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Thermoelectric Power of Germanium below Room Temperature*

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The thermoelectric power of germanium single crystals has been measured in the temperature range 10 to 300°K. N-type samples of various impurity content have been investigated. Results show that the thermoelectric power Q decreases with increasing concentration of carriers. A few values of the heat conductivity are also reported.

The conventional theory predicts a relation between the thermal emf and the Hall coefficient. The temperature dependence of the thermoelectric power is in good agreement with this relation at temperatures higher than 200°K. Below this temperature Q rises sharply above the value given by this expression, reaches a maximum of several millivolts per degree near 15°K and decreases again at lower temperatures.

Large deviations may be expected at low temperatures due to the disturbance of the phonon equilibrium. The phonon current has a strong influence on the interaction with electrons and may lead to a maximum in the thermoelectric power at low temperatures. The contribution due to the non-equilibrium of the lattice is proportional to the ratio of phonon and electron mean free path. The former is related to the thermal conductivity while the latter can be derived from electrical data.

I. INTRODUCTION

The thermoelectric power of germanium was measured several years ago by Scanlon and Middleton.[1] These authors investigated both N- and P-type material between 150 and 900°K. The results show within the experimental error good agreement with the theoretical treatment of Johnson and Lark-Horovitz.[2]

The purpose of this investigation was to extend these measurements to single crystals and to lower temperatures. The main problem was: to what extent is the above theory valid at low temperatures?

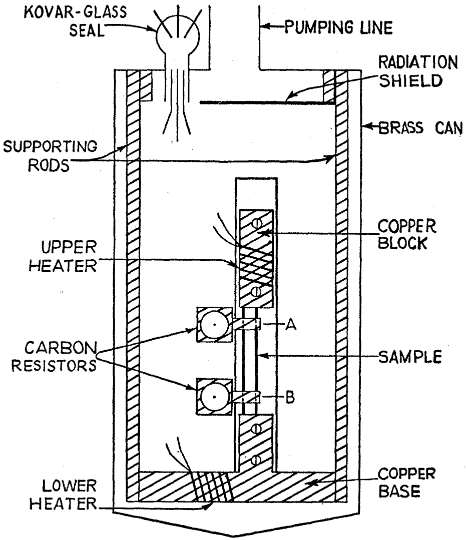

Fig. 1. Apparatus.

The results have led to a re-examination of the present theory of thermoelectric power in semiconductors. This theory contains the same assumption that Bloch[3] made for the case of metals, namely, that the lattice is in equilibrium. Peierls[4] has first questioned the general validity of this assumption. A few years later this problem was investigated in detail by Makinson[5] for the case of thermal conductivity in metals. This author shows that the non-equilibrium of the lattice has an important influence in Bi between 10 and 30°K. Gurevich[6] has made similar calculations for the thermoelectric power in metals. He describes the influence of the phonon current on the electrons as a carrying of the electrons by the lattice waves. In insulators and semiconductors where most of the heat is transported by the lattice vibrations, this effect is even larger.

It will be shown that the disturbance of the lattice vibrations leads to an additional term in the expression for the thermoelectric power of semiconductors, which plays an important role at low temperatures.

II. SAMPLES

The six samples studied are antimony-doped (N-type) germanium single crystals with different impurity content. All samples were cut from large crystals which were prepared by L. Roth of this department. The resistivities at room temperature for the six samples are indicated in Fig. 2. The surfaces of the samples were ground; the cross section is about 1×2.5 mm, while the length varies between 15 and 25 mm.

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[1] Lark-Horovitz, Middleton, Miller, Scanlon, and Walerstein, Phys. Rev. **69**, 259 (1946); W. W. Scanlon, Thesis, Purdue University, 1948 (unpublished).

[2] V. A. Johnson and K. Lark-Horovitz, Phys. Rev. **69**, 259 (1946); National Defense Research Council Report No. 14—585, 1946 (unpublished).

[3] F. Bloch, Z. Physik **52**, 555, 1928; **59**, 208 (1930).

[4] R. Peierls, Ann. Physik **4**, 121 (1930).

[5] R. E. B. Makinson, Proc. Cambridge Phil. Soc. **34**, 474 (1938).

