

Theory of the Ettingshausen Effect in Semiconductors

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The Ettingshausen effect in semiconductors is mainly due to the generation of electron-hole pairs at one side of the sample and their recombination at the other side. The Ettingshausen coefficient is calculated, in agreement with Putley, as $P = (E_g/\kappa e c) z (1+z)^{-2} (\mu_e + \mu_h)$ where $z = (n_h \mu_h / n_e \mu_e)$ —ratio of hole conductivity to electron conductivity. E_g is the gap energy, and κ the thermal conductivity. We discuss this formula for intrinsic, p -type and n -type semiconductors. P goes through a maximum for p -type semiconductors near the temperature at which the Hall voltage goes through zero. Our results agree reasonably well with the measurements of Mette, Gärtner, and Loscoe of P as a function of temperature for different samples of germanium and silicon.

1. INTRODUCTION

IN the presence of a magnetic field H perpendicular to an electric current J_x a thermal gradient is established in a direction perpendicular to both J_x and H . We choose the magnetic field along the z axis, the electric current along the x axis, and the thermal gradient dT/dy along the y axis. The ratio $(dT/dy)/J_x H = P$ is known as the Ettingshausen coefficient. In addition to the thermal gradient a Hall field E_y is also established along y . Early measurements of the Ettingshausen coefficient for metals and semiconductors are given, for example, in the International Critical Tables.¹ We shall measure temperature in degrees Kelvin, magnetic field in gauss, and the current density J in (practical) amperes/cm². In our units the early data give $P \approx -10^{-10}$ deg-cm/amp-gauss for "good metals" like Cu and Ag. On the other hand for the semiconductor Si, $P \approx +250 \times 10^{-6}$ deg-cm/amp-gauss. The usual sign convention for $P > 0$ is shown in Fig. 1. Here the positive current J is towards the right, the magnetic field H is into the paper, and the top surface is hot.

Recent measurements by Mette, Gärtner, and Loscoe^{2,3} on Ge and Si, respectively, (referred to as MGL) confirm the large positive value of the Ettingshausen coefficient for semiconductors. (However, the early measurements¹ give considerably larger value for P .) MGL have made detailed measurements of P

as a function of the temperature and of the impurity content of their samples.

The theory of Ettingshausen effect in metals is developed by Fieber, Nedoluha, and Koch.⁴ Physically we understand the temperature gradient as caused by the dependence of the mean time of collision τ of the carriers (free holes or electrons) on their energy. At a finite temperature the carriers are distributed in certain quasi-continuous energy levels. The $\tau(\epsilon)$ associated with each energy level determines the mean value of the drift velocity $\bar{v}(\epsilon)$ for a carrier in energy level ϵ : namely

$$\bar{v}(\epsilon) = E_x \mu(\epsilon) = E_x e \tau(\epsilon) / m. \quad (1)$$

The mobility is denoted by $\mu(\epsilon)$. In the presence of a magnetic field along z and Hall field E_y along y , the carriers are subject to a force $F(\epsilon)$ in the y direction where

$$F(\epsilon) = e H \bar{v}(\epsilon) / c + e E_y = E_x H e^2 \tau(\epsilon) / m c + e E_y. \quad (2)$$

In the steady state the Hall field will have such a value that will give no net current along y . That is, $F(\bar{\epsilon}) = 0$ for a suitable energy $\bar{\epsilon}$. But the value E_y which make $F(\bar{\epsilon}) = 0$ will certainly leave $F(\epsilon') \neq 0$ for $\epsilon' \neq \bar{\epsilon}$. Since for conductors $\tau(\epsilon)$ is a monotonically decreasing function of energy, we find that carriers of higher energy drift towards negative y and the carriers of lower energy drift towards positive y . (See Fig. 2.) It is this separation of high and low-energy carriers that leads to a heat current along the y axis.

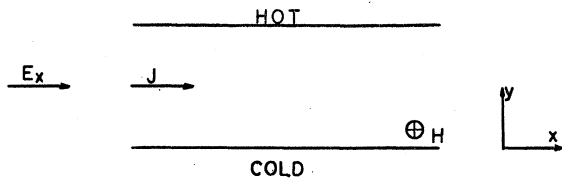


FIG. 1. Sign convention for a positive Ettingshausen coefficient. The top surface is hot when an electric field E_x and positive current J are directed to the right, with a magnetic field H into the paper.

¹ *International Critical Tables* (McGraw-Hill Book Company, Inc., New York, 1929), Vol. 6, p. 419.

