

Measurement of the Thermoelectric Power of Germanium at Temperatures above 78°K†*

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A systematic investigation of the thermoelectric power of germanium samples has been made in the temperature range between 78°K and about 925°K. The general method of measurement is the determination, through thermocouple readings, of the ratio $\Delta E/\Delta T$, where ΔE is the thermal emf (relative to chromel) measured between two points in the sample having a temperature difference ΔT . At first, difficulty was experienced in obtaining reliable and reproducible thermoelectric power data at the lower temperatures (78°K to about 350°K). A detailed discussion is given of the steps taken to eliminate this difficulty by reducing or removing the effects of thermal conduction by the thermocouple wires, convection currents around the sample, poor contacts between thermocouple junctions and the sample, and inhomogeneities in the thermocouple wires. In the impurity range the sign of the thermoelectric power is the sign of the Hall coefficient, and the magnitudes of thermoelectric power, resistivity, and Hall coefficient increase with decreasing impurity content. With rising temperature the thermoelectric power increases in magnitude and passes through an extremum at a temperature somewhat lower than that corresponding to the end of the exhaustion range or flat portion of the Hall curve. The thermoelectric power of a *p*-type sample passes through zero at a temperature higher than that at which the Hall coefficient of the same sample becomes zero. The thermoelectric power curves of both *p*-type and *n*-type samples approach a common curve, having negative values, in the intrinsic range.

I. INTRODUCTION

EARLY investigations¹⁻⁴ of the electrical properties of the elements silicon, germanium, and tellurium showed them to be quite different from the metals and to belong in the category now referred to as semiconductors. Occasional studies of thermoelectric power were included in the general search for information about the electrical properties of these semiconductors.

Wick⁵ measured the resistivity, Hall coefficient and thermoelectric power of two different silicon samples and found negative⁶ values for both the Hall coefficient and the thermoelectric power, measured with respect to copper. Zimmerman⁷ observed that silicon may show either positive or negative thermoelectric power with respect to copper. Smith⁸ found that silicon samples having positive Hall coefficients have positive thermoelectric powers and that negative thermoelectric powers accompany negative Hall coefficients. Buckley⁹

measured several electrical properties of each of four silicon samples as the temperature varied between 0°C and 100°C. He pointed out the variation from one silicon sample to another, even when cut from the same melt, is such that correlation between different electrical properties should be expected only when the properties are measured for the same sample.

Bidwell¹⁰ studied the temperature variation of resistivity and thermoelectric power of a sample of 99.9 percent pure germanium. Haken¹¹ investigated several properties of tellurium including thermoelectric power and the variation of thermoelectric power with known additions of tin and antimony to the tellurium. Wold¹² made a rather complete investigation of the electrical properties, including thermoelectric power, of tellurium samples at temperatures between 0°C and the melting point.

The experiments reported by the authors in this paper were undertaken, starting in 1942, because, with the preparation of germanium samples with controlled amounts of various impurity additions at the Purdue laboratories, it became possible to investigate systematically over a wide temperature range the dependence of thermoelectric power upon the impurity content of the sample and to correlate these data with other electrical properties, especially the Hall coefficient and resistivity.¹³

II. METHOD OF MEASUREMENT

A. General Method

The general method of measuring thermoelectric power may be described as follows. A temperature

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* The investigations reported here are based in part upon doctoral theses submitted to the Faculty of Purdue University by A. E. Middleton and W. W. Scanlon.

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¹ J. Königsberger and K. Schilling, *Ann. Physik* **32**, 179 (1910).

² K. Baedeker, *Die Elektrischen Erscheinungen in metallischen Leitern* (F. Vieweg und Sohn, Braunschweig, 1911).

³ J. Königsberger and G. Gottstein, *Physik. Z.* **14**, 232 (1913).

⁴ J. Königsberger and G. Gottstein, *Ann. Physik* **47**, 566 (1915).

⁵ F. G. Wick, *Phys. Rev.* **25**, 382 (1907); **27**, 76 (1908).

⁶ The thermoelectric power is defined to be positive if conventional current flows from the semiconductor to the reference metal at the cold junction. This convention produces agreement between the sign of the thermoelectric power and the sign of the charge carriers in an impurity semiconductor.

⁷ C. I. Zimmerman, *Trans. Am. Electrochem. Soc.* **15**, 395 (1909).

⁸ A. W. Smith, *Phys. Rev.* **30**, 1 (1910).

⁹ O. E. Buckley, *Phys. Rev.* **4**, 482 (1914).

¹⁰ C. C. Bidwell, *Phys. Rev.* **19**, 452 (1922).

¹¹ W. Haken, *Ann. Physik* **32**, 291 (1910).

¹² P. I. Wold, *Phys. Rev.* **7**, 169 (1916).

¹³ Preliminary measurements were carried out by E. P. Miller, I. Walerstein, and K. Lark-Horovitz.

