Magnetic Field Dependence of the Seebeck Effect in Germanium

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The thermoelectric power (Seebeck effect) of n -type Ge single crystals has been measured as a function of magnetic Geld at four temperatures ranging from 78'K to 278'K. At all temperatures the magnitude of the thermoelectric power increased with magnetic Geld. Such behavior is shown to be consistent with a simplified model of a semiconductor. It was also observed that to within $\frac{1}{2}\%$ the thermal conductivity of Ge did not change as the magnetic Geld increased from zero to 11 500 oersteds.

INTRODUCTION

A LTHOUGH there has been much work on galvanomagnetic effects in semiconductors, comparatively little has been done on thermomagnetic effects. The present investigation was undertaken to study the thermoelectric power (Seebeck effect) and thermal conductivity of Ge single crystals as a function of magnetic field strength. It was hoped that the results from such research would be useful in the better understanding of the scattering mechanisms which are operative in semiconductor transport properties. A preliminary report' of some of this work has already been given.

EXPERIMENTAL

A number of single-crystal n -type Ge specimens were used in the experiment, but only the results of a typical crystal will be presented. This was an n -type crystal with a resistivity of 7 ohm-cm at 273°K. It was in the form of a rectangular parallelepiped with dimensions 1 mm \times 2.5 mm \times 15 mm. The [111] axis was parallel to the long dimension while the $\lceil 110 \rceil$ axis was perpendicular to the 2.5 mm \times 15 mm face (within 5°). The heat current was parallel to the long dimension of the crystal.

The crystal, with appropriate heaters and thermocouples, was mounted vertically from the top of a vacuum can. During an experimental run the pressure in the can was less than $10⁻⁴$ mm of mercury. The vacuum can was within a glass Dewar flask which fit between the poles of an electromagnet. Magnetic fields up to 11 500 oersteds across a 1-inch gap were supplied by a 6-inch Varian magnet. Calibration of the magnet

TABLE I. Temperature dependences of the thermoelectric power of Ge in zero magnetic field; and the ratio of the change in resistance to the change in thermoelectric power for the same magnetic field. The ratio values are independent of magnetic field strength at any given temperature. $\qquad \qquad \bullet$ 0.01

TУK	$-Q_0 \mu v/^0K$	$(\Delta\rho/\rho_0)/(\Delta Q/Q_0)$
278	1150	15.5
238	1100	15.0
199	1250	13.0
78	1990	3.3

¹ M. C. Steele, Bull. Am. Phys. Soc. Ser. II, 1, 225 (1956).

to within 1% error was made with a Rawson fluxmeter. The fields were perpendicular to the heat current in the crystal, and parallel to the $[110]$ axis.

Data were taken at four temperatures corresponding to convenient fixed points between liquid nitrogen (773'K) and the ice point (273'K). Chromel-constantan thermo couples were used to measure the temperatures along the specimen. By appropriate switching, these thermocouples also served as the voltage probes for measuring the thermoelectric power of Ge referred to either chromel or constantan. Voltages were measured with a $K-2$ potentiometer.

In Fig. ¹ are plotted the results of the relative change in thermoelectric power as a function of magnetic field at 278'K, 238'K, and 199'K. The difference in the thermoelectric power produced by the magnetic Geld is

$$
\Delta Q = Q(H) - Q_0,
$$

where $Q(H)$ is the value in the magnetic field H and Q_0 is the zero-field value at the same temperature. The Q_0 values as a function of temperature are given in Table I. Since $\Delta Q/Q_0$ is a positive quantity, $|Q|$ had increased by applying H . The sign of this change is significant

FIG. 1. Relative change in thermoelectric power of Ge as a function of H at 278°K, 238°K, and 199°K.

FIG. 2. Magnetoresistance of Ge at 273°K, 232°K, and 195°K.

insofar as scattering mechanisms are concerned. This will be discussed below.

At 278°K the change in Q was only 1.5% at 11 500 oersteds. Since the relative error in measuring Q was 0.1% , the observed change is well beyond the uncertainty in the measurement.