² H. Mette, W. W. Gärtner, and C. Loscoe, *Phys. Rev.* **115**, 537 (1959).

³ H. Mette, W. W. Gärtner, and C. Loscoe, *Phys. Rev.* **117**, 1491 (1960).

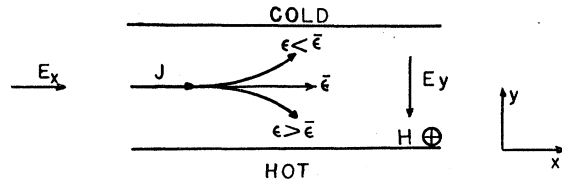


FIG. 2. The Ettingshausen effect for positive carriers. All carriers move towards the right, but due to the combined action of magnetic field H and electric field E_y , the low-energy carriers drift towards the top, and the high-energy carriers drift towards the bottom.

⁴ H. Fieber, A. Nedoluha, and K. M. Koch, *Z. Physik* **131**, 143 (1952).

The case of metals is complicated by the fact that both heat and electricity are transported by the same carriers. However, in semiconductors ordinary thermal conductivity is almost entirely due to the lattice vibrations. When the motion of the carriers in a semiconductor in a magnetic field produces a heat current, this current produces a temperature gradient which in turn creates a lattice heat current equal and opposite to the carrier heat current.

Clearly the magnitude of the heat current from the carriers will depend on the energy spread over which carriers are distributed. In a semiconductor where the energy gap E_g is small, one can produce appreciable numbers of free electrons and holes at temperatures somewhat above room temperature. The present theory is applicable only when a semiconductor has both types of carriers present. Electric current is then carried by the motion of electrons and holes in opposite directions. Figure 3 shows that in the presence of a magnetic field both carriers turn to the top side of the sample. We wish to discuss the simple case in which both electrons and holes have the same time of relaxation; and that their number densities are equal. We expect in this case that the Hall field will be zero. Because of the electric current and magnetic field there will be a constant particle current along y in which the number of holes moving along y will always be equal to the number of electrons moving in the same direction. This cannot go on by itself. We must introduce an additional process of generation of electron-hole pairs at one side G and the inverse process at the other side R . In the absence of any external mechanism the generation and recombination of electron-hole pairs lead to an absorption and liberation of heat from and to the lattice. We estimate the current density for both the electrons and the holes from Eqs. (1) and (2). In the above mentioned simplified case since $n_e = n_h = n$; $\mu_e = \mu_h = \mu$; $E_y = 0$ we have the particle current density towards positive y as $n\mu^2 E_x H / c$. Thus, the heat current due to recombination is $nE_g \mu^2 E_x H / c$. The lattice heat current density Q which will balance the free carrier heat current will be

$$Q = -\kappa \frac{dT}{dy} = -nE_g \mu^2 E_x H / c, \quad (3)$$

$$P = \frac{dT}{dy} (HJ_x)^{-1} = \frac{E_g n \mu^2 E_x H}{c \kappa H e E_x 2 n \mu} = \frac{E_g \mu}{2 e c \kappa}. \quad (4)$$

Here κ is the thermal conductivity and we have written $J_x = e E_x 2 n \mu$ since the electric current density along x is due to both electrons and holes.

It should be noted that since E_g is of the order of 1 ev every electron hole pair that recombines produces a relatively large amount of energy. In the case of metals the fast and the slow carriers have a difference in energy only of the order kT . We, therefore, expect that the magnitude of the Ettingshausen coefficient should be

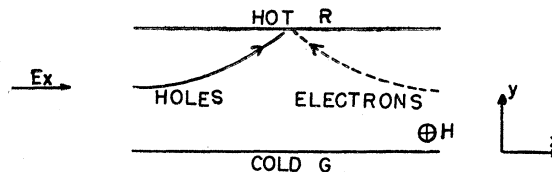


FIG. 3. The Ettingshausen effect for an intrinsic semiconductor. Holes and electrons move in opposite directions due to the electric field E_x , but in the same direction due to the magnetic field H . Electron-hole pairs are generated at the side G , which becomes cold; and recombination of electrons and holes occurs at the side R , which becomes hot.

considerably larger for semiconductors than for metals. In addition to the energy difference, we note that P is inversely proportional to κ , the thermal conductivity, which is larger for metals than for semiconductors. The observed difference in the absolute magnitudes of P in metals and semiconductors is of the order 10^4 .

Our simplified derivation gives the positive sign for P experimentally found for semiconductors.