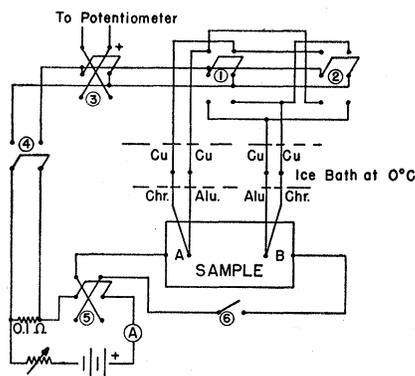


FIG. 1. Electrical circuit for measuring thermoelectric power and resistivity. Switches 4 and 6 are left open while measuring thermoelectric power; closing switch 2 upward with switch 1 open permits potentiometer measurement of the thermal emf in the germanium-chromel circuit. With switch 2 open, closing switch 1 upward and then downward gives the two emf's of chromel-alumel couples, the difference of which determines the temperature difference between points *A* and *B*. For resistivity determination, the PD between points *A* and *B* is measured with switches 2 and 6 closed; the PD is measured for both directions of current flow so that any thermal PD may be eliminated by subtraction. The current is found by measuring the PD across a 0.1-ohm standard resistor.

gradient is established in a sample so that the points *A* and *B* have the different temperatures T_1 and T_2 , respectively. Thermocouples (e.g., chromel and alumel) placed at these points are used to measure the temperatures. By use of suitable switching systems (Fig. 1) the thermal emf of the sample with respect to one or the other of the thermocouple wires and the thermal emf of each thermocouple can be measured on a potentiometer. The four thermocouple wires are joined to copper wires leading to the switching system, and the copper-chromel and copper-alumel reference junctions are electrically insulated from one another and placed in an ice-water bath maintained at a uniform temperature of 0°C with the aid of a mechanical stirrer.

The thermoelectric power is found from the relation

$$Q = \Delta E / \Delta T, \quad (1)$$

where ΔE represents the thermal emf produced in the germanium chromel circuit by the temperature difference ΔT between the junctions and $\Delta T = T_1 - T_2$.

One of the switching arrangements indicated in Fig. 1 permits the direct potentiometer reading of the emf ΔE . Other switching arrangements allow the potentiometric measurement of the thermal emf E_1 in the chromel-alumel couple with junctions at T_1 and 0°C and likewise the measurement of the thermal emf E_2 in the other chromel-alumel couple with junctions at T_2 and 0°C . From the values E_1 and E_2 one can determine, with the aid of National Bureau of Standards calibration data for chromel-alumel thermocouples, the average temperature $T_a = (T_1 + T_2)/2$ and thence q_a , the thermoelectric power of a chromel-alumel thermocouple at T_a . This information permits determination

of the temperature difference ΔT by the relation

$$\Delta T = (E_1 - E_2) / q_a. \quad (2)$$

Thus, the thermoelectric power of the germanium sample, relative to chromel, at the temperature T_a is computed from the equation

$$Q(T_a) = (q_a \Delta E) / (E_1 - E_2), \quad (3)$$

a quantity determined by three potentiometer readings and the quantity q_a taken from appropriate calibration tables. When advance-manganin, copper-constantan, or platinum-platinum rhodium thermocouples were substituted for the chromel-alumel couples, the same technique was employed and the $Q(T_a)$ values obtained from Eq. (3) were corrected to give readings relative to chromel.

For measurements above room temperature the samples were placed in a cylindrical electric heater which was closed at both ends to reduce convection currents. Because of the relative ease of establishing parallel isothermal planes in the sample and its surrounding medium at high temperatures, reproducible values of Q as a function of temperature were readily obtained independently of sample size, temperature gradient, or method of mounting the thermocouples on the sample.

At low temperatures, however, since the thermal gradient above the surface of liquid air in a Dewar flask was used to provide a variable range of sample temperatures, considerable difficulty was encountered in the earlier stages of this work in obtaining reliable thermoelectric power values. These difficulties called for careful consideration of certain aspects of the experimental procedure.

B. Problems of Measurement at Low Temperatures

The principal source of error in the measurement of Q occurs in the measurement of the difference in temperature between the points *A* and *B* on the surface of germanium. This difference is usually about 2°C so that the temperature difference should be known to within 0.1°C to determine Q to within five percent.

Investigations of precision thermometry with thermocouples¹⁴ have indicated the following conditions that must be met in measurements of surface temperatures: (1) since the emf of a thermocouple measures the temperature of the junction at *A* or *B*, the junction should have the same temperature as the germanium surface at the point of contact; (2) the thermocouples should not distort the established isotherms in the vicinity; and (3) the thermocouple wires should be uniform in composition and reproducible in calibration.

In the earlier low temperature experiments large thermal gradients due to convection currents occurred

¹⁴ American Institute of Physics Symposium, *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1941), pp. 180-316, 855-861.

near the sample surfaces. The resulting heat conduction in the thermocouple wires caused the junctions to assume temperatures intermediate between the surface temperature of the sample and the temperature of the surrounding medium a short distance away. This produced errors in the values of ΔT . The emf of a thermocouple is governed by the temperature of the junction at the point where the two wires leave it; for a large junction this temperature may be several tenths of a degree different from the temperature at the point where the junction contacts the sample. Thus the ideal junction is very small, and one aims at maximum heat conduction between the junction and sample and minimum heat conduction between the junction and its leads. These conditions can be approached by using thermocouple wires of very small cross section and by use of thermal insulation placed around the sample junction and a short section of lead wires.

