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.

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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

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the intrinsic carriers and the carriers released from impurity levels. In this range one allows for the presence of carriers of both signs, but one cannot take the electron density to be equal to the hole density. The term "intrinsic range" is reserved for those temperatures at which the intrinsic electrons and holes completely swamp the carriers from impurity levels. Under this condition the electron density equals the hole density.

The general thermoelectric power expression, which is now obtained, can be put into special forms applicable to the various temperature ranges. These results are then used to calculate thermoelectric power curves to be compared with measured values.

II. GENERAL EXPRESSION FOR THE THERMOELECTRIC POWER

The thermoelectric power is found by obtaining the Thomson coefficient from the thermal and electrical current densities and then integrating the appropriate Thomson relation.[7] When both holes and electrons are present, the electrical (j_x) and thermal (w_x) current densities may be written:

$$j_x=\frac{4\pi e}{3}\int_0^\infty v_1^3 l_1\left(\frac{\partial f_1^0}{\partial x}-eE_x\frac{\partial f_1^0}{\partial \epsilon_1}\right)dv_1 -\frac{4\pi e}{3}\int_0^\infty v_2^3 l_2\left(\frac{\partial f_2^0}{\partial x}+eE_x\frac{\partial f_2^0}{\partial \epsilon_2}\right)dv_2, \quad (1)$$

and

$$w_x=-\frac{4\pi m_1}{6}\int_0^\infty v_1^5 l_1\left(\frac{\partial f_1^0}{\partial x}-eE_x\frac{\partial f_1^0}{\partial \epsilon_1}\right)dv_1 -\frac{4\pi m_2}{6}\int_0^\infty v_2^5 l_2\left(\frac{\partial f_2^0}{\partial x}+eE_x\frac{\partial f_2^0}{\partial \epsilon_2}\right)dv_2, \quad (2)$$

where subscript 1 refers to electrons and subscript 2 to holes. Furthermore, no magnetic field is applied, the electric field intensity and temperature gradient possess only X components, l denotes mean free path, f^0 the unperturbed distribution function, v the carrier velocity, ϵ the carrier kinetic energy ($mv^2/2$), and m the effective mass.

The unperturbed distribution functions are

$$f_1^0=2m_1^3h^{-3}\left\{1+\exp\left(\frac{\epsilon_1-\zeta_1}{kT}\right)\right\}^{-1}, \quad (3a)$$

and

$$f_2^0=2m_2^3h^{-3}\left\{1+\exp\left(\frac{\epsilon_2-\zeta_2}{kT}\right)\right\}^{-1}, \quad (3b)$$

where ζ_1 and ζ_2 are the "partial" Fermi levels. The quantities ϵ_1 and ζ_1 are zero at the bottom of the conduction band and have positive values in the conduction band, negative in the forbidden band. The zeros of ϵ_2 and ζ_2 are at the top of the filled band with positive values in the filled band, negative in the forbidden band. The condition for thermal equilibrium requires that the partial Fermi levels be related to ζ, the Fermi level of the sample, by

$$\zeta_1=\zeta \quad\text{and}\quad \zeta_2=-E_G-\zeta, \quad (4)$$

where E_G is the width of the forbidden band.

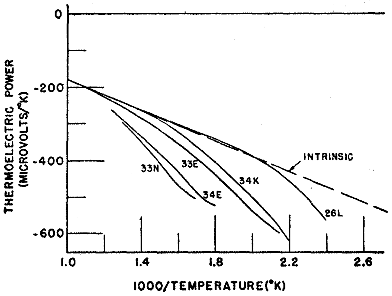

FIG. 1. Thermoelectric power as a function of reciprocal temperature for five n-type, antimony-doped polycrystalline germanium samples. The dashed line is drawn in to approximate the common line approached by all samples as they become intrinsic. The number of conduction electrons per cm^3 at exhaustion is 3.3×10^{16} for 26L, 7.7×10^{16} for 34K, 1.1×10^{17} for 33E, 6.2×10^{17} for 34E, and 8.2×10^{17} for 33N. The three purer samples become intrinsic within the range of investigation and so empirically determine the curve for intrinsic germanium as