MGL have examined mostly p -type crystals of Ge and Si. They find a maximum value of P as a function of temperature. A detailed theory given in the next sections gives an excellent qualitative agreement with the experimental results. In this more detailed theory we take into account $n_e(T)$, $n_h(T)$, $\mu_e(T)$, $\mu_h(T)$ as functions of temperature T . Here subscript e refers to electrons and h to holes. We continue to make several reasonable approximations: First, we neglect the dependence of n_e and n_h on position co-ordinate. Second, we neglect the Thomson emf caused by the temperature difference. We further neglect the contribution of electrons and holes to the thermal conductivity.

As we were preparing the final draft of this manuscript, we found a paper by Putley⁵ in which he gives a concise table of equations for the various thermomagnetic and galvanomagnetic coefficients. His formula for the Ettingshausen coefficient is

$$P = -\frac{3\pi kT}{16 e \kappa} \times \frac{(n_e^2 \mu_e^3 + n_h^2 \mu_h^3) - n_e n_h \mu_e \mu_h (\mu_e + \mu_h) (7 + 2E_g/kT)}{(n_e \mu_e + n_h \mu_h)^2}.$$

In our paper we neglect the first term $(n_e^2 \mu_e^3 + n_h^2 \mu_h^3)$ in the numerator: this term is due to variation of mobility with carrier energy ϵ , as discussed above for single-band carriers. We also neglect 7 in comparison with $2E_g/kT$. We assume that recombination of a pair produces only the gap energy E_g , while Putley has included the energy due to the thermal motion of the electron and hole. When these approximations are made, Putley's equation reduces to our Eq. (21) for the general two-band model, and to Eq. (4) for the intrinsic semi-

⁵ E. H. Putley, Proc. Phys. Soc. (London) **B68**, 35 (1955).

conductor with equal electron and hole mobilities. (We note that in his Lorentz-Drude calculation, Putley includes the characteristic factor $3\pi/8$.)

We have not been able to find in the literature a derivation of Putley's equation for P . *Note added in proof.*—We are grateful to Dr. Putley for a reference to his work: T. R. E. Journal, Oct. 1953, pp. 39–81. In this paper we provide a detailed derivation (of Eq. 21), and we also give a physical interpretation of the Ettingshausen effect in semiconductors. We also compare our calculations with the recent experiments of MGL.

We note that our calculation of the Ettingshausen coefficient can be combined with the Bridgman relation to give a calculation of the Nernst-Ettingshausen coefficient. The converse route has been followed by others,^{2,6} i.e., the calculation first of the Nernst-Ettingshausen coefficient, and subsequently of the Ettingshausen coefficient.

2. CALCULATION

In the presence of an electric field E_x along the x axis and a magnetic field H along the z axis a Hall field is produced along the y axis which we denote by E_y . Boltzmann's transport equation for electrons in electric and magnetic fields shown in Fig. 2 can be written as

$$-\left[\frac{\partial f}{\partial v_x} \left(\frac{eE_x}{m} + \frac{ev_y}{mc} H \right) + \frac{\partial f}{\partial v_y} \left(\frac{eE_y}{m} - \frac{ev_x}{mc} H \right) \right] = -\frac{f-f_0}{\tau}, \quad (5)$$

where electronic charge is $-e$, and f is the distribution function.

Assume the solution of (5) to be of the form

$$f = f_0 + v_x f_1 + v_y f_2. \quad (6)$$

Then

$$\begin{aligned} \frac{\partial f}{\partial v_x} &\approx \frac{\partial f_0}{\partial \epsilon} m v_x + f_1, \\ \frac{\partial f}{\partial v_y} &\approx \frac{\partial f_0}{\partial \epsilon} m v_y + f_2. \end{aligned} \quad (7)$$

Substituting (7) and (6) into Eq. (5) and equating coefficients of v_x and v_y we obtain:

$$(\partial f_0 / \partial \epsilon) e E_x - \omega f_2 = f_1 / \tau, \quad (8)$$

$$(\partial f_0 / \partial \epsilon) e E_y + \omega f_1 = f_2 / \tau, \quad (9)$$

where $\omega = eH/mc$. Assuming that $\omega\tau$ is small, we neglect $(\omega\tau)^2$ in comparison with unity, and solve for f_1 and f_2 , as follows

$$f_1 = (\partial f_0 / \partial \epsilon) e E_x \tau [1 - E_y \omega \tau / E_x]. \quad (10)$$

Similarly

$$f_2 = (\partial f_0 / \partial \epsilon) e E_x \tau [\omega \tau + E_y / E_x]. \quad (11)$$

⁶ P. J. Price, Phys. Rev. **102**, 1245 (1956).