The use of fine wires may introduce errors due to non-uniformity of the thermocouple wires. Samples of wire were tested for uniformity by moving a hot soldering iron along its length and measuring the emf developed; a discontinuity in emf appears when the iron touches a "junction" due to an inhomogeneity in the wire. This test led to the rejection of No. 40 chromel-alumel wires as too inhomogeneous, the acceptance of No. 36 chromel-alumel wires and No. 36 copper-constantan wires as sufficiently uniform, and also the acceptance of a special lot of one mil and two mil advance-manganin wires.

Sets of "matched" thermocouples were made to avoid errors due to non-uniformity between the two couples. The two junctions to be placed in contact with the sample were formed from as nearly identical material as possible by taking a long, homogeneous piece of each kind of thermocouple wire to be used, cutting them, and welding these freshly cut ends to form the junctions contacting the sample. The four free ends were soldered to copper leads from the switchboard, insulated from one another, bound together with wire, and submerged in the ice-water bath.

The effect of the method of mounting and size of temperature gradient upon the measurement of thermoelectric power may be shown by direct experiment. A germanium sample, ground to the customary shape of a rectangular parallelepiped 0.4 cm \times 0.5 cm \times 2.0 cm, was mounted vertically in the air column above liquid air in a Dewar flask. Two matched thermocouples of No. 36 chromel-alumel were soldered to the germanium surface near the ends of the sample with a minimum amount of solder. Wires of this size were chosen to emphasize the effects observed. An electric heater at the top was used to control the temperature gradient in the sample. The soldered junctions provided excellent electrical contacts and would not slip mechanically as might be the case with pressure contacts. Figure 2 shows the thermoelectric

power curves obtained for this sample for different values of the temperature difference between the contact points. The thermoelectric power curves tend to converge at the higher temperatures, indicating that the measured thermoelectric power above 100°C is not sensitive to the size of the temperature gradient, in marked contrast to the behavior at the lower temperatures. Consideration of heat transfer by convection yields an explanation for the results of Fig. 2 on the basis that convection currents in the air above the liquid air bath cause the thermocouple junctions to have a temperature difference which is at marked variance with the temperature difference between the points of the sample contacted by the thermocouples. The error from this source is dependent on the temperature gradient.

Next, the same sample was mounted in a horizontal position so that it lay on an isothermal plane in the Dewar flask and thus convection currents were reduced. The sample was held in position between two graphite blocks by spring pressure; one of the blocks was wound with several turns of No. 36 nichrome wire, insulated from the graphite by asbestos tape, to serve as a heater to produce a temperature gradient in the sample (Fig. 3). With this arrangement there was much less dependence of the thermoelectric power curve upon the temperature gradient. However, errors appeared whenever the heater held the sample temperature 20° or 30° higher than that of the surrounding air; these errors were eliminated by thermally insulating the sample and short sections of thermocouple wires leaving the sample.

The difficulty of thermally insulating the sample was reduced by substituting smaller diameter wires for

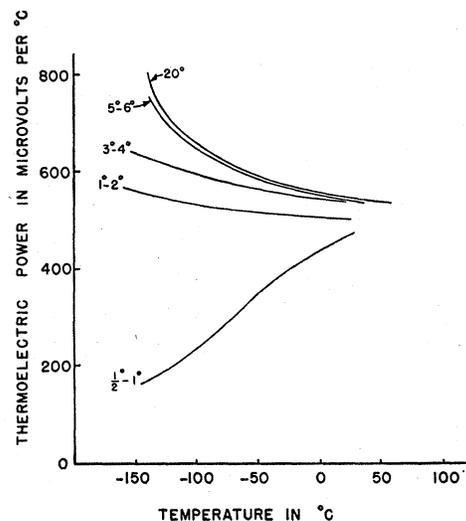


Fig. 2. Measured thermoelectric power for a germanium sample held vertically above the liquid air level in a Dewar flask. Numbers on the curves denote the approximate temperature difference maintained between ends of the sample during measurement.