$$Q=-86.3(2430°/T-0.34)\ \text{microvolts/°K}.$$

The integrals in Eqs. (1) and (2) are simplified by use of the relations

$$\frac{\partial f_1^0}{\partial x}=-\frac{\partial f_1^0}{\partial \epsilon_1}\frac{dT}{dx}\left\{\frac{\epsilon_1}{T}+T\frac{d}{dT}\left(\frac{\zeta}{T}\right)\right\} \quad (5a)$$

and

$$\frac{\partial f_2^0}{\partial x}=-\frac{\partial f_2^0}{\partial \epsilon_2}\frac{dT}{dx}\left\{\frac{\epsilon_2}{T}-T\frac{d}{dT}\left(\frac{E_G+\zeta}{T}\right)\right\}. \quad (5b)$$

Now Eqs. (1) and (2) may be rewritten as

$$j_x=-\frac{8\pi e}{3m_1^2}\left[\left\{eE_x+T\frac{d}{dT}\left(\frac{\zeta}{T}\right)\frac{dT}{dx}\right\}L_1(1)+\frac{1}{T}\frac{dT}{dx}L_2(1)\right]+\frac{8\pi e}{3m_2^2}\left[\left\{-eE_x-T\frac{d}{dT}\left(\frac{E_G+\zeta}{T}\right)\frac{dT}{dx}\right\}L_1(2)+\frac{1}{T}\frac{dT}{dx}L_2(2)\right] \quad (6)$$

and

$$w_x=\frac{8\pi}{3m_1^2}\left[\left\{eE_x+T\frac{d}{dT}\left(\frac{\zeta}{T}\right)\frac{dT}{dx}\right\}L_2(1)+\frac{1}{T}\frac{dT}{dx}L_3(1)\right]+\frac{8\pi}{3m_2^2}\left[\left\{-eE_x-T\frac{d}{dT}\left(\frac{E_G+\zeta}{T}\right)\frac{dT}{dx}\right\}L_2(2)+\frac{1}{T}\frac{dT}{dx}L_3(2)\right], \quad (7)$$

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[7] See, e.g., F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 174.

TABLE I. Values of electron mobility to hole mobility ratio (c) and temperature variation of forbidden band width (a) found from the measured thermoelectric power curve of intrinsic germanium.

E_0(ev)	$c=\mu_1/\mu_2$	a(ev/°K)
0.70	3.98	-4.43×10^{-4}
0.72	3.80	-4.45×10^{-4}
0.74	3.62	-4.48×10^{-4}
0.76	3.47	-4.52×10^{-4}

where

$$L_j(1)=\int^{\infty}\epsilon^j l_1\frac{\partial f_1{}^0}{\partial\epsilon}d\epsilon \tag{8}$$

and $L_j(2)$ is the corresponding integral containing l_2 and $f_2{}^0$.

These current density equations are used to find the Thomson coefficient σ_T from the expression for the rate of heat development per unit volume:[7]

$$\begin{aligned}dH/dt&=E_xj_x-\partial w_x/\partial x\\&=\rho j_x{}^2-\sigma_Tj_x\frac{dT}{dx}+\frac{d}{dx}\left(\kappa_{el}\frac{dT}{dx}\right),\end{aligned} \tag{9}$$

where ρ is the electrical resistivity and κ_{el}, the portion of the thermal conductivity due to electron transport. The development of dH/dt yields the result

$$\sigma_T=-\frac{T}{e}\frac{d}{dT}\left(\frac{1}{T}\frac{g_1}{g_2}\right)+\frac{T}{e}\left(\frac{g_3}{g_2}\right), \tag{10}$$

where the functions g_1, g_2, and g_3 are defined by

$$g_1=L_2(1)/m_1{}^2-L_2(2)/m_2{}^2,$$

$$g_2=L_1(1)/m_1{}^2+L_1(2)/m_2{}^2,$$

and

$$g_3=\frac{L_1(1)}{m_1{}^2}\frac{d}{dT}\left(\frac{\zeta}{T}\right)+\frac{L_1(2)}{m_2{}^2}\frac{d}{dT}\left(\frac{E_G+\zeta}{T}\right).$$