[6] L. Gurevich, J. Phys. (U.S.S.R.) **9**, 477 (1945).

III. APPARATUS

A. Temperature Region 10–85°K

The thermoelectric power is measured with the potential method as used in thermal and electrical conductivity experiments. Figure 1 shows the apparatus.

The sample is soldered vertically between a copper base and a rectangular copper block, which are both mounted on a piece of lavite. Both block and base are provided with a nichrome heater. The upper heater enables the establishment of a temperature gradient along the sample, while the lower heater makes it possible to reach temperatures somewhat higher than the boiling point of the refrigerant. The copper base is suspended by means of two copper rods. This entire arrangement is enclosed in a brass can which can be evacuated through a monel pumping tube.

The temperature difference is determined with thermometers at two points (*A* and *B*) about 2 mm from the ends of the sample. In the temperature region 10–85°K Ohmite carbon thermistors (room temperature resistance=570Ω) were used. After removal of the insulation the resistors were embedded in small copper blocks (4×4×10 mm) and electrically insulated by means of cigarette paper and glyptal. The connection with the sample consists of 1-mm copper strips, which are soldered around the germanium specimen at the points *A* and *B*. The solder used is low melting cerroseal.

A copper shield prevents radiation through the pumping line from entering the brass can. All leads leave the can through a kovar-glass seal, except the copper wires leading to *A* and *B*. The thermoelectric power is measured between the latter ones, which are brought out through the pumping line in order to avoid additional thermal emf's.

The vacuum can is immersed in a refrigerant bath. Nitrogen is used for temperatures between 48 and 90°K, hydrogen between 10 and 25°K, and helium below 10°K.

During measurement of the thermoelectric power, the vacuum jacket is evacuated to pressures smaller than 10^{-4} mm of mercury. In order to calibrate the thermometers, a small amount of helium gas is admitted into the can. The temperature of the bath is determined by measuring the vapor pressure.[7]

The resistance of the carbon thermistors is compared with a standard resistance by means of a Leeds and Northrup *K*-2 potentiometer. The corresponding temperature T can be obtained from the calibration curves (log resistance against $1/T$). For the measurement of the thermal emf, a Rubicon thermofree six-dial potentiometer has been employed.

The thermoelectric power has been measured under steady state conditions. The time required to reach this state is of the order of 30 sec at liquid hydrogen temperatures, while it never exceeds 30 min in the liquid nitrogen region.

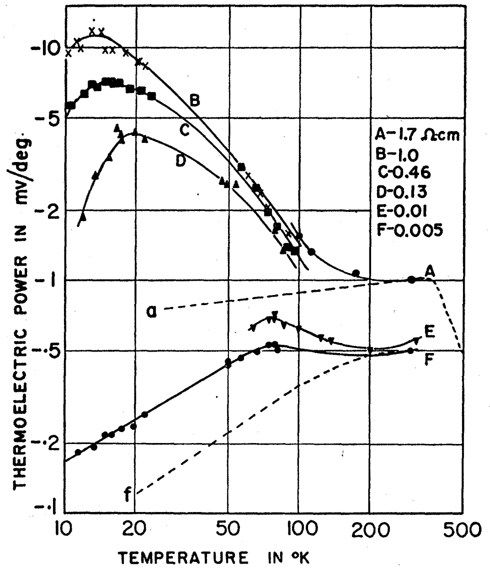

Fig. 2. Thermoelectric power of *N*-type germanium against copper as a function of temperature.

Heat Losses and Errors

The use of 5-mil advance wire to the resistors and 3-mil copper wire to the heater and to the sample makes the heat lost by conduction negligible. The heat leak through the wires is calculated to be 10^{-5} cal/sec, while the heat flow through the sample always exceeds 10^{-2} cal/sec.

The measuring current in the carbon resistors is kept very small ($\sim 10^{-4}$ amp). Taking into account the thermal conductivities of glyptal and copper, the temperature difference between thermometer and sample will be smaller than 10^{-3} degree.

Appreciable temperature gradients across the sample are difficult to obtain at low temperatures due to the high thermal conductivity of germanium (comparable with copper). Around 20°K the thermal resistance of the soldered contacts is much higher than that of the sample. The smallest temperature difference between *A* and *B* is 0.1 degree for which the accuracy of the thermoelectric power is estimated at 10 percent.

