band. Although the percentage of the fast holes is small, they affect considerably the magnetic field dependence of the Hall coefficient and the ratio of Hall mobility to drift mobility. This makes the calculation of the impurity concentration from the scattering due to ionized impurities as well as the calculation based on the temperature dependence of the carrier concentration very difficult. There are other uncertainties especially in the latter calculation, one of which is the presence of excited states of the impurities and another the dependence of the impurity activation energy on the concentration of charge carriers.[11]
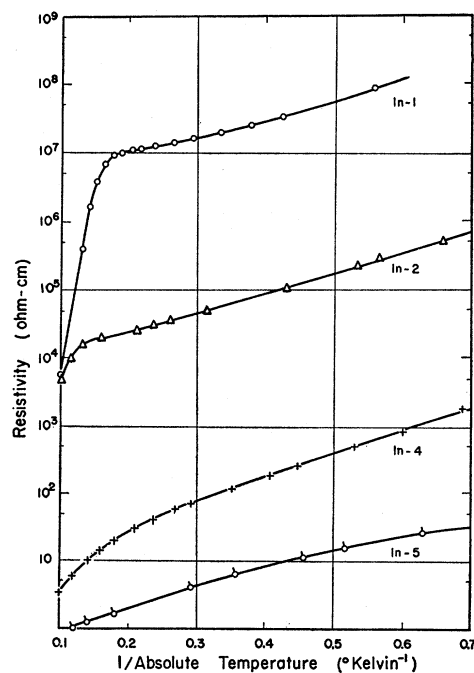
Because of these complications the concentrations of

FIG. 13. Resistivity measurements on indium-doped germanium between 1.5°K and 10°K.

donors and acceptors listed in columns 2 and 3 of Table II can be taken as order of magnitude values only. They were calculated from the mobility data at 78°K with the aid of the Brooks-Herring formula[12] for scattering by ionized impurities, assuming an effective mass of $m_e^* = 0.125 m_0$ for electrons[13] and $m_h^* = 0.33 m_0$ for holes[13] and ignoring the presence of the high-mobility holes in p-type material. The polycrystalline nature of In-3, In-4, and In-5 constitutes an additional factor of uncertainty for the concentration values obtained for these samples.

The indium-doped samples contain on the average a much larger concentration of minority impurities (donors) than the gallium-doped samples. This is to be expected[4] because of the difference in the segregation coefficients of indium and gallium in germanium.

DISCUSSION

The fact that the Hall maximum, the onset of the small slope of the log resistivity *versus* $1/T$ curve, and the sharp drop of the magnetoresistive ratio occur always at one and the same temperature for a given sample seems to indicate that one and the same process causes all three properties to deviate from their normal behavior.

In the following, the various explanations for the observed anomalies will be compared with the experimental results, and it will be shown why one has to discard them.

(1) Conducting surface layers cannot be the reason for the observed phenomena because measurements made on etched samples are independent of sample thickness; hence, conducting surface layers, although
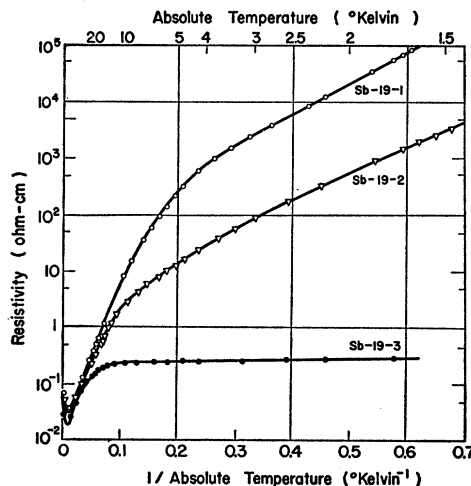

FIG. 14. Resistivity measurements on n-type germanium with large concentrations of antimony.