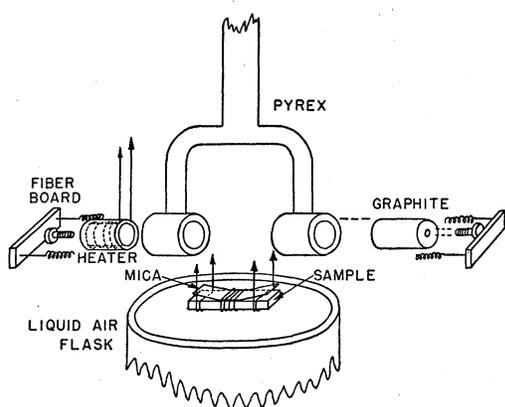


FIG. 3. Low temperature thermoelectric power apparatus. The mica strip bound to the sample is used with silicon, but not with germanium. One- or two-mil advance-manganin thermocouples are used.

the No. 36 thermocouple wires. A special lot of one- and two-mil advance and manganin wires were calibrated and used because this two-mil wire, considering its size and thermal conductivity, conducted about $1/2500$ of the amount of heat that would be conducted by No. 36 chromel-alumel wires under the same temperature gradient. The junction for these fine wires was a flattened bead of silver solder, about 2 mm^2 in area, which held the junction to the sample. With this arrangement thermoelectric power values were independent of temperature gradients within the sample and between the sample and the surrounding air. The high electrical resistance of the fine wires produced difficulty in balancing the potentiometer and consequent random errors in thermoelectric power values.

Another example of the importance of the foregoing precautions is found in thermoelectric power measurements on a group of *p*-type samples with 3×10^{15} , 2×10^{16} , 2×10^{17} , and 5×10^{18} carriers per cm^3 at 300°K . A family of curves was obtained similar to those shown in Sec. 3 (Fig. 5), but the magnitudes of the thermoelectric powers in the impurity range did not agree with the values calculated¹⁵ from the Hall curves of these samples. After introducing the techniques described, the thermoelectric power curves of two of these samples were remeasured, the magnitudes were found to be increased considerably in the impurity range, and agreement between theory and experiment was obtained.

The foregoing discussion can be summarized by saying that the sample holding arrangement (Fig. 3) finally adopted for the low temperature measurements satisfied the requirements of (1) excellent thermal contact between each junction and the sample, (2) horizontal mounting of the sample to reduce convection

current error, (3) smallest feasible values for the cross sections and thermal conductivities of the thermocouple wires, and (4) insulation of the thermocouple junctions from the surrounding air.

C. High Temperature Measurements

Thermoelectric power values at high temperatures (above 100°C) were readily measured. The sample was inserted vertically into a cylindrical electric furnace; the uniformity of the temperature inside this furnace made it unimportant whether the sample was held vertically or horizontally. Both ends of the furnace were closed off to reduce drafts. A small electric heater pressed against one end of the sample provided the necessary temperature gradient. Figure 4 shows the sample holder for high temperature measurements of thermoelectric power.

Holes were ground into the sample near each end, to a depth of about 3 mm, with a $\frac{1}{16}$ -inch nickel tube for a drill and a mixture of No. 600 carborundum and water as an abrasive. Platinum foil was pounded into the bottom of the hole so that good electrical and thermal contact could be obtained between junction and sample. No. 36 chromel-alumel wires were used for the thermocouples. The junctions were welded together and filed off smoothly. Small lavite plugs were used to press the junctions tightly against the platinum in the holes, and the plugs were bound in position by fine wire. The thermocouple wires were wound around the sample several times and insulated with asbestos string. The sample was then placed inside a glass tube with a graphite contact on one end and a heater wound around a graphite core at the other end. Springs outside the furnace pressed the contacts against the sample.

By attaching current leads to the graphite it was possible to make simultaneous determinations of

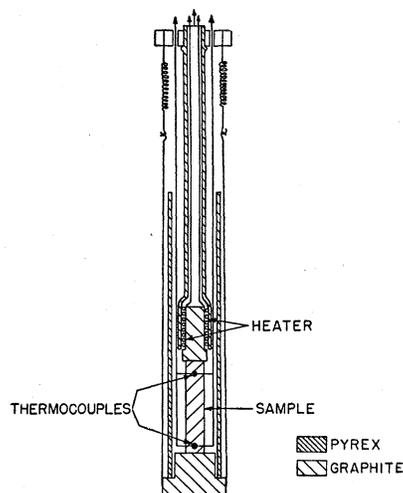


FIG. 4. High temperature thermoelectric power apparatus.

¹⁵ V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **69**, 259 (1946).

thermoelectric power and resistivity. Since no thermal contact problem is involved, the resistivity data obtained with this arrangement were reliable and reproducible over the entire range from -190°C to above 600°C , whereas reliable thermoelectric power data were obtained only at temperatures above 50° or 100°C .