B. Temperature Region 78–300°K

The apparatus is essentially the same as the one shown in Fig. 1. Carbon resistors, however, are unsuitable at these temperatures and are therefore replaced by thermocouples. The combination of 5-mil manganin and 5-mil advance wire has been selected. Calibration points have been taken in the liquid nitrogen range, at 90.1°K (boiling point of oxygen), at 194.6°K (sublimation point of CO_2), and at room temperature. Agreement was found with the data of Scanlon,[8] who calibrated these thermocouples between 150 and 900°K.

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[7] Westinghouse Research Report R-94433-2A-1950 (unpublished).

[8] W. W. Scanlon, reference 1, p. 36.

IV. RESULTS

Figure 2 shows the results for the 6 samples *A–F*. Above 200°K these curves fit in very well with the measurements of Scanlon[1] on polycrystalline germanium which cover the temperature range 150–900°K.

Although the apparatus described in this paper was not designed to measure the thermal conductivity with a high degree of accuracy, it is nevertheless possible to estimate the magnitude of this quantity. A few values are given in Table I. The data in the liquid nitrogen range agree fairly well with the very accurate results of thermal conductivity measurements carried out by Goff.[9]

V. DISCUSSION

For a nondegenerate semiconductor (*N*-type), the conventional theory[2] predicts the following relation between the thermoelectric power Q and the Hall coefficient R in the impurity range:

$$\text{(I)}\quad Q=-\frac{1}{e}\left(\text{const}-\frac{\zeta}{T}\right)=-\frac{\kappa}{e}(\ln RT^{\frac{3}{2}}-\text{const}),$$

in which κ = Boltzmann constant and ζ = chemical potential. In order to check this formula, Hall measurements were carried out on the samples A, D and F.[10] The values of Q for sample A as calculated from (I) are indicated by the dashed line *a*. The other samples give similar results. It is clear that good agreement is obtained at temperatures higher than 200°K. Below this temperature all samples show larger values of Q than theoretically predicted, depending on the impurity content.

TABLE I. Resistivity and thermal conductivity of *N*-type germanium.

Samples	Resistivity at room temperature (Ω-cm)	Thermal conductivity (watts/cm °C)				
		20°K	50°K	60°K	70°K	80°K
B	1.0	11.5	7.5	5.1	4.2	3.5
C	0.46	10.5	—	5.1	3.5	2.9
D	0.13	10.5	—	4.7	3.3	2.7
F	0.005	4.7	4.2	3.3	3.0	2.3

Sample F has a degeneracy temperature of 55°K. The above formula therefore cannot be applied in this case at low temperatures. Johnson[11] has calculated the thermal emf using Fermi-Dirac statistics taking both impurity and lattice scattering of the electrons into account. The dashed line *f* represents the results.

An attempt has been made to explain the large values of the thermoelectric power at low temperatures. In the next section an expression for Q will be derived taking into account the deviation of the phonon distribution from its equilibrium value.

Electron-Phonon Interaction

Let us consider the semiconductor under the influence of a temperature gradient (in the x direction) and an electric field. A dynamic equilibrium is established through the interaction of electrons and phonons.

The following scattering mechanisms can occur:

- I. *a.* electron—phonon
  - *b.* electron—impurities;
- II. *a.* phonon—phonon
  - *b.* phonon—impurities
  - *c.* phonon—electrons
  - *d.* phonon—boundaries.

Under equilibrium conditions, the classical distribution function for the electrons is given by

$$f_0=\exp[-(E-\zeta)/\kappa T], \tag{1}$$

where E = kinetic energy of the electron ($\epsilon=E/\kappa T$).

The phonon distribution is represented by

$$N_0=1/(e^z-1), \tag{2}$$

where $z=h\nu/\kappa T$ and $h\nu$ = energy of the phonons.