The boundary condition is

$$-e \int f v_y \rho d^3 v = J_y = 0 = -e \int f_2 v_y^2 \rho d^3 v. \quad (12)$$

Quantities of interest are

$$J_x = -e \int f v_x \rho d^3 v = -e \int f_1 v_x^2 \rho d^3 v, \quad (13)$$

$$Q_y = \int \epsilon f v_y \rho d^3 v = \int \epsilon f_2 v_y^2 \rho d^3 v. \quad (14)$$

Q_y is the heat current along y and $\rho d^3 v$ is the number of states in the volume element $d^3 v$ in velocity space.

3. APPLICATION TO SEMICONDUCTORS

The formulas developed in the last section are applicable to both the free electrons and holes. Using appropriate signs and mobilities one can calculate their combined effects on J_x , J_y , and Q_y . If only one type of carriers is present as will be the case in n - or p -type semiconductors at room temperature or below, one can use a Maxwellian distribution function and calculate a heat current using Eq. (14) in a straight-forward manner. One will then get a nonzero heat current only if one takes into account the dependence of collision time τ on the energy as discussed in the introduction.

The present paper considers the case of high temperatures where the conduction is due to both the electrons and the holes. It should be noted that when we consider two-band conduction in semiconductors, the dependence of τ on energy becomes much simplified. One can within a very small error associate a mean collision time τ_e with the electrons and τ_h with the holes. The mean energy of the electrons and holes is $E_c + \frac{3}{2}kT \simeq E_c$ and $E_v - \frac{3}{2}kT \simeq E_v$, where E_c and E_v are the energies associated with the bottom and the top of the conduction and valence bands.

Equation (12) under the above assumptions becomes

$$H E_x n_e \mu_e^2 / c + E_y n_e \mu_e = H E_x n_h \mu_h^2 / c - E_y n_h \mu_h, \quad (15)$$

where n_e and n_h are the numbers of free electrons and holes; μ_e and μ_h their mean mobilities: e.g., $\mu_e = e\tau_e/m$. The Hall field E_y is found from Eq. (15):

$$E_y = H E_x (n_h \mu_h^2 - n_e \mu_e^2) / (n_e \mu_e + n_h \mu_h). \quad (16)$$

We can interpret each side of Eq. (15) as an electronic or hole current in a field along y

$$H E_x \mu_e / c + E_y. \quad (17)$$

Thus, each side divided by e denotes the actual number of holes or electrons moving in the positive direction. [See Eq. (2).]

Equation (14) determines the temperature gradient. In semiconductors heat conductivity is largely due to

the lattice. Since Q_y is the heat current due to charged carriers in electric and magnetic fields,

$$-Q_y = -\kappa dT/dy. \quad (18)$$

Using Eq. (17) one finds

$$-\kappa \frac{dT}{dy} = -\left(\frac{E_c - E_v}{e}\right) (HE_x n_e \mu_e^2 / c + E_y n_e \mu_e). \quad (19)$$

Here we have used E_c as the mean energy of free electrons and E_v as the mean energy of holes with $E_c - E_v = E_g$. Ettingshausen coefficient P is defined as

$$P = \frac{dT}{dy} / HJ_x = \frac{dT}{dy} / HE_x (n_e \mu_e + n_h \mu_h) \quad (20)$$

$$= \frac{E_g}{\kappa c} \frac{n_e \mu_e^2}{n_e \mu_e + n_h \mu_h} (1 + E_y c / E_x H \mu_e).$$

Substituting for E_y from (16),

$$P = \frac{E_g}{\kappa c} \frac{n_e \mu_e n_h \mu_h}{(n_e \mu_e + n_h \mu_h)^2} (\mu_e + \mu_h). \quad (21)$$

4. DISCUSSION

Equation (21) gives the Ettingshausen coefficient P in terms of four variables n_e , n_h , μ_e , and μ_h . We consider first the special case of an intrinsic semiconductor where $n_e = n_h$. (Note that any sample behaves like an intrinsic semiconductor at sufficiently high temperatures.) Here we note that P is independent of the number of carriers and we have

$$P = \frac{E_g}{\kappa c} \frac{\mu_e \mu_h}{\mu_e + \mu_h}, \quad \text{intrinsic.} \quad (22)$$

Since μ_e and μ_h are continuously decreasing functions of temperature (μ_h decreasing more rapidly), we conclude that for an intrinsic semiconductor P decreases with the temperature. At sufficiently high temperatures $\mu_e \gg \mu_h$, giving

$$P \approx E_g \mu_h / \kappa c, \quad \text{intrinsic.} \quad (23)$$

Consider next a p -type sample. Here n_h is always greater than n_e . At low temperatures, i.e., below room temperature, we have only free holes and practically no free electrons. The problem is then a one band carrier problem, and our formulas will not be applicable.