One of the Thomson relations states that, if Q is the thermoelectric power in a semiconductor-metal circuit with junctions at temperatures T and $T+dT$, the product $T\,dQ/dT$ equals the difference between the Thomson coefficients of the semiconductor and metal. In this derivation, the Thomson coefficient of the metal is taken as zero, and so

$$\sigma_T=T\,dQ/dT \tag{11}$$

is the equation for determining thermoelectric power. Although the following thermoelectric power values are thus found for the semiconductor relative to a metal of zero Thomson coefficient, the values are approximately applicable relative to any metal because metals have σ_T values very much smaller than those of most semiconducting samples. The sign of Eq. (11) is consistent with the convention that the thermoelectric power is positive if conventional current flows from the semiconductor to the reference metal at the cold junction.

III. THE INTRINSIC RANGE

At temperatures high enough that the effects of impurity atoms may be neglected and only intrinsic carriers considered, one can assume that:

(A) Classical statistics apply and the distribution functions of Eqs. (3a) and (3b) may be replaced by

$$f_1{}^0=2m_1{}^3h^{-3}\exp\{(-\epsilon_1+\zeta)/kT\}, \tag{12a}$$

$$f_2{}^0=2m_2{}^3h^{-3}\exp\{(-\epsilon_2-E_G-\zeta)/kT\}. \tag{12b}$$

(B) The only important scattering of carriers is due to the lattice,[8] and hence the mean free paths l_1 and l_2 are independent of the energies ϵ_1 and ϵ_2.

(C) The conduction electron and hole densities are equal, i.e., $n_1=n_2$. Thence,

$$\zeta=-\tfrac{1}{2}E_G-\tfrac{3}{4}kT\ln(m_1/m_2). \tag{13}$$

Assumptions A and B lead to the following values for the integrals appearing in Eq. (10):

$$\left.\begin{aligned}L_1(1)&=-2l_1m_1{}^3h^{-3}kT\exp(\zeta/kT);\\L_1(2)&=-2l_2m_2{}^3h^{-3}kT\exp\{-(E_G+\zeta)/kT\};\\L_2(1)&=-4l_1m_1{}^3h^{-3}(kT)^2\exp(\zeta/kT);\\L_2(2)&=-4l_2m_2{}^3h^{-3}(kT)^2\exp\{-(E_G+\zeta)/kT\}.\end{aligned}\right. \tag{14}$$

Also, when assumptions A and B are valid, the mean free paths can be expressed in terms of the electron and hole mobilities, μ_1 and μ_2, respectively:

$$l_{1,2}=\tfrac{3}{4}\mu_{1,2}(2\pi m_{1,2}kT)^{\frac{1}{2}}/e. \tag{15}$$

Insertion of expressions (14) and (15) into Eq. (10) and simplification yields a Thomson coefficient expression valid at high temperatures:[9]

$$\begin{aligned}\sigma_T=&-\frac{T}{e}\frac{d}{dT}(2k\tanh z)\\&+\frac{T}{e}\left\{-\frac{1}{2}\tanh z\frac{d}{dT}\left(\frac{E_G}{T}\right)+k\frac{dz}{dT}\right\},\end{aligned} \tag{16}$$

where z is defined by

$$z=\frac{\zeta}{kT}+\frac{E_G}{2kT}+\frac{1}{2}\ln\left(\frac{cm_1{}^{\frac{3}{2}}}{m_2{}^{\frac{3}{2}}}\right), \tag{17}$$

in which c denotes the mobility ratio μ_1/μ_2.