III. RESULTS

Thermoelectric power curves are presented here for those germanium samples for which the precaution described in Sec. 2B were employed in making the low temperature measurements. Figure 5 shows the thermoelectric power curves of four aluminum-doped, *p*-type, polycrystalline germanium samples; the carrier concentration at 300°K ranges from 5×10^{15} per cm^3 to

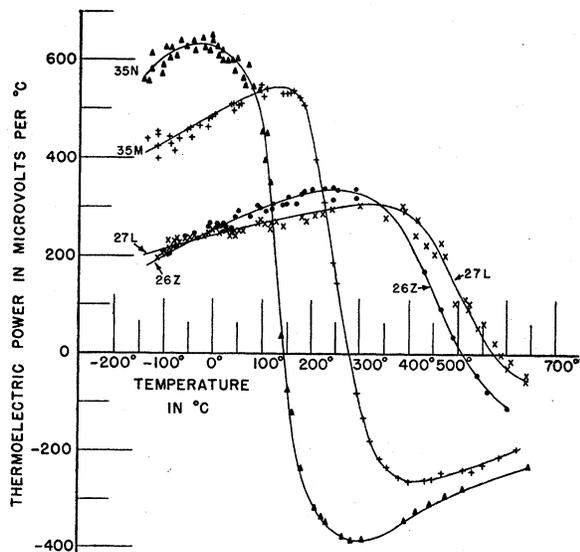


FIG. 5. Thermoelectric power curves for four polycrystalline, aluminum-doped germanium samples. The number of holes per cm^3 , at exhaustion, is 5.6×10^{15} for sample 35N, 1.5×10^{17} for 35M, 4.1×10^{18} for 26Z, and 7.0×10^{18} for 27L.

7×10^{18} per cm^3 . So that the thermoelectric power behavior of these samples may be correlated with their other electrical properties, their Hall curves are given in Fig. 6 and their resistivity curves in Fig. 7. Figure 8 presents the thermoelectric power curves of five antimony-doped, *n*-type, polycrystalline germanium samples with conduction electron concentrations ranging from 3×10^{15} per cm^3 to 7×10^{17} per cm^3 . The Hall coefficients of these samples are given in Fig. 9 and the resistivities in Fig. 7.

Figure 10 shows the effect upon thermoelectric power of a heat treatment used to convert a germanium sample from *n*-type to *p*-type and then back to *n*-type. Sample 21V_a was originally prepared¹⁶ by melting

¹⁶ This sample was prepared by R. M. Whaley of Purdue University and was heat treated by the method recommended by him.

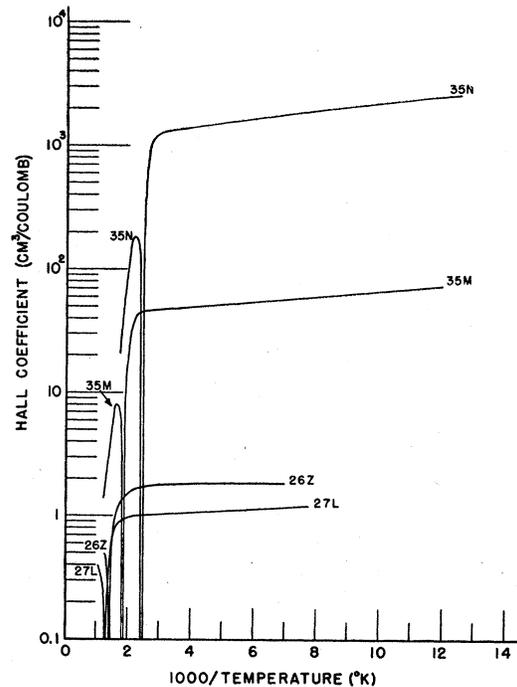


FIG. 6. Hall curves for the four *p*-type germanium samples for which thermoelectric power is given in Fig. 5. Hall values to the right of the zero point of each curve are positive, to the left negative.

spectroscopically pure germanium powder in a commercial helium atmosphere; a polycrystalline *n*-type sample was obtained. This sample could be converted

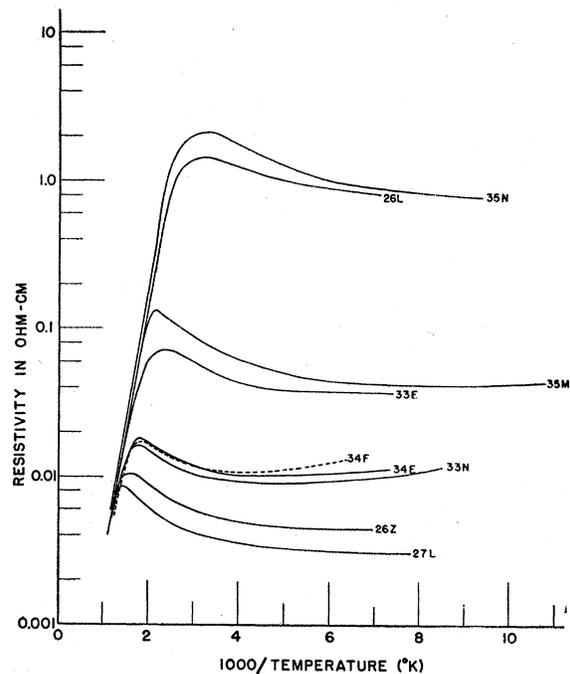


FIG. 7. Resistivity curves for the nine germanium samples for which thermoelectric power curves are given in Figs. 5 and 8.