[12] H. Brooks, Phys. Rev. **83**, 879 (1951).
[13] Lax, Zeiger, and Dexter, Physica **20**, 818 (1954); C. Kittel, Physica **20**, 829 (1954).
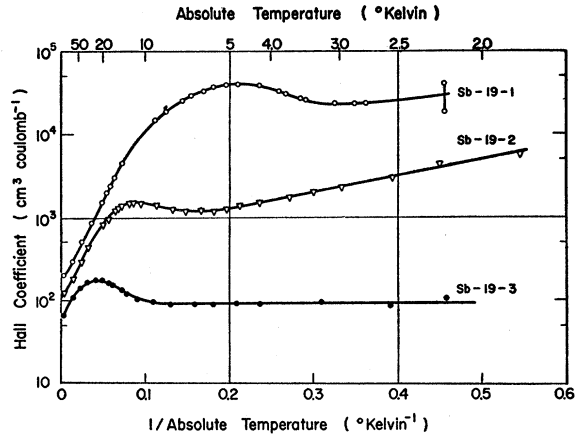

FIG. 15. Hall measurements on n-type germanium with large concentrations of antimony.

found on ground samples, are not detectable on etched or electropolished samples.[14]

(2) Soldered contacts also do not seem to influence the measurements, since cross-shaped samples and ordinary Hall plates show the same results. Furthermore, no difference is found after removing and re-soldering the leads several times.

(3) In the very low electric fields applied, it is very difficult to picture an avalanche excitation of charge carriers, particularly in view of the ohmic behavior of the resistivity (Fig. 1).

(4) The possibility of light excitation of charge carriers at low temperatures due to radiation from warmer parts of the cryostat or to stray light from outside has to be excluded. The sample is surrounded by a copper cylinder of the same temperature and thus is shielded against radiation from warmer parts. The experimental arrangement excludes also the possibility that stray light reaches the samples.[15]

(5) The strong magnetic field dependence of the Hall coefficient might suggest that the anomalies are purely a magnetic field effect which disappears in the limit of vanishing fields. This, without doubt, is not the case. The resistivity is measured without an applied magnetic field, and even the limiting value of the Hall coefficient as the magnetic field goes to zero passes through a maximum (Figs. 2 and 3).

(6) The possibility of explaining the anomalies as being due to the fact that the surfaces of constant energy are nonspherical has to be excluded, because the small difference which has been found in the Hall

[14] If one plots the maximum value of the observed Hall coefficient against sample thickness, then for etched samples one obtains a horizontal line indicating a Hall coefficient independent of sample thickness. The same experiment carried out with ground samples shows a Hall coefficient which increases with increasing thickness approaching the value of the etched samples.
[15] Further evidence for this is that heating effects due to light were never observed even at very low temperature where the atomic heat of the sample is exceedingly small and absorption of radiation would lead to a rise in temperature, which was not observed.

coefficient of two of the oriented samples (Fig. 5) is the same before and after the onset of the anomaly and does not affect the shape of the Hall curve.

Since all explanations offered so far do not fit the experimental arrangement, one must conclude that the Hall coefficient, resistivity, and magnetoresistive ratio of the bulk germanium do not show the behavior at low temperatures which is predicted by the usual semiconductor theory, and that this theory has to be altered to account for the observed phenomena.

Before discussion of the theories that postulate additional conduction in an impurity band, some regularities in the electrical behavior of the gallium-doped samples will be summarized here.

The conductivity of these samples can approximately be described by a sum of three exponential terms as in Eq. (2). The first term represents conduction by holes in the valence band. The second term is only found in the case of samples with impurity content larger than about 10^{16}/cc; it becomes much smaller than the first term when the impurity content is smaller than 10^{16}/cc, since ϵ_2 increases rather strongly with decreasing concentration of impurities, whereas the factor C_2 remains constant (see Table II).

The third term consists of an exponential with an ϵ_3 of the order of 10^{-3} ev and a factor C_3 which decreases very rapidly with decreasing impurity concentration. Since the second and the third terms depend on the concentration of impurities in quite different ways, two different mechanisms are probably responsible for their appearance.

The strong decrease of the factor C_3 with decreasing impurity concentration makes the assumption of additional conduction in an impurity band a very plausible explanation for the presence of the third term and for the maximum in the Hall curve, since the mobility in such a band would be expected to decrease rapidly with increasing distance between the impurity atoms.