At higher temperature there will be some free electrons in the conduction band. As the temperature increases both n_e and n_h will increase. The mobility μ_h decreases faster with the temperature than μ_e . Hence, a variable z defined as $z = n_h \mu_h / n_e \mu_e$ which will be nearly infinite at room temperatures, will become comparable to unity at high temperatures and smaller

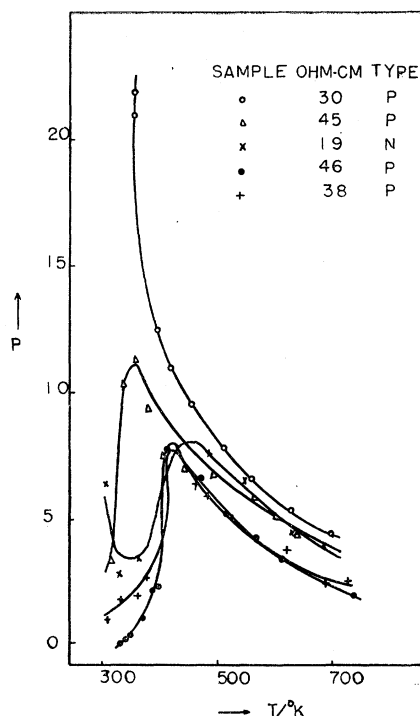


FIG. 4. Measurements of the Ettingshausen coefficient P for five different samples of Ge, by Mette, Gärtner, and Loscoe, reference 2. P is given in units of $\mu\text{deg-cm/gauss-amp}$. The resistivities should read 30, 4.5, 1.9, 0.46, and 0.38 ohm-cm.

than unity at still higher temperatures. Expressing P in terms of z we have

$$P = \frac{E_g}{\kappa c} \frac{z}{(1+z)^2} (\mu_e + \mu_h). \quad (24)$$

Since z varies much more rapidly with temperature than μ_e or μ_h near the region where $z \approx 1$ we approximate P as a function of z only. P then has a maximum near $z = 1$. In terms of the variable z we note from Eq. (16) that the Hall field goes through zero at $z = \mu_e / \mu_h$. Since μ_e / μ_h in this temperature range is of the order unity, we conclude that for a p -type semiconductor there must be a maximum P_{max} in the Ettingshausen coefficient plotted against temperature; and the temperature T_m at which the maximum occurs must lie in the neighborhood of the temperature at which the Hall field is zero. From Eq. (24),

$$P_{\text{max}} = \frac{E_g (\mu_e + \mu_h)}{\kappa c \cdot 4}, \quad (25)$$

which is the maximum value of P for any sample at this temperature.

In n -type semiconductors above room temperature z is always less than unity. At room temperature z is nearly zero, at higher temperature it increases but remains less than unity, and at very high temperatures

z falls as μ_h/μ_e . Thus z as a function of temperature has a maximum value less than unity. Since z goes through a maximum Eq. (24) shows that P must also go through a maximum.

5. COMPARISON WITH THE EXPERIMENTS

Recently Mette, Gärtner, and Loscoe² have measured Ettingshausen coefficients of germanium within a temperature range of 300°K to 700°K. MGL have measured four p -type and one n -type samples of Ge: their results are reproduced in Fig. 4. The purest of the samples (room temperature resistivity equals 30 ohm-cm) does not show a maximum in the Ettingshausen coefficient. Instead, P decreases continuously with increasing temperature. This is to be expected since for the purest sample ($n_h\mu_h/n_e\mu_e \approx 1$ at room temperature. If the temperature is sufficiently high so that $z < 1$, $\mu_h \ll \mu_e$, and $n_h \approx n_e$, then Eq. (24) gives $P \approx (E_g/\kappa e)z\mu_e = (E_g/\kappa e)\mu_h$. This is exactly the behavior of P for an intrinsic sample as given in Eq. (23). Numerical values compare favorably with the experimental values obtained by MGL. An estimate at 400°K shows $P = 19 \times 10^{-6}$ deg-cm/gauss-amp as against their observed value $P = 14 \times 10^{-6}$. (In our estimate we use $E_g/e = 0.75$ volt; $\mu_h/c = 1.05 \times 10^9 T^{-2.33} = 1000$ cm²/volt sec; and $\kappa = 0.4$ watt/deg cm = 0.4×10^8 gauss-cm² amp/sec deg cm.) Variation of P as a function of temperature arises from the dependence of μ_h on temperature which agrees with the experimental observation of the sample of highest purity in the range of 400°K to 700°K: The ratio P_{400}/P_{700} is estimated as $\mu_h(400)/\mu_h(700) = 3.7$, while the observed ratio P_{400}/P_{700} is 3.