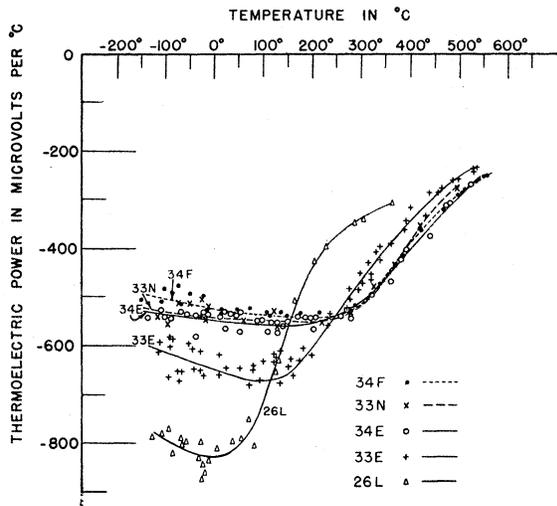


FIG. 8. Thermoelectric power curves for five polycrystalline, antimony-doped germanium samples. The number of conduction electrons per cm^3 , at exhaustion, is 3.4×10^{15} for sample 26L, 9.6×10^{16} for 33E, 5.8×10^{17} for 34E, 7.1×10^{17} for 34F, and 7.4×10^{17} for 33N.

to p type by holding it at 800°C in a high vacuum furnace for four hours. It was converted back to n type by holding it at 500°C in a high vacuum furnace for eighteen hours. Hall coefficient, resistivity, and thermoelectric power curves were measured for this sample (1) in an initial n -type state, (2) after conversion to p type, and (3) after conversion back to n type. Figure 11 gives the resistivity and Hall curves corresponding to the thermoelectric power curves of Fig. 10; the third Hall curve was not obtained because of the accidental destruction of the sample.

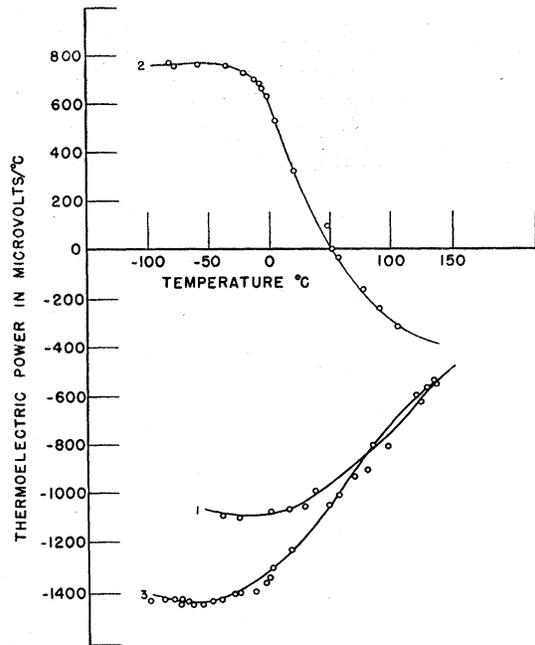


FIG. 10. The effect of heat treatment upon the thermoelectric power of germanium sample 21Va. Curve 1 was taken in the initial condition, curve 2 after holding the sample at 800°C in vacuum for 4 hours, and curve 3 after holding the sample an additional 18 hours in vacuum at 500°C .

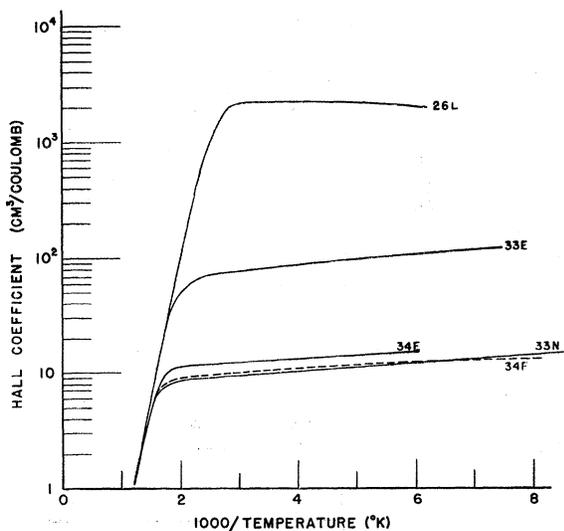


FIG. 9. Hall curves for the five n -type germanium samples for which thermoelectric power curves are given in Fig. 8. All Hall values in this figure are negative.