Under the influence of the external forces, f and N will deviate from their equilibrium values and can be developed according to Fröhlich in spherical harmonics:

$$f=f_0+f_1=f_0+c(k)\frac{k_x}{\kappa T}\frac{\partial f_0}{\partial\epsilon}; \tag{3}$$

$$N=N_0+N_1=N_0+b(q)\frac{q_x}{\kappa T}\frac{\partial N_0}{\partial z}, \tag{4}$$

where $\mathbf{k}$ = electron wave vector and $\mathbf{q}$ = phonon wave vector.

The conditions for a steady state are given by the Boltzmann equations:

$$(\partial f/\partial t)_{\text{coll}}=-(\partial f/\partial t)_{\text{drift}}, \tag{5a}$$

$$(\partial N/\partial t)_{\text{coll}}=-(\partial N/\partial t)_{\text{drift}}. \tag{5b}$$

The solutions f and N can be substituted into the formulas for the electric current density and the heat current density of the electrons which are respectively given by:

$$J=-\frac{e}{4\pi^3}\int v_x f d^3k; \tag{6}$$

$$W=\frac{1}{4\pi^3}\int v_x E f d^3k. \tag{7}$$

From (6) and (7) expressions for the electrical conductivity σ, the thermal conductivity of the electrons λ_e, and the thermoelectric power Q can be derived.

We now proceed to the solution of Eqs. (5a) and (5b). In treating the perturbations of N_0, we will limit ourselves to the case of rather pure crystals, so that the

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[9] J. F. Goff, Thesis, Purdue University, 1953 (unpublished).

[10] I want to thank Dr. Finlayson and Mr. Fritzsche for performing these measurements.

[11] V. A. Johnson and K. Lark-Horovitz, Bull. Am. Phys. Soc. **28**, No. 2, 32 (1953).

scattering of phonons by electrons and impurities may be neglected.

It will be assumed that the phonon-phonon processes (IIa) can be described by a mean free path $l_{ph}(q)$ which is defined by

$$(\partial N/\partial t)_{\mathrm{coll}}=-sN_1/l_{ph}(q), \tag{8}$$

where s = velocity of sound.

When the external force is a temperature gradient, the parameter $b(q)$ can be calculated from (5b) with the result[12]

$$b(q)=-\frac{\hbar s}{T}l_{ph}(q)\frac{dT}{dx}. \tag{9}$$

The collisions of electrons and phonons (Ia) result in transitions in the state of the electron gas under absorption or emission of lattice quanta. These processes can be represented by

$$\mathbf{k}'=\mathbf{k}+\mathbf{q}_a,\quad E(\mathbf{k}')=E(\mathbf{k})+h\nu; \tag{10a}$$

$$\mathbf{k}''=\mathbf{k}+\mathbf{q}_e,\quad E(\mathbf{k}'')=E(\mathbf{k})-h\nu. \tag{10b}$$

The change of the number of electrons $f(\mathbf{k})$ due to collisions with phonons becomes in the case of semiconductors:

$$\left(\frac{\partial f}{\partial t}\right)_{e\varphi}=\Phi_k\sum_{\mathbf{q}}[(1+N_q)f(\mathbf{k}+\mathbf{q}_a)-N_qf(\mathbf{k})$$
$$+N_qf(\mathbf{k}+\mathbf{q}_e)-(1+N_q)f(\mathbf{k})], \tag{11}$$

where Φ_k = transition probability $=C/NMsk$,[13] C = constant, M = atom mass, and N = number of atoms. Substitution of (3) and (4) in (11) gives the result

$$\left(\frac{\partial f}{\partial t}\right)_{e\varphi}=\frac{C}{NMsk\kappa T}\sum_{\mathbf{q}}\frac{1}{e^z-1}\frac{\partial f_0}{\partial \epsilon}q(\cos\beta_a+\cos\beta_e)(c-b),$$

where β_a and β_e are respectively the angles between $\mathbf{q}_a$ and the x axis, and $\mathbf{q}_e$ and the x axis. We can now introduce polar coordinates with the polar axis in the direction of $\mathbf{k}$ and transform the sum over q to an integral. Integration over the aximuth ϕ yields

$$q\int_0^{2\pi}\cos\beta_a d\phi+q\int_0^{2\pi}\cos\beta_e d\phi=-2\pi k_x\frac{q^2}{k^2}. \tag{13}$$

The upper limit for the integration over q is in the case of semiconductors equal to $2k$.[14] Furthermore, e^z-1 can be approximated by $z=h\nu/\kappa T=\hbar sq/\kappa T$. We will also assume for the time being that l_{ph}—and therefore b—is energy independent. Then,

$$\left(\frac{\partial f}{\partial t}\right)_{e\varphi}=-C'kTc\frac{k_x}{\kappa T}\frac{\partial f_0}{\partial \epsilon}+C'kTb\frac{k_x}{\kappa T}\frac{\partial f_0}{\partial \epsilon}, \tag{14}$$

where $C'=4CV/\kappa\pi NMs^2\hbar$ and V = volume of sample.