Figure 2 shows the corresponding magnetoresistance changes $(\Delta\rho/\rho_0)$ as a function of H. These measurements were made for purposes of comparing the thermomagnetic and galvanomagnetic behavior of a given specimen. It is noted that the shapes of the curves in Figs. 1 and 2 are very similar. In fact, at any given temperature the ratio $(\Delta \rho / \rho_0) / (\Delta Q / Q_0)$ is constant over the entire field range (see Table I). This is rather an unexpected result and suggests the strong interrelation between the two effects.

The results at 78'K are given in Fig. 3. At this temperature saturation effects are already evident in both $\Delta Q/Q_0$ and $\Delta \rho/\rho_0$ at fields above 6000 oersteds.

At each temperature used in this experiment, measurements were made of the thermal conductivity as a function of magnetic field. Up to 11 500 oersteds there was no observable change in the thermal conductivity of Ge. A change of $\frac{1}{2}\%$ would have been within the detectable limit of the experiment. The absence of any magnetic field dependence of the thermal conductivity for a Ge specimen of this resistivity is in accordance with the theoretical work of Tolpygo² and the experimental work of Amirchanov et al^3 Such a result is easily understood when one considers that the electronic contribution to the thermal conductivity of Ge is negligible.

DISCUSSION

It can be shown that with simplifying assumptions, the phenomenological theory of transport effects in semiconductors leads to an expression

$$
\frac{\Delta Q}{Q_0} = \frac{9\pi^2 \left[(4/\pi) - \frac{1}{2} \right]}{64 \left[2 - \left(\frac{\zeta}{k} \right)^2 \right]} \left(\frac{\mu H}{c} \right)^2, \tag{1}
$$

where

$$
\zeta = kT \ln \left[\frac{4\pi^3 n \hbar^3}{(2\pi mkT)^{\frac{3}{2}}} \right] \tag{2}
$$

is the Fermi energy, μ is the carrier mobility, and n is the carrier density. Equation (1) is valid for nondegenerate extrinsic semiconductors (either n or p type) with spherical energy surfaces, when lattice scattering is dominant. All terms in H higher than quadratic have been neglected in deriving Eq. (1). This requires that $(\mu H/c) \ll 1$ for Eq. (1) to be valid. For electrons, ζ is zero at the bottom of the conduction band and has positive values in the conduction band, negative in the forbidden band. For holes, ζ is zero at the top of the valence band with positive values in the filled band, negative in the forbidden band. No account is taken of Q_p , the phonon-drag effect, 4^{-6} in Eq. (1), so that Eq. (1) is valid only at temperatures high enough to neglect that contribution to the thermoelectric power. Actually the field dependence of Q_p should be calculated or established by further measurement in order to say that Eq. (1) is valid even at higher temperatures. Although Q_p is only 5% of Q at $\overline{T} \simeq 300^\circ K$, it is not known what part of $\Delta Q/Q_0$ can be attributed to Q_p .

Although Ge has a multi-ellipsoid electronic band structure, it was thought to be pertinent to compare the results with the simple spherical model. It is expected that a more detailed calculation, utilizing the parameters available from cyclotron resonance, would show the same field dependence but give a different coefficient than that in Eq. (1) . Further, the multiellipsoid calculation would give information on the anisotropy⁷ of the magneto-Seebeck effect which could then be checked experimentally. In the present experiments, no longitudinal magnetic fields were employed.

Equation (1) predicts an increase in the absolute value of Q upon applying a transverse magnetic field. This is in agreement with the sign observed at all temperatures, although one might expect that Eq. (1) would only be valid at the higher temperatures (238'K and 278'K). The results shown in Fig. ¹ do follow an

- ^rJ.I. Kaplan, Phys. Rev. 99, ¹⁸⁰⁸ (1955).
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² K. P. Tolpygo, Tr. Inst. Fiz. An USSR 3, 52 (1952).

³ Amirchanov, Daibov, and Zhuzie, Doklady Akad. Naul U.S.S.R. 98, 557 (1954).

⁴ H. P. R. Frederikse, Phys. Rev. 92, 248 (1953). ^s T. H. Gehalle and G. W. Hull, Phys. Rev. 94, 1134 (1954). C. Herring, Phys. Rev. 96, 1163 (1954).

 $H²$ dependence for fields below 4000 oersteds. At stronger fields, the field dependence approaches a linear law and at very strong values one would expect to see saturation (such as is evident in Fig. 3).

