

Thermal Conductivity of Germanium from 3°K to 1020°K

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(Received June 10, 1960)

The thermal conductivity of germanium has been measured from 3°K to 1020°K. From 3°K to 300°K a longitudinal heat flow method was used. A radial flow method employing small samples was used from 300°K to 1020°K. The advantages and special experimental techniques required in this radial method are discussed. From 3°K to 10°K the results are explained by a simple combination of boundary plus isotope scattering in which all phonon-phonon processes can be neglected. At all temperatures below 940°K the heat is carried by phonons, but at 940°K a sharp rise in the thermal conductivity indicates the presence of a second conduction mechanism which may be electron-hole pairs.

INTRODUCTION

THE thermal conductivity of germanium at high temperatures has been measured several times by longitudinal heat flow methods. See, for example, McCarthy and Ballard,¹ Pankove,² Ioffe,³ Kettel⁴ and Abeles.⁵ This method has also been used extensively below room temperature by White and Woods,⁶ Carruthers *et al.*⁷ and Geballe and Hull.⁸

This conventional method of measuring thermal conductivity employs a steady-state flow of heat along a rod-shaped sample. A heater is attached to one end of the rod, and the other end is in thermal contact with a heat sink. Two thermocouples are also fastened to the sides or ends of the rod at appropriate points a distance L apart. Under steady-state conditions the heat generated in the heater flows down the rod and establishes a thermal gradient. The thermal conductivity K is then computed from the formula

$$K = QL/A\Delta T, \quad (1)$$

where Q is the heat energy input per unit time, A is the cross-sectional area of the sample, ΔT is the temperature difference between the thermocouples.

Serious errors due to radiation losses can occur in this method at high temperatures, but it is satisfactory at low temperatures. To compensate for these losses one of the two techniques is usually used: (A) One provides one or more radiation shields around the sample. Ideally these shields should fit snugly around the sample. Heaters must be attached to the shield so that the temperature gradient along its length exactly matches that of the sample. (B) An alternate method is to compute the radiation losses from an estimated emissivity of the sample, and combine this with the measured radiation loss of the heater alone. In the present high-temperature

experiment a radial geometry was used in order to eliminate such radiation troubles. In the low-temperature part of the experiment below 300°K the longitudinal method was employed.

THE RADIAL FLOW METHOD

In the radial flow method heat is generated along the axis of a cylinder. It flows radially outward and under steady-state conditions establishes a steady temperature gradient along the radius. See Fig. 1 for a description of the samples. Therefore, a heater wire must be placed along the axis of the cylinder and two thermocouples be placed at different radii. The thermal conductivity is then computed from the formula

$$K = \frac{Q \ln(r_2/r_1)}{2\pi L \Delta T}, \quad (2)$$

where Q is the heat energy input per unit time along the axis of the sample, r_1 and r_2 are the radial positions of the inner and outer thermocouples, respectively, ΔT is the measured temperature difference, and L is the length of the sample.

The advantage of this method for germanium is that radiation loss from the heater is completely eliminated. This method was first reported for solids by Callendar

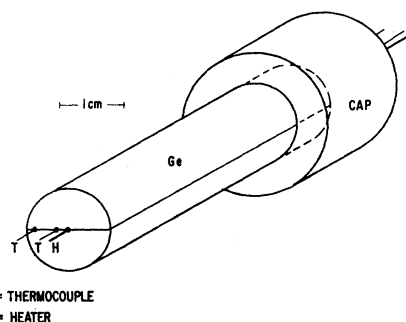


FIG. 1. The radial heat flow method for measuring the thermal conductivity of germanium. The heater wire and the two thermocouples are shown embedded in the split cylinder. One of the two end caps is shown.

¹ K. A. McCarthy and S. S. Ballard, *Phys. Rev.* **99**, 1104 (1955).

² J. Pankove, *Rev. Sci. Instr.* **30**, 495 (1959).

³ A. F. Ioffe, *Can. J. Phys.* **34**, 1342 (1956).

⁴ F. Kettel, *J. Phys. Chem. Solids* **10**, 52 (1959).

⁵ B. Abeles, *J. Phys. Chem. Solids* **8**, 340 (1959).

⁶ G. K. White and S. B. Woods, *Phys. Rev.* **103**, 569 (1956).

⁷ J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A238**, 502 (1957).

⁸ T. H. Geballe and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).

and Nicolson.⁹ Kingery¹⁰ has demonstrated that the radial heat flow from a cylinder will have negligible error from end effects if the length-to-diameter ratio is greater than 12 to 1. By an actual analysis¹¹ of the problem of the finite cylinder it can be shown that an error of less than 0.5% is made if the length-to-diameter ratio is greater than 4 to 1.