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[8] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Verlag. Julius Springer, Berlin, Germany, 1933), Vol. 24, No. 2, pp. 509–521, 558–560.

[9] A similar expression is given in a discussion of the thermoelectric power of tellurium samples by T. Fukuroi and S. Tanuma, Science Repts. Research Insts., Tôhoku Univ., 4, 353 (1952).

For an intrinsic semiconductor, one introduces Eq. (13) into Eq. (17) to obtain $z=\frac{1}{2}\ln c$ and thence

$$\sigma_T=-\frac{T}{e}\frac{d}{dT}\left\{\frac{2k(c-1)}{c+1}\right\}+\frac{T}{e}\frac{k(c-1)}{(c+1)}\frac{d}{dT}\left(\frac{-E_G}{2kT}\right). \quad (18)$$

Now Eq. (11) may be readily integrated to yield for the thermoelectric power

$$Q=-\frac{k(c-1)}{e(c+1)}\left(\frac{E_G}{2kT}+2\right). \quad (19)$$

Both experimental and theoretical considerations[10–14] indicate that E_G varies with temperature in an approximately linear manner:

$$E_G=E_0+aT. \quad (20)$$

Thence Eq. (19) becomes

$$Q=-\frac{k}{e}\frac{(c-1)}{(c+1)}\left(\frac{E_0}{2kT}+2+\frac{a}{2k}\right). \quad (21)$$

This predicts that a plot of Q as a function of the reciprocal of the temperature, in the intrinsic range, should be a straight line with parameters determined by E_0, a and c. Figure 1 shows a plot of Q *vs* $1/T$, at high temperatures, for several of the n-type germanium samples investigated by Middleton and Scanlon.[2] The approach of these curves to a common straight line may be seen; the empirical equation of this line is

$$Q=-\frac{k}{e}\left(\frac{2430°}{T}-0.34\right). \quad (22)$$

One can determine a and c for germanium by comparing Eqs. (21) and (22) and inserting an experimentally determined value[1,12,13,15] of E_0. The results are shown in Table I.

The value of a obtained in this manner is in good agreement with the value obtained for germanium from optical data,[12] but higher than the value found from other data.[11–13] The c values of Table I are much larger than values found by methods[16–18] which employ data taken at lower temperatures (usually 300°K) and which give c between 1.5 and 2.1. Such a temperature difference in c values is to be anticipated if the electron mobility follows the expected $T^{-1.5}$ law[8] while the hole mobility varies with temperature about as $T^{-2.2}$, as has been indicated by recent experiments.[18,19]

IV. THE TRANSITION RANGE

In the transition range, both holes and electrons are present as carriers, but the carriers released by impurities are comparable with those due to intrinsic conduction; thus one cannot take n_1 equal to n_2. However, the temperature is high enough that assumptions A and B and, hence, Eq. (16) are still valid. When Eq. (16) is inserted into Eq. (11) and the integration performed, one obtains

$$\begin{aligned}Q&=-\frac{2k}{e}\tanh z+\frac{k}{e}z-\frac{k}{e}\int\tanh z\frac{d}{dT}\left(\frac{E_G}{2kT}\right)dT\\&\approx-\frac{2k}{e}\tanh z+\frac{1}{eT}\left(\zeta+\frac{E_G}{2}\right)-\frac{E_G}{2eT}\tanh z. \quad (23)\end{aligned}$$

The approximation made in evaluating the integral above is that of taking $\tanh z$ as a slowly varying function of T in comparison with $(d/dt)(E_G/2kT)$. The error from this approximation vanishes at the low temperature end of the transition range, but increases to $\frac{3}{4}(k/e)\ln(m_2/m_1)$ as the sample becomes intrinsic. The measurements of Benedict and Shockley[20] indicate that m_2/m_1 is probably less than 1.6 for germanium. Hence the maximum difference between the exact and approximate forms of Eq. (23) is probably less than 30 microvolts/°C.