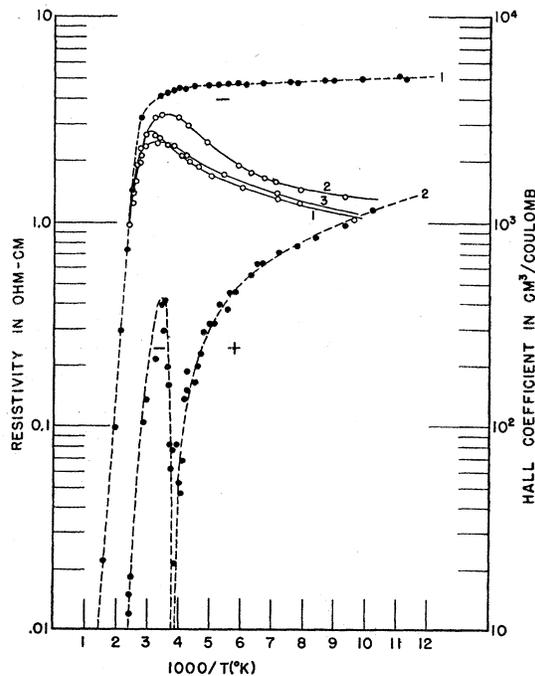


FIG. 11. The resistivity and Hall curves of heat-treated germanium sample 21Va. Curves 1, 2, and 3 correspond to the conditions given for Fig. 10. (The solid lines are resistivity curves and the broken lines Hall curves.)

Two silicon samples, obtained from Bell Telephone Laboratories, were studied. Both were *p* type and polycrystalline, but sample 112 was aluminum-doped and sample 26 G was boron-doped. The high temperature thermoelectric power was measured with an arrangement similar to that of Fig. 4, with quartz replacing glass and with No. 36 platinum-platinum, rhodium thermocouple wires being used. The low temperature thermoelectric power (200°C down to about -100°C) was obtained with the use of one-mil advance-manganin thermocouples and a holder arrangement similar to that of Fig. 3. The thermocouple junctions were pressed against nickel spots electroplated on the silicon to improve electrical contact. Figure 12 shows the thermoelectric power curves obtained for these samples, and Fig. 13 gives the corresponding Hall and resistivity curves.

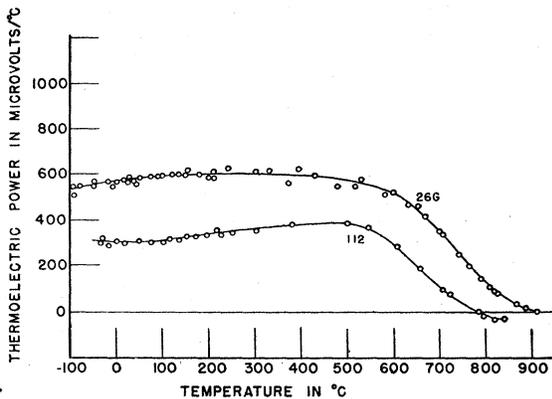


FIG. 12. Thermoelectric power curves for two silicon samples. Both are *p* type; sample 26 G was boron-doped and 112 aluminum-doped.

On the basis of the results presented in Figs. 5 through 13, one can draw the following qualitative conclusions about thermoelectric power behavior:

1. The sign of the thermoelectric power in the low temperature range, where conduction is due to impurity-introduced carriers (impurity range), is the sign of the carrier, i.e., *p*-type samples have positive thermoelectric powers and *n*-type samples negative thermoelectric power. Thus the signs of the Hall coefficient and the thermoelectric power are the same in the impurity range.

2. In the impurity range the magnitudes of thermoelectric power, resistivity, and Hall coefficient increase together with decreasing impurity content and decrease together with increasing impurity content.

3. The thermoelectric power of an *n*-type sample remains negative throughout. Beginning at the low temperature end of the curve, thermoelectric power slowly increases in magnitude with rising temperature and passes through an extremum at a temperature lower by about 50°K than the temperature at which

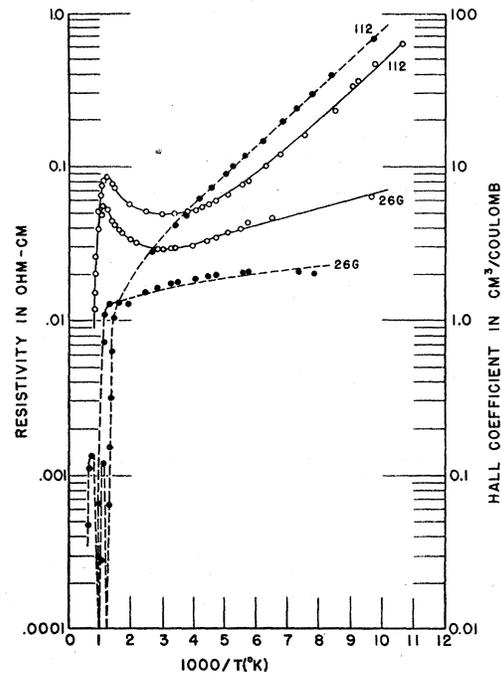


FIG. 13. Resistivity and Hall curves for the two silicon samples for which thermoelectric power curves are given in Fig. 12. (The solid lines are resistivity curves and the broken lines Hall curves.)

the Hall curve of the same sample breaks away from the flat portion characteristic of the exhaustion range. As the temperature continues to rise, the thermoelectric power decreases in magnitude and eventually approaches a curve common to all samples because it is determined by the properties of the intrinsic semiconductor. The magnitude of the extremum thermoelectric power value is roughly proportional to the logarithm of the Hall coefficient in the impurity range, when one compares various *n*-type germanium samples with one another.