Normally most investigators that have used the radial flow method for solids have tended towards large samples, e.g., 15 cm in diameter and 60 cm in length. This is not necessary. As shown here, this method can be used on small samples if sufficient care is exercised. As the sample size is made progressively smaller the thermocouple locations come closer together. Hence large heat inputs are necessary for a reasonable temperature gradient. With the thermocouples close together it is difficult to measure the exact radial distance of each thermocouple from the center. Fortunately the precise location of the thermocouples is not as critical as in the longitudinal flow method, since the radial distances of the thermocouples appear as $\ln(r_2/r_1)$. In the present experiment the uncertainty in this term is about $\pm 20\%$, and accounts for most of the error in the absolute value of K .

EXPERIMENTAL DETAILS

For the radial flow experiments above 300°K a bar of very pure (zone melted, $\rho = 30$ ohm-cm at 300°K, n -type) polycrystalline germanium was carefully ground to 1.27 cm in diameter and cut to about 6.1 cm long. The average crystallite size was measured as 0.2 cm by standard metallographic techniques. The sample was carefully sliced in half lengthwise using a 0.0254-cm thick diamond cutting wheel. The flat surface of each half was carefully polished to remove cutting marks. Thus the two halves fitted together quite well upon assembly. In this manner there is little chance for loss of heat by radiation, conduction, or convection out through the cut. Then three square slots 0.0254 cm wide were cut lengthwise in one of the halves for the center heater, the inner thermocouple, and the outer thermocouple, respectively. The heater was a single strand of nichrome wire, and platinum vs platinum-10% rhodium was used for the thermocouples. These wires were then cemented in their respective slots. Figure 1 shows a drawing of the leads imbedded in the sample. Sauereisen Insalute No. 1 was used for the high-temperature cement. It is a sodium silicate base cement. By careful use of this cement it was possible to avoid contact of the wires with the germanium up to the highest temperatures used. The halves were then assembled and held together using two aluminum oxide ceramic end caps. Stainless steel screws in these caps were used to provide

a radial compression of the sample. The screws were isolated from the sample by platinum spacers resting on germanium. This method held the two halves very tightly together at all temperatures.

In high-temperature work it is very important to avoid low-melting eutectic points. Unfortunately germanium will alloy with many metals at high temperature. This temperature of alloying may be quite low. For example gold and germanium will alloy at 623°K. Nickel and germanium alloy at 1048°K. While no eutectic temperature for platinum and germanium has been reported in the literature, it was discovered that one exists at about 1070°K. For the thermocouples 0.0127 cm platinum vs platinum-10% rhodium wires were used. The thermocouple junction could not be any larger than the wire because of the narrow slot in which the thermocouple was placed. For this reason the junction was gold brazed. Gold near its melting point (1336°K) alloys slightly with platinum, and makes an excellent brazed joint barely discernible from the platinum wire. Silver would also make a useful brazing material but its melting point (1236°K) is only slightly above the melting point of germanium (1210°K).

The heater circuit consisted of a single wire through the center of the cylindrical sample, and this appeared to be the best arrangement. Nichrome wire, 0.0127 cm in diameter, was chosen for the heater wire. This gave a heater resistance of about 1 ohm per cm. The Nichrome was spot-welded to platinum lead wires. Since in this method one only needs the power input per unit length, it was feasible to place the potential leads at the ends of the sample. Since the resistivity of Nichrome does not vary appreciably over a maximum temperature difference of 20°C, the power input per unit length at the middle of the sample is nearly the same as the average value over the whole length. The heater was powered by direct current supplied from an 18-v battery of wet cells.

At room temperature the thermal conductivity of germanium is 0.60 w/cm-deg. For a reasonable temperature difference of about 2°C approximately 6 w/cm must be supplied to the heater. With the power input and simple radiation cooling in air the sample would quickly increase its temperature to about 600°K. Hence in order to obtain room temperature measurements a good heat sink of low thermal impedance is required. It was found that a water cooled bath of silicone oil (G. E. No. SF8140) met this requirement. The oil bath was constantly stirred to keep its temperature uniform. This bath was used for measurements up to 523°K. For thermal conductivity measurements from 573°K to 1020°K the sample was placed in air inside an aluminum oxide tube in a resistance-heated furnace. Even at 1020°K the oxidation of the germanium sample was negligible. The heater power of the furnace and the power delivered to the heater wire in the sample were varied such that a temperature difference of about 2°C was maintained between the inner and outer thermocouples in the sam-

⁹ H. L. Callendar and J. T. Nicolson, British Assoc. Report, 1897; *Encycl. Brit.* 6, 890 (1910-11), 11th ed.

¹⁰ W. C. Kingery, *J. Am. Ceram. Soc.* 37, 88 (1954).