Equations (12a) and (12b) can be used to convert Eq. (23) into an expression for calculating the thermoelectric power from the electron and hole densities:

$$\begin{aligned}Q=-\frac{k}{e(n_1c+n_2)}\Bigg[2(n_1c-n_2)-n_1c\ln\left\{\frac{n_1h^3}{2(2\pi m_1kT)^{\frac{3}{2}}}\right\}\\+n_2\ln\left\{\frac{n_2h^3}{2(2\pi m_2kT)^{\frac{3}{2}}}\right\}\Bigg]. \quad (24)\end{aligned}$$

The comparison of measured thermoelectric power with values calculated from Eq. (24) is discussed in Sec. 6.

TABLE II. Dependence of the Hall coefficient factor r, defined as $ne|R|$, and thermoelectric power upon relative proportions of lattice and impurity scattering.

$\frac{\rho_I}{\rho_I+\rho_L}$	$\frac{\rho_I}{\rho_L}$	r	$q=\frac{L_2}{kTL_1}$
0.0	0	1.1781	2.000
0.1	1/9	1.0289	2.379
0.2	1/4	1.0411	2.558
0.3	3/7	1.0650	2.698
0.4	2/3	1.0962	2.809
0.5	1	1.1348	2.947
0.6	3/2	1.1833	3.065
0.7	7/3	1.2475	3.199
0.8	4	1.3399	3.380
0.9	9	1.4963	3.639
1.0	∞	1.9328	4.000

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V. THE IMPURITY RANGE

At the lower temperatures the number of intrinsic carriers is negligible compared to the number of carriers released by impurities. When the terms pertaining to hole conduction are dropped from Eq. (10), one obtains

$$\sigma_T(n\text{-type}) = -\frac{T}{e}\frac{d}{dT}\left\{\frac{1}{T}\frac{L_2(1)}{L_1(1)}\right\} + \frac{T}{e}\frac{d}{dT}\left(\frac{\zeta}{T}\right), \tag{25a}$$

and dropping out the electron-conduction terms in Eq. (10) leaves:

$$\sigma_T(p\text{-type}) = \frac{T}{e}\frac{d}{dT}\left\{\frac{1}{T}\frac{L_2(2)}{L_1(2)}\right\} + \frac{T}{e}\frac{d}{dT}\left(\frac{E_G+\zeta}{T}\right). \tag{25b}$$

Equation (11) may be integrated to yield the results,

$$Q(n\text{-type}) = -\frac{1}{eT}\frac{L_2(1)}{L_1(1)} + \frac{\zeta}{eT}, \tag{26a}$$

and

$$Q(p\text{-type}) = \frac{1}{eT}\frac{L_2(2)}{L_1(2)} + \frac{E_G+\zeta}{eT}. \tag{26b}$$

For most germanium, silicon, and tellurium samples, the carriers obey classical statistics above liquid air temperature. In this case the distribution functions are given by Eqs. (12a) and (12b), and the Fermi level may be related to the carrier density by the equation:

$$\zeta = kT \ln\left\{\frac{n_1h^3}{2(2\pi m_1kT)^{\frac{3}{2}}}\right\}. \tag{27}$$

If most of the carrier scattering is due to the lattice, the mean free path is independent of the carrier kinetic energy, and Eqs. (14) and (27) may be used to obtain

$$L_2(1)/L_1(1) = L_2(2)/L_1(2) = 2kT. \tag{28}$$

Inserting this result into Eqs. (26a) and (26b) produces the expression:

$$Q = \pm\frac{k}{e}\left[2 - \ln\left\{\frac{n_{1,2}h^3}{2(2\pi m_{1,2}kT)^{\frac{3}{2}}}\right\}\right], \tag{29}$$

where the sign of Q is the sign of the carrier. Equation (24), when either n_1 or n_2 is set equal to zero, reduces to Eq. (29).