At the present time, nothing can be said about the mechanism which gives rise to the presence of the second term in the expression for the conductivity and to the complicated behavior of the Hall coefficient which is always connected with it. Since this mechanism seems to be not effective in purer samples, it will be tried to discuss the possibility of a conducting impurity band as an explanation for the anomalies without considering this additional effect which becomes noticeable only in the electrical behavior of samples in a certain impurity concentration range.

If one tries to compare the experimental results with any kind of model which assumes conduction in impurity bands, one encounters great difficulties.

According to James and Ginzbarg,[5] an impurity band is formed by the interaction between localized impurity states, or the overlapping of their electron wave functions. The distribution of energy states of a perfect crystal differs from that of a crystal in which one n-type impurity atom replaces a regular lattice atom by the fact that in the latter case two energy states are missing from the conduction band and one doubly degenerate energy state appears in the forbidden gap. The degeneracy is due to the two alternative spin directions. The two corresponding eigenfunctions are localized in that they have an appreciable amplitude only in the neighborhood of the impurity. If two impurities replace regular lattice atoms, two doubly-degenerate energy states appear in the forbidden gap and a corresponding number of states are missing from the conduction band. The energy difference between these two states can be computed in terms of an exchange integral involving the single-impurity wave functions. The eigenfunctions belonging to these energy states again have an appreciable amplitude only in the neighborhood of the two impurities. When there are many impurities, the group of energy states in the forbidden energy gap is called an impurity band.

In the hypothetical case of a periodic arrangement of the impurity atoms, the impurity band is separated from the bottom of the conduction band (or from the top of the valence band in p-type) by a forbidden gap, and it contains twice as many energy states as there are impurity atoms. James and Ginzbarg[5] have shown that, if the random distribution of impurities is taken into account, then the impurity band appears as an energy range of high-level density, separated from the conduction band merely by a range of smaller level density and that the number of states in the impurity band is less than twice the number of impurity atoms.

Some difficulties, which arise in discussing conduction in an impurity band, will be given in the following. For this discussion, a periodic arrangement of impurity atoms will be assumed. The realistic case of a random distribution of impurity atoms will probably be more complicated, although Aigrain[5] has shown that the band-type approximation holds for lower impurity densities rather in the random than in the ordered case.

A basic property of a band, formed by an ideal lattice, is that the average value of the ratio free electron mass to effective mass, m_0/m^*, over the whole band vanishes. This means that the net current vanishes if the band is completely filled. The ratio m_0/m^* must therefore depend on energy inside the band, and it must assume positive and negative values. Since at most temperatures the impurity band width will be small compared to kT, carriers with positive and with negative effective masses will exist at the same time and will move in opposite directions.

The excess carrier concentration which produces a net current flow in an applied electric field will depend strongly on the distribution of charge carriers over the quantum states in the impurity band, hence on temperature, and will, therefore, be quite different from the true concentration of carriers occupying the band. The average mobility will also depend on temperature through the averaging process which involves states with very different effective masses.

The theory for the Hall coefficient and the resistivity of an impurity band has not yet been worked out. The formulas will certainly look very different from those of the ordinary band because of the drastic changes of the effective mass within the impurity band. One cannot expect, for instance, that the Hall coefficient is proportional to the reciprocal of the concentration of charge carriers occupying the impurity band. Some factors similar to $r = |R|/en$ of the ordinary conduction band might depend on temperature since the averaging process includes states of very different properties.

The simplest model which assumes conduction in an impurity band is that of Hung.[2,3] The impurity band of his model is formed by the interaction between the ground states of the impurities. The approximate agreement obtained by Hung is based on the assumption that (a) the expressions for the Hall coefficient and the resistivity for simultaneous conduction in two bands still hold in this case[16]

$$R = \frac{1}{e}\frac{r_c n_c \mu_c^2 + r_i n_i \mu_i^2}{(n_c \mu_c + n_i \mu_i)^2}, \tag{3}$$

$$\rho = 1/(en_c\mu_c + en_i\mu_i), \tag{4}$$

where the subscripts refer to the conduction band and the impurity band, respectively, and (b) that the factors r_c and r_i do not deviate appreciably from unity.

With these assumptions the concentration of charge carriers in the impurity band at very low temperatures is equal to the carrier concentration in the conduction band at exhaustion and the calculated curves of the resistivity and the Hall coefficient are both flat in the lowest temperature region.