When $b=0$ $(N=N_0)$, a mean free path can be defined for the electron-phonon interaction. Thus,

$$\left(\frac{\partial f}{\partial t}\right)_{e\varphi}=-\frac{\hbar k}{ml_{e\varphi}}f_1+C'kTb\frac{k_x}{\kappa T}\frac{\partial f_0}{\partial \epsilon}, \tag{15}$$

where

$$l_{e\varphi}=\hbar/C'mT. \tag{16}$$

The scattering of electrons by impurities (I*b*) has been treated by Conwell and Weisskopf.[15] The mean free path for this interaction l_{ei}, is energy dependent. The change of $f(\mathbf{k})$ due to electron-impurity scattering is given by

$$(\partial f/\partial t)_{ei}=-(\hbar k/ml_{ei})f_1. \tag{17}$$

The change of the electron distribution function caused by an electric field F and a temperature gradient dT/dx is

$$\left(\frac{\partial f}{\partial t}\right)_{\mathrm{drift}}=\frac{\hbar}{m}\frac{k_x}{\kappa T}\frac{\partial f_0}{\partial \epsilon}\left\{-eF-T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)-\frac{E}{T}\frac{dT}{dx}\right\}. \tag{18}$$

From Eqs. (5a), (14), (17), and (18) it now follows that:

$$\left(\frac{1}{l_{e\varphi}}+\frac{1}{l_{ei}}\right)kc+\frac{1}{l_{e\varphi}}kb=\left\{-eF-T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)-\frac{E}{T}\frac{dT}{dx}\right\}. \tag{19}$$

$1/l_{e\varphi}+1/l_{ei}$ can be replaced by $1/l_e$, where l_e is the electron mean free path for the case $N_1=0$ (Bloch approximation[3]). l_e can be determined experimentally when the only external force is an electric field.

Equation (19) determines c and therefore f_1. The expression for the electrical and heat current densities are then obtained from Eqs. (6) and (7):

$$J=-\mathcal{K}_1\left\{e^2F+eT\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)\right\}-\mathcal{K}_2\frac{e}{T}\frac{dT}{dx}-\mathcal{K}'e\frac{dT}{dx}; \tag{20}$$

$$W=\mathcal{K}_2\left\{eF+T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)\right\}+\mathcal{K}_3\frac{1}{T}\frac{dT}{dx}+\mathcal{K}''\frac{dT}{dx}, \tag{21}$$

where

$$\mathcal{K}_i=\frac{16\pi m}{3h^3}\int E^il_e\frac{\partial f}{\partial E}dE; \tag{22a}$$

$$\mathcal{K}'=\frac{16\pi m}{3h^3}\int E\frac{l_e}{l_{e\varphi}}\frac{\hbar s}{T}\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}l_{ph}\frac{\partial f}{\partial E}dE; \tag{22b}$$

$$\mathcal{K}''=\frac{16\pi m}{3h^3}\int E^2\frac{l_e}{l_{e\varphi}}\frac{\hbar s}{T}\left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}}l_{ph}\frac{\partial f}{\partial E}dE. \tag{22c}$$

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[12] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (Julius Springer Berlin, 1933), Vol. 24, No. 2, p. 547.

[13] H. Fröhlich, *Elektronen Theorie der Metalle* (Julius Springer, Berlin, 1936).

[14] H. Fröhlich, reference 13, p. 234.