With the same assumptions used to derive Eq. (1) , it can be shown⁸ that

$$
\frac{\Delta \rho}{\rho_0} = \frac{9\pi}{16} \left(1 - \frac{\pi}{4} \right) \left(\frac{\mu H}{c} \right)^2.
$$
 (3)

The validity of the H dependence of Eq. (3), in the appropriate field region, has been established experimentally by several observers. The present results (Figs. 2 and 3) confirm the previous conclusions.

From Eq. (1) and Eq. (3) it follows that the ratio $(\Delta \rho/\rho_0)/(\Delta Q/Q_0)$ would be independent of H. The results of this experiment confirm this at all temperatures and over the entire range of field used. This is both surprising and revealing. It is surprising when it is recalled that Eqs. (1) and (3) are low-field approximations derived with many simplifying assumptions. It is revealing in that it points to the similarity of the two effects even in the saturation region of H .

For strong magnetic fields and other types of scattering, the calculation from Boltzmann's equation becomes quite complicated. Some special cases have recently been considered by Rodot.⁹ He finds for a degenerate semiconductor that

 $(\Delta Q/Q_0) > 0$ for lattice scattering,

while

$$
(\Delta Q/Q_0) < 0
$$
 for ionized-impurity scattering.

Both of these results are applicable over the entire magnetic field range. In addition, at strong fields he finds a saturation effect similar to that given by the simple theory of magnetoresistance.¹⁰ simple theory of magnetoresistance.¹⁰

For nondegenerate extrinsic semiconductors, Rodot only considers the limiting values of Q in zero and infinite fields for both lattice and impurity scattering. However, he does show that lattice scattering still increases $|0|$ while ionized-impurity scattering decreases $|0|$. It is in this sense that experiments on the magnetic field dependence of the Seebeck effect can contribute to an understanding of the transport mechanisms in semiconductors.

At 78'K, the thermoelectric power of Ge (even in the absence of a magnetic field) already has an appreciable phonon-drag contribution.^{4,5} Hence, at this temperature, it is important to consider how the magnetic field changes the phonon-drag effect. From a qualitative viewpoint, one would expect $|Q_p|$ to increase with the application of a magnetic field. The argument proceeds from the knowledge that a magnetic field increases the

FIG. 3. Data at $78^{\circ}K$. The solid circles refer to the change in Q while the solid triangles refer to ρ .

resistance of Ge. This corresponds to decreasing the mean free path of the carriers, and Herring' had shown that Q_p is inversely proportional to the mean free path of the mobile carriers. Hence, Q_p should increase like the magnetoresistance. This dependence could easily explain the saturation effects noted in Fig. 3 for both $\Delta \tilde{Q}/Q_0$ and $\Delta \rho/\rho_0$. This argument has recently been $\Delta Q/Q_0$ and $\Delta \rho/\rho_0$. This argument has recently bee
put into a more analytical form by Herring.¹¹ Furthe work is needed at lower temperatures and for various orientations in order to get the detailed dependence of Q_{ν} on magnetic field. This aspect of the experiment may also have some interesting implications on thermomagnetic effects in metals at low temperatures. For example, it is well known that in the absence of a magnetic field, the phonon-drag effect plays a very small role in the thermoelectric power of either metals or semimetals such as Bi. But the situation may be quite different in strong magnetic fields if the particular material exhibits a large magnetoresistance. Such is the case for Bi at low temperatures. Thermomagnetic experiments¹² on Bi crystals at low temperatures have already shown that $|Q|$ increases 500-fold in a field of 10000 oersteds. Since there was no mechanism advanced to explain those results, it is pointed out here that the phonon-drag effect aided by the magnetic field could possibly bring about such a large effect.

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⁸ See, for example, F. Seitz, Phys. Rev. **79**, 372 (1950).
⁹ M. Rodot, Compt. rend. 243, 129 (1956).
¹⁰ See, for example, F. Seitz, *Modern Theory of Solids* (McGraw Hill Book Company, Inc., New York, 1940), p. 184.

¹¹ C. Herring (to be published in Garmisch Conference Proceedings, 1956). "
¹² M. C. Steele and J. Babiskin, Phys. Rev. 98, 359 (1955).