The finite slopes of the resistivity curves and the Hall curves in the lowest temperature region and the fact that the Hall coefficient does not approach its exhaustion value as the temperature is lowered disagree with Hung's picture. One concludes that either the model of a conduction in the ground states of the impurities or the Eqs. (3) and (4) must be altered so that they account for the special properties of the impurity band which were mentioned above.

Since at the present time, Eqs. (3) and (4) are the only ones available for the Hall coefficient and the resistivity of two-band conduction, it will be attempted to show that they can describe the observations obtained from the purer samples without making use of Hung's original assumption that the impurity band is formed by the ground states. It will only be assumed that a certain concentration of charge carriers flows in another band with an impurity band mobility μ_i much smaller than the mobility μ_c in the valence band so that

$$r_c n_c \mu_c^2 \gg r_i n_i \mu_i^2 \tag{5}$$

in the temperature range under consideration.

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[16] In general, one might write $R = \Sigma_j R_j \sigma_j^2/(\Sigma_j \sigma_j)^2$.
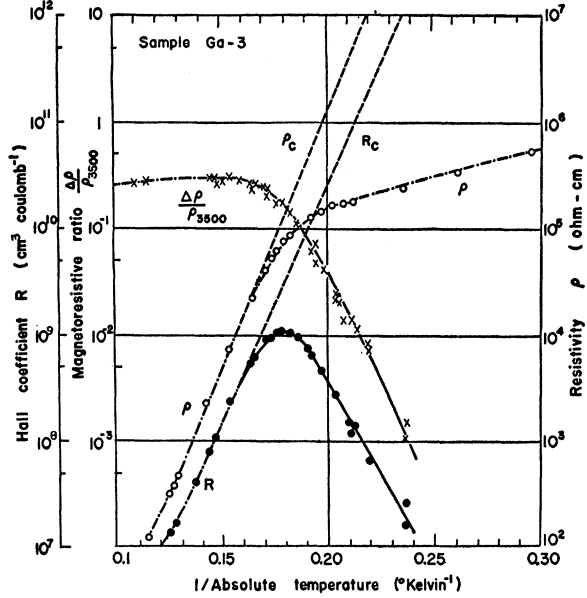

FIG. 16. $\Delta\rho/\rho_H$ and R calculated from ρ, R_c and ρ_c (see text).

If one denotes by

$$R_c = r_c/en_c, \quad \rho_c = 1/en_c\mu_c, \quad R_i = r_i/en_i, \quad \rho_i = 1/en_i\mu_i, \tag{6}$$

the Hall coefficient and the resistivity in the conduction band and in the impurity band, respectively, one obtains by use of Eqs. (3), (4), and (5):

$$R/R_c = \rho^2/\rho_c^2. \tag{7}$$

From Eqs. (4) and (8), one obtains the magneto-resistive ratio for two-band conduction as follows:

$$\sigma(H) = \sigma_c(H) + \sigma_i(H),$$

$$\sigma_c(H) = \sigma_c(0)(1 - B_c H^2),$$

$$\sigma_i(H) = \sigma_i(0)(1 - B_i H^2).$$

One can neglect $B_i H^2$ as being small compared with unity as found experimentally. By using resistivities instead of conductivities, one finds

$$(\rho_H - \rho_0)/\rho_H = \Delta\rho/\rho_H = B_c H^2 \rho/\rho_c. \tag{8}$$

Here ρ_c may be calculated from the n_c extrapolated from the Hall curve and μ_c extrapolated from the mobility curve. The Hall coefficient R and the magneto-resistive ratio $\Delta\rho/\rho_H$ calculated from ρ and ρ_c by using (7) and (8) show that this description is self-consistent (see Fig. 16).

These considerations are very hypothetical, and the agreement which was demonstrated previously does not yet prove the validity of the assumptions in the case of such a complicated picture.

Because of the finite slopes of the resistivity curves

and the Hall curves in the lowest temperature range, Erginsoy[5] suggested that the impurity band is formed by the excited states instead of the ground states of the impurities. The finite slopes would then find their explanation in the excitation energy which is necessary to bring charge carriers from the ground states into the band of the first excited states.