¹¹ H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Clarendon Press, Oxford, 1959), 2nd. ed., No. VIII, p. 221.

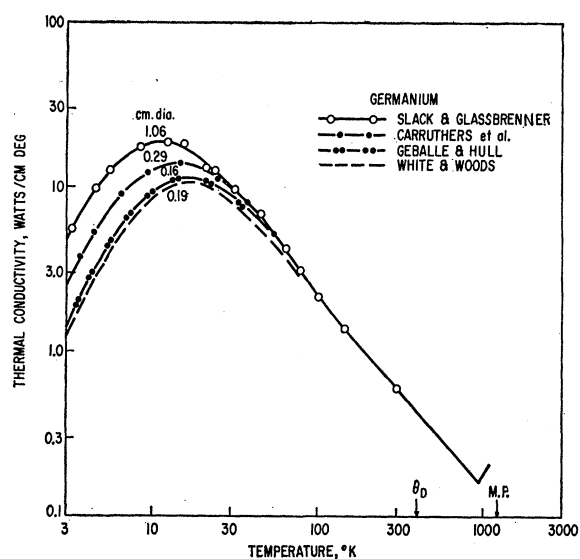


FIG. 2. The thermal conductivity of germanium from 3°K to 1020°K. The data below 300°K were measured in a longitudinal heat flow apparatus, and are compared with previous work. The curve above 300°K is from Fig. 4.

ple. The maximum temperature of 1020°K was enforced by the accidental burnout of the heater wire at a hot spot.

The measurements in the longitudinal flow experiment below 300°K were made on a high-purity single crystal of germanium in a different apparatus,¹² and have an absolute accuracy of about $\pm 5\%$. This crystal was *p* type containing about 10^{14} residual copper atoms per cm^3 , and thus it was intrinsic *n* type at 300°K. It was made from natural Ge in which all of the Ge isotopes

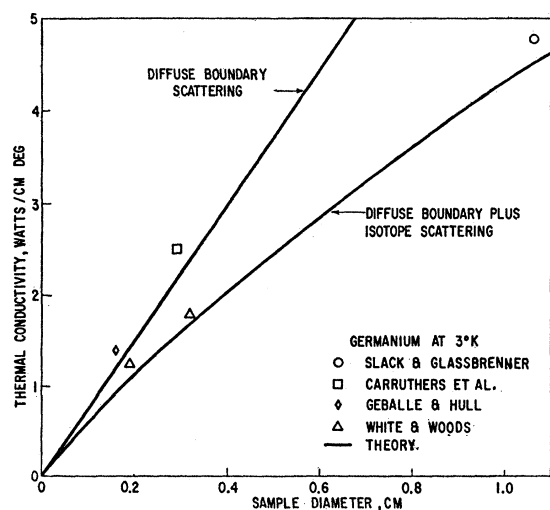


FIG. 3. The thermal conductivity of germanium at 3°K as a function of the sample diameter. A combination of boundary plus isotope scattering is needed to explain the results.

¹² G. A. Slack and R. Newman, Phys. Rev. Letters **1**, 359 (1959).

occur in their natural abundances.^{8,13} Its dislocation density was about 3×10^8 per cm^2 , and its size was 0.94 cm by 0.94 cm by 3.2 cm long.

EXPERIMENTAL RESULTS

The results of the low-temperature experiment are shown in Fig. 2 together with those of several previous investigators.⁶⁻⁸ The agreement at temperatures above 50°K is quite good. Both the present work and that of Carruthers *et al.*⁷ give a thermal conductivity of 0.60 watt/cm deg at 300°K. At temperatures below 50°K the present conductivity values are higher than previous ones because the sample diameter is larger. The fact that there is a size effect even up to 50°K has been noted before.¹⁴ This size effect is quite pronounced at the

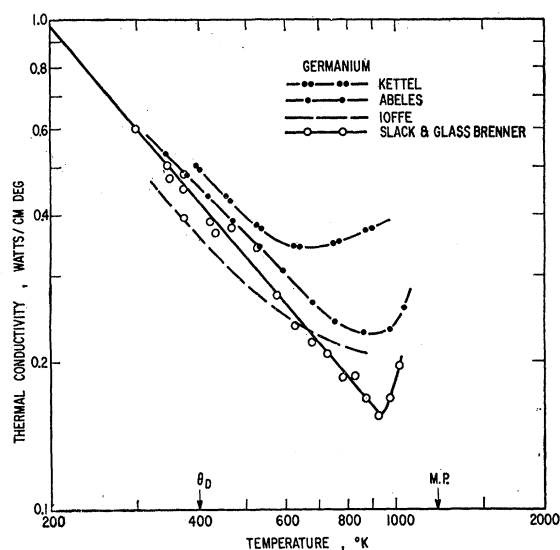


FIG. 4. The thermal conductivity of germanium from 300°K to 1020°K as determined by the radial heat flow method. Note the rise at 940°K. Data of previous authors are also shown.

lowest temperature of 3°K, and the conductivity vs sample diameter is plotted in Fig. 3. For the present sample the thermal conductivity at 3°K is about two-thirds of the limit imposed¹⁵ by diffuse boundary scattering alone.