With the other three p -type samples, MGL have observed a maximum in the Ettingshausen coefficient. The temperature T_m shifts to higher values as the sample is more and more p type. The theory explains this observation, because if initially the sample has more holes then it will require a much higher temperature for the ratio $n_h\mu_h/n_e\mu_e = z$ to be of order unity. Therefore, T_m will be larger if the sample is impure. The value of P_{\max} will, however, be smaller for the impure sample than P_{\max} for the purer sample because the mobilities will decrease with higher temperature. [See Eq. (25) for P_{\max} .]

The prediction of the present theory that the Hall coefficient changes sign near T_m is confirmed by preliminary experiments of MGL (private communication).

One concludes from Eq. (25) that if a maximum occurs at some temperature for a certain sample, then it is the maximum value of Ettingshausen coefficient for all samples at that temperature. This conclusion does not seem to hold for the p -type Ge samples as measured by MGL: specifically the values of P for the purest sample lie somewhat above P_{\max} for the other p -type samples. This conclusion seems to be valid for p -type Si from the experimental curves of MGL, shown in Fig. 5.

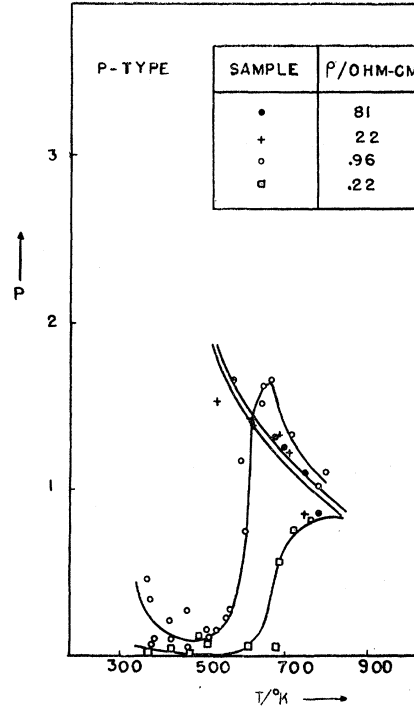


FIG. 5. Measurements of the Ettingshausen coefficient P for four different samples of Si, by Mette, Gärtner, and Loscoe, reference 3. P is given in units of $\mu\text{deg-cm/gauss-amp}$.

The ratio

$$\frac{P_m(\text{Ge})}{P_m(\text{Si})} = \frac{P_m}{P_m'} = \frac{E_g}{E_g'} \frac{\kappa'}{\kappa} \frac{\mu_e}{\mu_e'} \frac{(T_m)}{(T_m')},$$

where the primed and unprimed quantities refer, respectively, to Si and Ge. Comparing results of Ge sample (0.38 ohm-cm room temperature resistivity) and Si sample (0.22 ohm-cm room temperature resistivity) one finds from Figs. 4 and 5 an experimental ratio of $P_m/P_m' = 5$. Using $\kappa'/\kappa = 0.6/0.4$, $E_g/E_g' = 0.74/1.12$ and $\mu_e(450^\circ)/\mu_e'(650^\circ) = 1800/280$ we obtain the theoretical estimate $P_m/P_m' \approx 6.5$, which indicates a reasonable agreement with the experiment. The thermal conductivities are taken from MGL^{2,3}; the Ge mobility $\mu_e(450)$ is from the formula $4.9 \times 10^7 T^{-1.6}$ while $\mu_e'(650)$ is obtained from an extrapolation of Morin and Maita's data.⁷

For lack of experimental data we cannot compare the theory with n -type samples. One expects the maximum in these to be lower than the corresponding maxima for p -type because $z < 1$.

ACKNOWLEDGMENT

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⁷ F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).