The calculations of the lower band-edge energies of the $2s$, $2p$, and $3s$ bands of hydrogen-like impurities, which were carried out by Erginsoy[5] and Baltensperger,[5] show, however, that the bands of the excited states are concentrated near the edge of the conduction band.[17]

Another objection to the model of Erginsoy is that the excited states of an impurity cannot be treated as ordinary acceptor states, since one of them can be occupied only if all the other excited states and the ground state of the corresponding impurity atom are empty. This limits the number of available excited states so much, expecially at low temperatures when most of the ground states are occupied, that conduction through excited states should be extremely small.

Busch and Labhart[5] used a slightly different model to explain their experimental findings on SiC. They assumed a conducting acceptor band in an n-type crystal (a corresponding donor band between the acceptors and the valence band in the case of a p-type crystal). These authors determined the energy gap between their postulated band and the impurity states, as well as the number of states forming the additional band, from the experimental curves using Eqs. (3) and (4).

In order to explain the temperature dependence of the Hall coefficient and resistivity of the gallium-doped samples on the basis of Busch's model, it is necessary to assume a conducting impurity band about 10^{-3} ev below the acceptor states. This band should be filled with electrons at 0°K and partly empty at elevated temperatures, to account for the observed positive sign of the Hall coefficient. This discussion shows clearly that additional experimental work will be necessary to provide an adequate foundation for theoretical discussion.

SUMMARY

The resistivity ρ, the Hall coefficient R, and the transverse magnetoresistive ratio $\Delta\rho/\rho$ of single-crystal samples of n-type and p-type germanium have been reinvestigated in the temperature range from 300°K to 1.5°K. It was found that Hung's observations of an anomalous behavior of resistivity and Hall coefficient are correct.

The $\log\rho$ versus $1/T$ curve has either two or three different slopes at temperatures below about 25°K, depending on the range of impurity concentrations.

The Hall coefficient first increases with decreasing temperature, as expected from semiconductor theory, but, in the temperature range in which the slope of the resistivity curve changes, the Hall coefficient goes through a maximum. At still lower temperatures, the Hall coefficient decreases by orders of magnitude in the case of samples with lower impurity concentrations. At the lowest temperatures the Hall coefficient of samples with high impurity concentrations is either completely constant with temperature or shows one or even two slopes in the $\log R$ vs $1/T$ plot. These slopes are significantly different from the corresponding slopes of the resistivity curves in the same temperature range.

Throughout the whole temperature range the Hall coefficient does not change sign. Samples which are found to be p-type at higher temperatures remain p-type down to the lowest temperature investigated and the same holds for n-type samples.

In the same temperature range where Hall coefficient and resistivity become anomalous, the magnetoresistive ratio decreases when the temperature is lowered.

Special precautions were taken to exclude the effect of surface conduction, the influence of heat radiation, and electric field excitation.

Investigation of the Hall coefficient as a function of magnetic field strength shows clearly that the anomaly cannot be due to a magnetic field effect. That the effects observed can also not be due to the influence of the direction of the current flow, and the magnetic field with respect to the symmetry axes of the Brillouin zones, has been shown by measurements on carefully selected and crystallographically oriented specimens in which the symmetry axes of the sample had different crystal orientations.

The explanation of these observations due to Hung, who assumed that the localized impurity states interact and form a conduction band, seems plausible for the following reasons. The width of the impurity band should drastically decrease with increasing separation between the impurity atoms. Therefore one would expect the mobility of the charge carriers in the impurity band to decrease rapidly with decreasing concentration of impurities. This effect is demonstrated by the following observations: (a) In the lowest temperature range where conduction in the impurity band should outweigh conduction in the ordinary conduction band, the resistivity increases rapidly, if the impurity concentration of the sample is decreased; (b) the Hall maximum decreases in magnitude and shifts to higher temperature when the impurity concentration is increased, and (c) the magnetoresistive ratio is exceedingly small in the lowest temperature range where conduction in the impurity band should predominate.

Hung's hypothesis on the other hand cannot account for the complicated behavior of Hall coefficient and resistivity of germanium samples with impurity concen-

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[17] There is reason to believe that excited states are much closer to the ground state in antimony-doped n-type germanium, as E. M. Conwell [Phys. Rev. (to be published)] pointed out to me.

trations larger than 2×10^{16}/cc and smaller than about 10^{17}/cc.