Under the conditions assumed in deriving Eq. (29), the carrier density is related to the Hall coefficient of the sample, R, by the relation:[21]

$$n = 3\pi/(8e|R|), \tag{30}$$

where R is measured in cm^3/coulomb, e in coulomb, and n per cm^3. When Eq. (30) is substituted into Eq. (29) along with the values of the various quantities, including the free electron mass for $m_{1,2}$, a simple thermoelectric power expression is obtained:

$$Q = \pm(k/e)[\ln(|R|T^{\frac{3}{2}}) - 5.32]. \tag{31}$$

When this expression is valid, the thermoelectric power as a function of temperature may be found from a measured Hall curve which gives R as a function of T; and, conversely, measurement of the thermoelectric power curve gives an approximate determination of the Hall curve and carrier density curve of the same sample.

The assumption of predominant lattice scattering is best satisfied for relatively high purity samples at the higher temperature end of the impurity range. It has been found, especially in germanium, that, with decreasing temperature and increasing impurity content, a substantial portion of the carrier scattering is caused by the randomly distributed impurity ions.[22,23] An approximate correction for the effect of impurity scattering upon the thermoelectric power is based upon the result of Conwell and Weisskopf[22] that the mean free path due to impurity scattering is about proportional to the square of the kinetic energy, whereas Sommerfeld and Bethe[8] have found the mean free path due to lattice scattering (l_L) to be independent of energy. When both kinds of scattering are present, the mean free path l is given by

$$1/l = 1/l_L + 1/l_I. \tag{32}$$

If $l_I = a\epsilon^2$, the energy dependence of l is given by

$$l = \frac{al_L\epsilon^2}{l_L + a\epsilon^2}. \tag{33}$$

This expression enters into the determination of the Hall coefficient so that Eq. (30) should be replaced by

$$n = r/e|R|, \tag{34}$$

where r depends[24,25] on the ratio of a/l_L (or ρ_L/ρ_I) in the manner given in Table II.[26]

The quantity $q = L_2(1)/\{kTL_1(1)\} = L_2(2)/\{kTL_1(2)\}$ also depends upon the relative amounts of lattice and impurity scattering in a manner found by inserting Eq. (33) into Eq. (8); the results of this computation are also given in Table II. When the corrections due to impurity scattering are considered and allowance is made for the difference between free electron mass m_0 effective mass, Eq. (31) is replaced by

$$Q = \pm(k/e)[\ln(|R|T^{\frac{3}{2}}) - \ln r - 7.16 + q + \tfrac{3}{2}\ln(m_{1,2}/m_0)]. \tag{35}$$

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[26] A later paper will describe corrections required in resistivity, thermoelectric power, and Hall effect by the deviation of l_I from a simple ϵ^2 energy dependence.

Since modifications due to using Fermi-Dirac statistics in place of Boltzmann statistics are usually not important above liquid air temperature, thermoelectric power is degenerate semiconductors is not discussed here but will be presented in a later paper.

VI. COMPARISON WITH EXPERIMENT

The theoretical expressions developed in the preceding sections have been compared with the thermoelectric power curves measured by Middleton and Scanlon.[2]

The thermoelectric power curves in the impurity range are calculated by applying Eq. (31), or Eq. (35) where required, to the measured Hall curves of the samples.[2] Equation (35) is used for quite impure samples at relatively low temperatures; m_1 and m_2 are taken equal to m_0, but proper values of r and q are inserted on the basis of analysis[27] of the resistivity curves of the samples.