The results of the radial experiment at temperatures above 300°K are given in Fig. 4, as well as results of previous investigators.³⁻⁵ The geometrical factor $L^{-1} \ln(r_2/r_1)$ in Eq. (2) is somewhat uncertain because of the small value of r_1 . This uncertainty is a constant factor independent of temperature. Hence the absolute value of K determined from Eq. (2) was multiplied by 1.24 in order to match the high-temperature results to a

¹³ G. T. Seaborg and I. Perlman, Revs. Modern Phys. **20**, 585 (1948).

¹⁴ T. H. Geballe and G. W. Hull, Bull. inst. intern. froid, Annexe 1955-3, p. 460.

¹⁵ H. B. G. Casimir, Physica **5**, 495 (1938).

conductivity of 0.60 watts/cm deg at 300°K. The temperature dependence of the results in Fig. 4 is exactly that which was measured. The present results lie between those of Ioffe and Abeles at 300°K, and lower than either above 700°K. It is believed that the present data are more nearly characteristic of germanium than previous work since spurious radiation losses from either the heater or the sample have been eliminated. Such losses only tend to make the apparent thermal conductivity too large, particularly at high temperatures. The data of Kettel are rather noticeably affected by this trouble.

The results show that above 300°K the thermal conductivity of germanium varies as $T^{-1.2}$, and that the extrapolated lattice thermal conductivity at the melting point is 0.12 watt/cm deg. An abrupt rise in the thermal conductivity is observed at 940°K, and is qualitatively similar to that found by the other investigators.

ANALYSIS OF RESULTS BELOW 300°K

A comprehensive study of the thermal conductivity of germanium below 100°K has been published by Callaway,¹⁶ and will not be repeated here. His main conclusion was that the thermal conductivity below 100°K of germanium with its natural isotopes is determined by phonon-phonon scattering, point impurity (i.e., isotope) scattering, and boundary scattering. The effects of normal three-phonon scattering are included since they modify the phonon spectrum. The analysis of the data below 10°K can be made in a much simpler fashion, as Callaway points out, since both the normal and umklapp processes are unimportant at these low temperatures. Consider the following expression¹⁷ for the thermal conductivity in the Debye approximation:

$$K = \frac{4\pi k^4 T^3}{v^2 h^3} \int_0^{\theta/T} \frac{l(x) x^4 e^x dx}{(e^x - 1)^2}, \quad (3)$$

where $x = (h\nu/kT)$, $l(x)$ is the phonon mean free path as a function of temperature T and phonon frequency ν , the average phonon velocity is v , the Debye temperature is θ , and k and h are Boltzmann's and Planck's constants, respectively. The only important variables in Eq. (3) are T and $l(x)$. If at all temperatures $l(x) = L$, the sample diameter, then K is always finite and has the same temperature dependence as the specific heat of the solid. This gives an upper limit to K at room temperature and above of about 10^6 w/cm deg for germanium when $L = 1$ cm. Clearly this is much too high. The next step is to include point impurity scattering in the theory. It was pointed out by Peierls¹⁸ that point impurity scattering by itself will not lead to a finite

thermal conductivity. Most authors¹⁸⁻²⁰ have resorted to invoking phonon-phonon scattering combined with the point impurity scattering in order to produce a finite thermal conductivity. However, since boundary scattering alone yields a finite thermal conductivity at all temperatures, a combination of boundary and point impurity scattering will yield a finite value. Furthermore, since phonon-phonon scattering becomes relatively unimportant at temperatures below the maximum in the thermal conductivity curve, this simple combination of point impurity plus boundary scattering provides an accurate prediction of the results at these temperatures. When impurity scattering alone is present $l(x)$ is given by¹⁷

$$l_p = (H/x^4)(\theta^4/T^4), \quad (4)$$

where $H = a_0/220BT$, a_0^3 is the average volume per atom, and BT is the isotope scattering parameter. In deriving Eq. (4) the following approximation²¹ was used:

$$\theta = h\nu/1.161ka_0.$$

This approximation is not too bad for germanium. The mean free path for boundary scattering is the sample diameter, L . The appropriate²⁰ $l(x)$ to substitute in Eq. (3) is $(l_p^{-1} + L^{-1})^{-1}$. It is convenient to introduce a reciprocal temperature parameter, t^{-1} , which is the value of x when $l_p = L$. In the low-temperature region, where $T \ll \theta$, the result is