4. Beginning at the low temperature end for a *p*-type sample, the thermoelectric power is positive and rises slowly to a maximum as the temperature becomes comparable with the temperature at which the Hall curve leaves the exhaustion range. Then, with rising temperature, the thermoelectric power decreases rapidly and, like the Hall coefficient of a *p*-type sample, changes sign from + to - because of the thermal release of intrinsic electrons and holes and the fact that electron mobility exceeds hole mobility. The thermoelectric power passes through zero at a temperature somewhat above that at which the Hall coefficient becomes zero for the same sample. Then the thermoelectric power passes through a minimum at a temperature considerably higher (by 50° to 150°) than the temperature of the minimum in the Hall curve. Finally, if the temperature range is extended far enough, the thermoelectric power approaches the common curve characteristic of intrinsic germanium. In comparing different

p-type samples with one another, one finds the heights of the maxima roughly proportional to the logarithms of the Hall coefficients in the impurity range and the depths of the minima roughly proportional to the logarithms of the Hall coefficients at the negative maxima.

The authors wish to thank K. Lark-Horovitz for

suggesting this problem and for his continued interest and encouragement during the course of this investigation. They also wish to thank E. P. Miller and I. Walerstein for the use of their preliminary results and equipment and V. A. Johnson for helpful discussions during the progress of the work and for assistance in preparing this material for publication.

Theory of Thermoelectric Power in Semiconductors with Applications to Germanium*

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The thermoelectric power Q of a semiconductor is found by calculating the Thomson coefficient σ_T from electrical and thermal current density expressions and then integrating the relation $\sigma_T = T dQ/dT$. This procedure yields a general expression for Q in terms of the Fermi level, forbidden band width, temperature, ratio of electron to hole mobility, and effective electron and hole masses. In the impurity range the general formula for Q reduces to a simple dependence on the Hall coefficient and temperature if carrier scattering is largely due to the lattice of the semiconductor; the same expression may be used with the addition of a correction term when carrier scattering by impurity ions becomes important at the lower temperatures. When both holes and electrons must be considered as carriers, Q can be evaluated at any temperature from the resistivity and Hall coefficient at that temperature. An expression is also obtained for the thermoelectric power of an intrinsic semiconductor in a form depending on the mobility ratio, forbidden band width at 0°K, and the temperature rate of change of this band width. Hall and resistivity data measured for six polycrystalline germanium samples and two silicon samples have been inserted into the theoretical expressions derived in this paper. The thermoelectric power curves so calculated are found to give generally good agreement with the measured curves.

I. INTRODUCTION

LARK-HOROVITZ, Middleton, Miller, Scanlon, and Walerstein^{1,2} have measured the thermoelectric power curves of a number of aluminum-doped and antimony-doped polycrystalline germanium samples, with carrier densities ranging from 10^{15} per cm^3 to 7×10^{18} per cm^3 . The resistivity and Hall coefficient, as well as thermoelectric power, were measured over a temperature range as wide as 78°K to 925°K for some samples.² The calculations described in this paper were carried out in an attempt to explain the behavior of the thermoelectric power of a semiconducting sample on the basis of its Hall curve and resistivity.

Early theoretical work on the behavior of semiconductors contains references to thermoelectric power.³⁻⁵ However, the results of these authors are not given in

form suitable for comparison with experiment or for prediction of thermoelectric power behavior from measured Hall and resistivity data.

For use in comparison with experiment, a theoretical thermoelectric power expression must be adaptable for application in the impurity, transition, and intrinsic ranges. In the impurity range of temperatures the numbers of intrinsic electrons and holes due to thermal excitation of electrons from the filled band to the conduction band are negligible compared to the number of conduction electrons excited from impurity donor levels (*n* type) or the number of holes formed by ionization of acceptor levels (*p* type). Thus, one need consider, in the impurity range, only one sign of carriers. Many samples show "exhaustion" in the impurity range, i.e., all of the donors or acceptors become ionized and the number of carriers per cm^3 remains effectively constant with temperature rise until intrinsic conduction becomes important. Low resistivity samples may show "degeneracy" at low temperatures,⁶ hence a general theory of the thermoelectric power of semiconductors must provide for the use of Fermi-Dirac statistics where appropriate.

"Transition range" is a suitable term to apply to those temperatures at which one must consider both

* This work was assisted first by a National Defense Research Committee contract with the Purdue Research Foundation and later by a Signal Corps Contract, and was reported in part to American Physical Society meetings at New York in January, 1946 and at Durham, North Carolina in March, 1953.

¹ Lark-Horovitz, Middleton, Miller, Scanlon, and Walerstein, *Phys. Rev.* **69**, 259 (1946).

² A. E. Middleton and W. W. Scanlon, preceding article [*Phys. Rev.* **92**, 219 (1953)].

³ M. Bronstein, *Physik. Z. Sowjetunion* **2**, 28 (1932).

⁴ R. H. Fowler, *Proc. Roy. Soc. (London)* **A140**, 505 (1933).

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