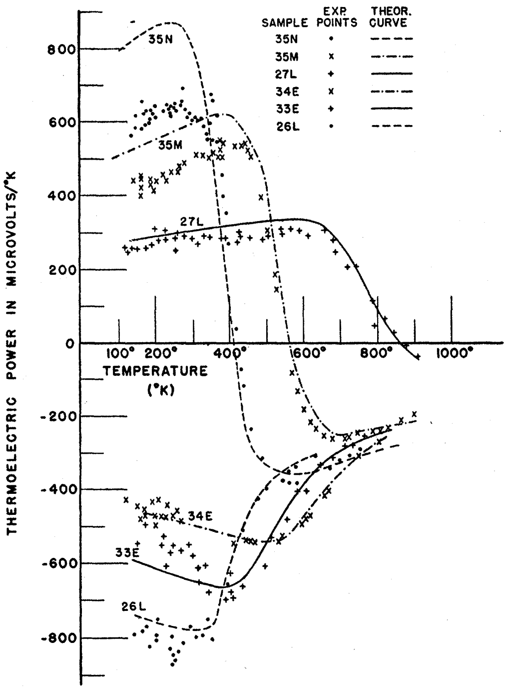

FIG. 2. Comparison of calculated and measured thermoelectric power curves for polycrystalline germanium samples. The smooth curves are calculated, and experimental points are indicated by dots and crosses. The number of holes per cm³ at exhaustion is 5.7×10^{15} for 35*N*, 1.7×10^{17} for 35*M*, and 7.2×10^{18} for 27*L*; the number of electrons per cm³ at exhaustion is 3.3×10^{16} for 26*L*, 1.1×10^{17} for 33*E*, and 6.2×10^{17} for 34*E*.

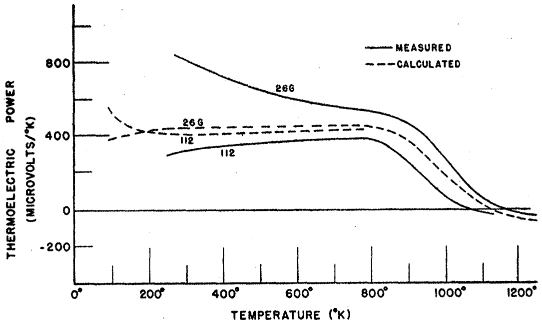

FIG. 3. Comparison of calculated and measured thermoelectric power curves for two *p*-type silicon samples, aluminum-doped 112 and boron-doped 26*G*.

The theoretical curves in the transition range are computed by putting into Eq. (24) values obtained from measured Hall and resistivity curves.[2] The carrier densities n_1 and n_2 are found, for a given temperature, from the values of R and σ (electrical conductivity) at that temperature by using the equations:

$$R = -\frac{3\pi}{8e}\,\frac{n_1c^2 - n_2}{(n_1c + n_2)^2}, \tag{36}$$

$$\sigma = n_1e\mu_1 + n_2e\mu_2 = 1/\rho, \tag{37}$$

and

$$n_2 - n_1 = \pm N, \tag{38}$$

where N is the number of carriers per cm³ in the exhaustion range (the $+$ sign applies to *p*-type samples, the $-$ sign to *n* type). Algebraic elimination of n_1 and n_2 yields expressions for the mobility ratio c:

$$(n\text{-type})\quad 1 - \frac{1}{c} = -\left\{\frac{8R}{3\pi e}\left(\frac{\sigma}{\mu_1}\right)^2 + N\right\}\left(\frac{\sigma}{\mu_1 e} - N\right)^{-1}, \tag{39a}$$

and

$$(p\text{-type})\quad c - 1 = \left\{N - \frac{8R}{3\pi e}\left(\frac{\sigma}{\mu_2}\right)^2\right\}\left(\frac{\sigma}{\mu_2 e} - N\right)^{-1}. \tag{39b}$$

Only lattice scattering is important in the transition range, and so the electron mobility as a function of temperature[8] is given by

$$\mu_1 = BT^{-\frac{3}{2}}, \tag{40}$$

where B is about 1.8×10^7 °K$^{\frac{3}{2}}$ cm²/volt-sec for electrons in single crystal germanium and less for the polycrystalline samples investigated by Middleton and Scanlon. For these polycrystalline samples mobility was extrapolated, following Eq. (40), from values at the high temperature end of the impurity range. The extrapolated mobility and measured R and σ at a chosen T are put into Eq. (39a) or (39b) to determine c at that temperature for the chosen sample. This process yielded c values for germanium, at temperatures in the 600°-900°K range, that averaged to about 3.0. No systematic variation of c with temperature or impurity content was observed. When c has been found, n_1 and n_2 may be evaluated from Eqs. (37) and (38), thus completing