$$K(t) = \left[\int_0^\infty \frac{x^4 e^x dx}{(e^x - 1)^2 (1 + x^4 t^{-4})} \right] \left(\frac{4\pi k^4}{v^2 h^3} \right) LT^3, \quad (5)$$

$$T(t) = (\theta/t)(H/L)^{1/4}. \quad (6)$$

The dependence of K on T can now be determined. This gives the pure boundary scattering value at very low temperatures ($t \rightarrow \infty$) of

$$K = 25.98(4\pi k^4/v^2 h^3)LT^3, \quad (7)$$

which is independent of Γ . At intermediate temperatures the integral in Eq. (5) can be evaluated from values of I_4 previously published.¹⁷ At very high temperatures ($t \rightarrow 0$) the value of K is independent of temperature and finite. Its value is very nearly

$$K = \frac{4}{3}(4\pi k^4/v^2 h^3)L^3 H^3 \theta^3. \quad (8)$$

Here K varies as Γ^{-3} . The expression for $K(T)$ in Eq. (5) can be evaluated for germanium using¹⁷ $v = 3.81 \times 10^5$ cm/sec, $\theta = 362^\circ\text{K}$ at 0°K ,²² $a_0 = 2.83 \times 10^{-8}$ cm, $\Gamma = 5.86 \times 10^{-4}$,¹³ and B has its theoretical value of $1/12$. At high temperatures ($t < 0.1$, $T > 150^\circ\text{K}$) this gives $K = 45$ watt/cm deg for $L = 1$ cm. The behavior of K vs T

¹⁶ J. Callaway, Phys. Rev. **113**, 1046 (1959).

¹⁷ G. A. Slack, Phys. Rev. **105**, 829, 832 (1957).

¹⁸ R. Peierls, Ann. Phys. **3**, 1055 (1929).

¹⁹ I. Pomeranchuk, J. Phys. U.S.S.R. **6**, 238 (1942).

²⁰ P. G. Klemens, Proc. Roy. Soc. (London) **A208**, 108 (1951).

²¹ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, New York, 1940), p. 111.

²² P. H. Keesom and N. Pearlman, Phys. Rev. **91**, 1347 (1953).

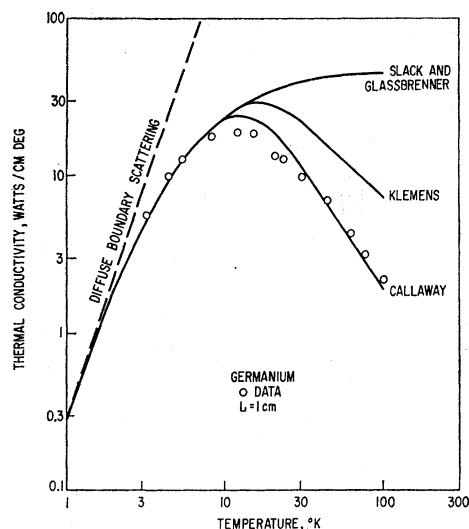


FIG. 5. Several theories of the low-temperature thermal conductivity of germanium. All of the theories give the correct behavior below 10°K. The curve by Slack and Glassbrenner neglects all phonon-phonon processes, while the other two authors consider them in different approximations.

for this simple combination of boundary plus isotope scattering is shown in Fig. 5, as the uppermost curve. It should be noted that this curve was computed exactly from the numbers above using no adjustable constants. The fit to the experimental data points is surprisingly good on the low-temperature side of the maximum.

The thermal conductivity of germanium has also been computed with the effects of phonon-phonon scattering included. In the method suggested by Klemens²⁰ the effects of the normal phonon processes are included by use of a cutoff approximation. The integrals involved in this method have been evaluated,¹⁷ and the results are shown as the middle curve in Fig. 5. This curve is a calculation from the approximate theory without any adjustable parameters. The effects of both normal and umklapp phonon processes are included by Callaway.¹⁶ By use of one adjustable parameter he was able to fit the data up to 100°K, as shown in Fig. 5. All three approximations give the same results at temperatures below 10°K, and shown that the neglect of phonon-phonon scattering is valid here.