Cohesive Energy of Noble Metals

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The method, developed by Kuhn and Van Vleck, and later simplified and extended by Brooks, for calculating the cohesive energy of monovalent metals, is here further extended to include the effects of the deviation of the effective ion-core potential from pure hydrogenic form in the vicinity of the surface of the s-sphere. A formula is derived for calculating the logarithmic derivative of the wave function at the surface of the s-sphere. From the logarithmic derivatives of the s- and p-functions the ground-state energy and the Fermi energy can be evaluated. The method thus extended is applied to the calculation of the cohesive energy of the monovalent noble metals. For these metals, the repulsion between ion cores is important. Combining the repulsive energy, which is calculated by Fuchs with a modified Thomas-Fermi method, with the energy of valence electrons calculated by the present method, we obtain the total cohesive energy of copper. Since there is no calculation of the repulsive energy for silver and gold, the ion cores are assumed to be rigid and the energies of the valence electrons at the observed lattice spacings are determined and considered as the approximate total energies. The cohesive energies calculated at the observed lattice spacings with the rigid ion-core assumption are 61.7 for Cu, 55.8 for Ag, and 49.2 for Au in comparison with the experimental values of 81.2, 68.0, and 92.0 respectively. Here the energy unit is kcal/mole.

1. INTRODUCTION

$\mathbf{V}$AN VLECK and Kuhn[1] have given simplified methods of calculating the cohesive energies of monovalent metals. Recently, Brooks[2] has pointed out a number of simplifications of their methods and obtained reasonable theoretical predictions of the cohesive energy and lattice constants of all the alkali metals. The Van Vleck-Kuhn method is based on the following facts: (1) The effective potential in the vicinity of the surface of the s-sphere in the Wigner-Seitz sphere approximation[3] is essentially hydrogenic, therefore, (2) the wave function in the same region can be excellently approximated by a linear combination of the confluent hypergeometric functions, viz.,

$$U_h^{(l,n)}(r) = \overline{W}^{(l,n)}(r) + k_l\widetilde{W}^{(l,n)}(r), \tag{1}$$

where the functions $\overline{W}^{(l,n)}$ and $\widetilde{W}^{(l,n)}$ are related to the standard Whittaker functions by Eqs. (11a, b) in Van Vleck and Kuhn, and (3) k_l can be determined by the function matching method. Brooks, however, has shown that

$$k_l = -\tan(\delta_l\pi), \tag{2}$$

where δ_l is the quantum defect.

In the present paper, the cohesive energy of the noble metals will be computed by the Brooks method, incorporating the correction due to the deviation of the effective potential from the pure hydrogenic form. In the case of copper, Fuchs[4] has calculated the cohesive energy by numerical integration of the radial wave equation in a Hartree-Fock potential. His results for copper as well as the observed values for all noble metals will be compared with our results in the last section.

2. EXTENSION OF THE BROOKS METHOD

We shall first explain a further extension of the Brooks method of determining k_l, and then derive the expression for the logarithmic derivative of the wave function with the correction due to the deviation of the effective potential from the pure hydrogenic form.

In calculating s- as well as p-functions by (1) and (2), Brooks has determined the dependence of δ_l on the energy ϵ by straight forward extrapolation from the free atom term values for both s- and p-levels. For s-levels, $l=0$, the straightforward extrapolation of δ_0 is legitimate and nearly linear in most cases. For $l\gtrless1$, however, Ham[5] has pointed out that the straight-forward extrapolation of δ_l is often not adequate. Instead of δ_l the quantity η_1, which is related to δ_1 by

$$\tan(\eta_1\pi) = \frac{\tan(\delta_1\pi)}{1+\epsilon}, \tag{3}$$

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[1] J. H. Van Vleck and T. S. Kuhn, Phys. Rev. **79**, 382 (1952).
[2] H. Brooks, Phys. Rev. **91**, 1027 (1953).
[3] E. P. Wigner and F. Seitz, Phys. Rev. **43**, 804 (1933).
[4] K. Fuchs, Proc. Roy. (London) **A151**, 585 (1935).
[5] F. Ham (private communication).