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[27] K. Lark-Horovitz, National Defense Research Committee Report 14-585, pp. 36, Nov. 1945 (unpublished); K. Lark-Horovitz and V. A. Johnson, Phys. Rev. **69**, 258 (1946); K. Lark-Horovitz, Elec. Eng. **68**, 1047 (1949); H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), pp. 58-61 and Figs. 3-7.

the data required for evaluation of thermoelectric power from Eq. (24).

Figure 2 shows a comparison between the measured and calculated thermoelectirc power curves for three n-type, antimony-doped polycrystalline germanium samples and three p-type, aluminum-doped polycrystalline germanium samples. It is apparent that consistently good agreement exists in the transition range, where there is little scatter of the experimental points, and also quite good agreement in the impurity range in view of the rather wide scatter of the experimental points at these lower temperatures.

Figure 3 shows a similar comparison between theory and experiment for two polycrystalline silicon samples, both p type, one (26G) boron-doped and the other (112) aluminum-doped. While there is a fair degree of agreement between theory and experiment, it is not as good as for the germanium samples, perhaps because all measurements on silicon were more difficult than on germanium because pressure contacts were used instead of soldered ones.

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Luminescence Studies of KI-TlI

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The characteristics of the electron traps present in the KI-TlI phosphor have been investigated. Determination of trapping depth and frequency factor yields evidence for representation as a reaction rate process with a division into two distinct trapping systems, while absorption and emission studies indicate a common excited state. Evaluation of concentration and cross section of traps substantiates the above hypothesis.

A. INTRODUCTION

CRYSTALS composed of alkali-halides with small percentages of added thallium-halide have been studied extensively as model impurity-activated phosphors. The original work of Pohl's school[1] and Bünger[2] has been supplemented more recently by that of Garlick[3] and Randall[4] who have also extended studies of the thermoluminescence phenomenon originally investigated by Urbach.[5] The theoretical aspects of the problem, first treated by Seitz,[6] have been advanced quantitatively by Williams.[7] The specific system, potassium iodide-thallium iodide, had been investigated earlier at this laboratory[8] and also by Bonanomi.[9]

A complete analysis of a complex electron-trapping system requires a knowledge of the kinetics involved. For a monomolecular process, the activation energy and frequency factor are required constants for the various trapping levels, as well as the concentration and cross section for trapping under given excitation. Absorption and emission characteristics indicate the processes involved while knowledge of intertrap and nonradiative transitions are necessary to estimate the efficiency of the phosphorescent processes. We have attempted in this investigation to extend the preliminary results previously reported and to discuss certain quantitative aspects of a long-lived phosphorescent system hitherto not mentioned.

B. THERMOLUMINESCENCE STUDIES

If a phosphor is irradiated at a temperature T, the phosphorescent intensity I will be determined by the rate of release of trapped electrons, $-(dn/dt)$, and can be described, for a monomolecular process, by

$$I \propto -(dn/dt) = n/\tau, \tag{1}$$

where the decay time τ is given by

$$\tau = s^{-1} \exp(E/kT). \tag{2}$$

E is the activation energy required to raise the electron from trapped to emitting state, and s is defined as the frequency factor. If the irradiation is stopped after n_0 electrons are trapped and the temperature increased at a rate $\beta = dT/dt$, the emission will continue at a rate

$$dn/dt = -sn_0 \exp\left[-\int_0^T \frac{s}{\beta} e^{-E/kT} dT\right] e^{-E/kT}. \tag{3}$$

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