The size dependence of the thermal conductivity at 3°K can now be analyzed in terms of a combination of boundary plus point impurity scattering. It is assumed that the boundary scattering mean free path is equal to the equivalent sample diameter. This is the diameter of a circle of the same cross-sectional area as the sample. This is a good approximation if the phonon scattering at the crystal surface is perfectly diffuse. If the scattering is partially specular, then the mean free path will exceed the sample diameter.²³ For no point impurity

(i.e., isotope) scattering K increases linearly with L , as shown in the diffuse boundary scattering curve in Fig. 3. For the combination of isotope plus diffuse boundary scattering the variation of K with L at 3°K was determined from Eq. (5). The results are the lower curve in Fig. 3. The experimental points from the different authors agree reasonably well with the theory. The preparation of the crystal surface was not the same in all cases. The fact that no points fall below the lower curve in Fig. 3 indicates some specular reflection probably occurred. In the present experiment the crystal surface was cut on a diamond wheel and then moderately etched to provide a diffuse reflecting surface. The agreement of this point at 1.06 cm with the theory is almost too good. Previous experiments on the size dependence of boundary scattering show that KCl,²⁴ SiO₂,²⁴ and diamond²⁵ exhibit a slower than linear increase of K with L , whereas experiments on Al₂O₃²⁵ exhibit a linear increase. The difference is probably caused in part by the fact that in the first three cases a combination of boundary plus point impurity scattering is present, whereas in Al₂O₃ boundary plus umklapp scattering is present.¹⁷ The umklapp scattering decreases more rapidly with decreasing temperature than point impurity scattering, and so it is not important at temperatures below the conductivity maximum.

ANALYSIS OF RESULTS ABOVE 300°K

For temperatures above the high-temperature value of the Debye temperature of germanium²⁶ of 400°K the theory²⁷ of phonon-phonon scattering indicates that λ should vary as T^{-1} . This is close to the observed variation of $T^{-1.2}$. The difference between -1.2 and -1.0 is, however, thought to be real, but of no tremendous theoretical significance. The polycrystalline nature of the sample cannot alter the behavior above 300°K, since the 0.2-cm crystallite size will produce crystallite boundary scattering only below about 30°K.

From 3°K to 940°K practically all of the thermal energy is transported by phonons. The abrupt rise in the thermal conductivity at 940°K makes it appear as though another mechanism of heat transfer enters the problem. This mechanism might be photons,^{28,29} excitons,³ or electron-hole pairs.^{30,31} There is also the possibility that a phase change or a specific heat anomaly in germanium might exist at high temperatures. Phase

²⁴ W. J. deHaas and T. Biermasz, *Physica* **5**, 47, 619 (1938).

²⁵ R. Berman, E. L. Foster, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A231**, 130 (1955).

²⁶ F. A. Johnson and J. M. Lock, *Proc. Phys. Soc. (London)* **72**, 914 (1958).

²⁷ G. Leibfried and E. Schlömann, *Nachr. Akad. Wiss. Göttingen, Math. physik. Kl.* **4**, 71 (1954).

²⁸ L. Genzel, *Z. Physik* **135**, 177 (1953).

²⁹ F. R. Charvat and W. C. Kingery, *J. Am. Ceram. Soc.* **40**, 306 (1957).

³⁰ B. I. Davydov and I. M. Shmushkevitch, *Uspekhi Fiz. Nauk* **24**, 21 (1940).

³¹ P. J. Price, *Phil. Mag.* **46**, 1192 (1955).

²³ R. Berman, F. E. Simon, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A220**, 171 (1953).

changes are ruled out by x-ray studies³² between 20°K and 1110°K, heat capacity studies³³ between 870°K and 1170°K, and electrical resistivity measurements³⁴ from 770°K to 1250°K.

The photon contribution to the heat transport depends on the optical absorption coefficient as a function of photon wavelength, $\alpha(\lambda)$, the index of refraction, n , the absolute temperature, T , suitably integrated over the Planck distribution, $E(\lambda, T)$. The theory has been carefully worked out by Genzel.²⁸ Only when $\alpha d \gg 1$, where d is an average dimension of the sample, and where $d \text{grad} T \ll T$ can a true photon thermal conductivity be defined. In this case the photon thermal conductivity, K_r , is

$$K_r = \frac{4\pi n^2}{3} \int_0^\infty \frac{1}{\alpha(\lambda)} \frac{\partial E(\lambda, T)}{\partial T} d\lambda. \quad (9)$$

If α is independent of wavelength this reduces to

$$K_r = 16n^2 \sigma T^3 / 3\alpha, \quad (10)$$

where σ is the Stefan-Boltzmann constant. The values

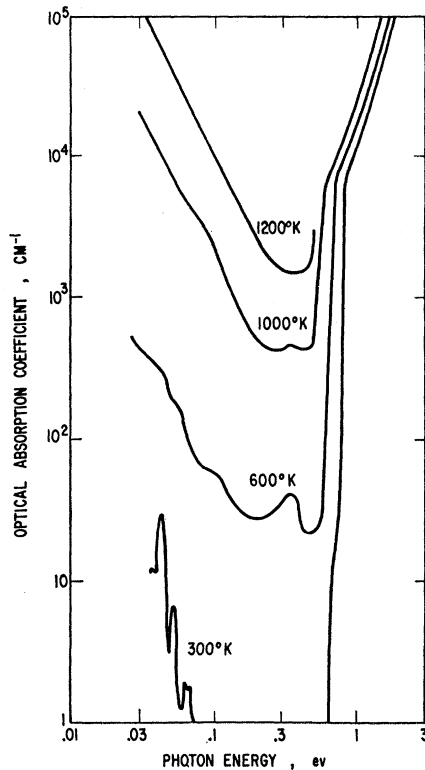


FIG. 6. The optical absorption coefficient of intrinsic germanium versus photon energy at several temperatures. The curve at 300°K is based on literature data. The other curves are estimated from literature data on free carrier absorption.