[15] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

The thermoelectric power may be derived from (20) and (21). The result is:

$$Q=-\frac{1}{e}\left(\frac{\mathcal{K}_2}{\mathcal{K}_1 T}-\frac{\zeta}{T}+\frac{\mathcal{K}'}{\mathcal{K}}\right). \tag{23}$$

It follows from (22a) that the first term is a constant. Comparison of this formula with the expression (I) shows that the non-equilibrium of the lattice ($N\neq N_0$) leads to an additional term $\mathcal{K}'/\mathcal{K}_1$.

In the analysis of Q we will begin with the second term. Using the classical chemical potential we find:

$$\frac{\zeta}{T}=\kappa\ln\frac{nh^3}{2(2\pi m\kappa T)^{\frac{3}{2}}}. \tag{24}$$

Hung and Gliessman[16] have shown that in many germanium samples the number of carriers n—as calculated from the Hall coefficient—changes little between 20 and 300°K. The temperature dependence of ζ/T in this region is therefore $(3/2)\ln T$.

Johnson[11] has evaluated the term $\mathcal{K}_2/\mathcal{K}_1 T$ for the two cases where either lattice scattering or impurity scattering predominates, and finds values ranging from 2κ to 4κ.

At very low temperatures Fermi-Dirac statistics has to be used; the first two terms will then be proportional to T.

It is readily seen from (22a) and (22b) that the scattering mechanism for the electrons has its influence also on the third term. When the electrons are mainly scattered by the lattice, $l_e\simeq l_{e\varphi}$ and

$$\frac{\mathcal{K}'}{\mathcal{K}_1}=\tfrac{3}{4}\pi^{\frac{1}{2}}\frac{l_{ph}}{l_{e\varphi}}\left(\frac{2ms^2}{\kappa T}\right)^{\frac{1}{2}}\kappa. \tag{25a}$$

On the other hand, when $l_{e\varphi}\gg l_{ei}$, then $l_e\simeq l_{ei}$ and

$$\frac{\mathcal{K}'}{\mathcal{K}_1}=\frac{35}{32}\pi^{\frac{1}{2}}\frac{l_{ph}}{l_{ep}}\left(\frac{2ms^2}{\kappa T}\right)^{\frac{1}{2}}\kappa. \tag{25b}$$

The essential factor in both expressions is the ratio of phonon and electron mean free paths. Taking $s=5\times 10^5$ cm/sec, the factor $(2ms^2/\kappa T)^{\frac{1}{2}}$ is of the order 1 at $T=1$°K.

The evaluation of l_{ph} is a very complicated problem. Klemens[17] has discussed the different interactions of phonons in a paper concerning the thermal conductivity of dielectrics. Both he and Peierls[18] have shown that the Umklapp processes play a major role at low temperatures. The mean free path for these interactions $l_u(q)$, is inversely proportional to q^2 and contains the factor $e^{\theta/2T}$ (θ=Debye temperature). The quantity l_{ph} is related to l_u. The electrons interact mainly with phonons of low energy; Klemens has shown that for low energy phonons $l_{ph}\sim l_u(q_0)$ where $q_0=\kappa T/\hbar s$. To obtain a value for l_{ph} however, requires extensive data on the thermal conductivity which are still lacking at the moment. A rough estimate shows, nevertheless, that already at 100°K the phonon mean free path l_{ph} is larger than $l_{e\varphi}$, and rises more rapidly than the electron mean free path when the temperature decreases. Thus $\mathcal{K}'/\mathcal{K}_1$ increases with decreasing temperature.

At very low temperatures boundary scattering will become important. The phonon mean free path for this type of scattering is constant and of the order of the crystal size. The electron mean free path, on the other hand, will continue to rise as $1/T$ with decreasing temperature and $\mathcal{K}'/\mathcal{K}_1$ will decrease.

From these considerations the conclusions may be drawn that the third term in the expression for Q(23) will offer an important contribution to the thermoelectric power at low temperatures. The thermal emf will increase with decreasing temperature, then reach a maximum at very low temperature, and tend to zero for $T\rightarrow 0$. This temperature dependence agrees qualitatively with the experimental results.

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[16] C. Hung and J. H. Gliessman, Phys. Rev. **79**, 726 (1950).

[17] P. G. Klemens, Proc. Roy. Soc. (London) **208**, 108 (1951).

[18] R. Peierls, Ann. Physik **3**, 1055 (1929).