³² H. Nitka, *Physik. Z.* **38**, 896 (1937).

³³ E. S. Greiner, *J. Metals* **4**, 1044 (1952).

³⁴ A. I. Blum, N. P. Mokrovskii, and A. R. Regel, *Izvest. Akad. Nauk. S.S.S.R. Ser. Fiz.* **16**, 139 (1952).

TABLE I. Approximate photon contribution to the thermal conductivity of germanium.

$T^\circ\text{K}$	$\text{Av } \alpha$ in cm^{-1}	K_r w/cm deg
600	30	3.5×10^{-3}
1000	630	0.8×10^{-3}
1200	3500	0.2×10^{-3}

of n and $\alpha(\lambda)$ for germanium at temperatures near 1000°K have not appeared in the literature, so it is necessary to estimate these quantities from other data. The temperature and wavelength dependence of n up to 300°K has been studied,³⁵ as has its value at high impurity concentrations,³⁶ and for the desired accuracy of a factor of 3 in K_r , a constant value of $n=4.0$ is taken. The optical absorption coefficient, $\alpha(\lambda)$, has been carefully measured^{37,38} at 300°K, and is plotted in Fig. 6. Above 300°K the absorption of light by free electrons and holes becomes important in germanium for $\lambda > 2$ microns. At shorter wavelengths intrinsic absorption is always present. The concentration of free carriers at high temperatures can be obtained from electrical measurements.³⁹ The α values corresponding to these concentrations can be estimated for electrons⁴⁰ and for holes⁴¹ from data taken on heavily doped samples at room temperature. The total absorption coefficient is the sum of the values for electrons and holes taken separately.⁴² Employing these data and the shift of the band gap with temperature,⁴³ the value of $\alpha(\lambda)$ for several temperatures, estimated to within a factor of 3, is given in Fig. 6. Just below the melting point of germanium the minimum value of α is above 10^3 cm^{-1} . Approximate average values of α over the Planck distribution were used to compute K_r from Eq. (10) as shown in Table I. These K_r values are negligible compared to the measured values of K . For temperatures below about 500°K germanium becomes optically transparent (i.e., $\alpha d \sim 1$), and Eq. (10) is no longer applicable. The important quantity becomes the direct radiative heat loss, Q_r , from the heater wire compared to the amount of heat, Q_e , conducted away by the germanium. This direct radiative loss, Q_r , is about a 0.004% correction at 500°K in the present experiment, and less at lower temperatures. It

³⁵ M. Cardona, W. Paul, and H. Brooks, *J. Phys. Chem. Solids* **8**, 204 (1959).

³⁶ W. G. Spitzer and H. Y. Fan, *Phys. Rev.* **106**, 882 (1957).

³⁷ R. J. Collins and H. Y. Fan, *Phys. Rev.* **93**, 674 (1954).

³⁸ W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955).

³⁹ F. J. Morin and J. P. Maita, *Phys. Rev.* **94**, 1525 (1954).

⁴⁰ H. Y. Fan, W. Spitzer, and R. J. Collins, *Phys. Rev.* **101**, 566 (1956).

⁴¹ R. Newman and W. W. Tyler, *Phys. Rev.* **105**, 885 (1957).

⁴² H. Y. Fan, M. L. Shepherd, and W. Spitzer, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge *et al.* (John Wiley & Sons, New York, 1956), p. 184.

⁴³ G. G. Macfarlane, T. P. McLean, J. E. Quarraington, and V. Roberts, *Phys. Rev.* **108**, 1377 (1957).

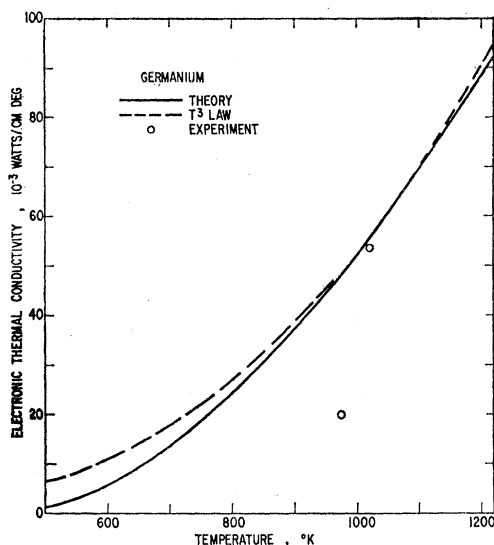


FIG. 7. The electronic contribution to the thermal conductivity of germanium versus temperature. The theory of bipolar diffusion is an approximate T^3 law. The two experimental points are shown.

should be noted that in optically transparent materials like alkali halides²⁹ K_r is important at high temperatures. The intrinsic free carriers in germanium at high temperatures make K_r negligible. The result of a negligible radiation heat loss, Q_r , from the radial sample heater, because it is imbedded in optically opaque germanium at high temperatures, is to be compared with the large radiation losses from the heater which are possible in a longitudinal heat flow method. This is the main advantage of the radial method of measuring thermal conductivity.

The possibility of an exciton contribution to the thermal conductivity has been suggested by Ioffe.³ Excitons in germanium have been studied by Macfarlane *et al.*,⁴³ and found to have a binding energy of 0.006 ev. This binding energy is quite small compared to kT at 1000°K of 0.086 ev. Thus excitons will be easily dissociated, and there will be very few at high temperatures to contribute to the thermal conductivity, as has been pointed out by Herring.⁴⁴ The unbound electrons and holes, will, on the other hand, contribute to the heat transport.

The contribution of the free electrons and holes to the thermal conductivity is composed of two parts. The first of these is the Weidemann-Franz contribution produced by the electron (and hole) gas. The second is the bipolar diffusion of electron-hole pairs under the influence of a temperature gradient. In the first process each carrier transports an energy of about kT , whereas in the second the energy transported per carrier is of the order of the band gap. Price's³¹ formulation gives for the sum of these two terms the electronic thermal conduc-

tivity, K_e , of

$$K_e = 2(\sigma_1 + \sigma_2)T \left(\frac{k}{e} \right)^2 + \frac{\sigma_1 \sigma_2}{\sigma_1 + \sigma_2} T \left(\frac{k}{e} \right)^2 \left[\frac{\Delta}{kT} + 4 \right]^2, \quad (11)$$

where σ_1 is the electrical conductivity due to electrons alone, σ_2 that due to holes, e is the electronic charge, k is Boltzmann's constant, and Δ is the indirect band gap of germanium at temperature T . The electrical conductivity as a function of temperature of intrinsic germanium has been measured from 260°K to above the melting point.^{34,39} The electrical conductivity increases monotonically up to the melting point with a nearly constant activation energy. There is no abrupt change in the electrical conductivity near 940°K as there is in the thermal conductivity. The data of Morin and Maita³⁹ have been used to estimate σ up to 1210°K. The variation of Δ with temperature was taken to be⁴⁸ $\Delta = 0.772 - 0.000365T$ ev from 300°K to 1210°K. With these numbers the value of K_e was computed as a function of temperature, and the results are given in Fig. 7. It turns out accidentally that between 900°K and 1210°K the theoretical value of K_e increases almost proportionally to T^3 . This is the same temperature dependence possessed by any errors caused by poor corrections for thermal radiation. See Kettel⁴ for example. Thus considerable care has to be exercised in order to obtain true experimental values of K_e .

The two available experimental points from Fig. 4 are also plotted in Fig. 7. For these points it has been assumed that

$$K_{\text{tot}} = K_g + K_e, \quad (12)$$

where the lattice thermal conductivity, K_g , above 940°K is obtained from an extrapolation of the linear portion of the curve. The experimental values of K_e are of the same magnitude as the theoretical ones computed from Eq. (11), but they appear to rise much more rapidly with temperature than the theory would predict. This discrepancy is not understood. Further experimental work is necessary in order to obtain data between 940°K and the melting point of 1210°K. The most that can be said is that bipolar diffusion of electron-hole pairs is the only mechanism that is of the right order of magnitude to account for the excess thermal conductivity of germanium above 940°K. The agreement with the experimental data is, however, only qualitative.

CONCLUSIONS

The thermal conductivity of high-purity germanium has been measured from 3°K to 1020°K. From 3°K to 300°K a longitudinal heat flow method was used. The results agree well with previous data. Germanium might be a useful thermal conductivity standard in this temperature range. In the region from 3°K to 10°K the data are explained in terms of a simple combination of

⁴⁴ C. Herring, *J. Phys. Chem. Solids* **8**, 543 (1959).

boundary and isotope scattering. The predicted variation of thermal conductivity with sample diameter was found. From 300°K to 1020°K a radial heat flow method was used which reduced the problem of heat transport by spurious thermal radiation to negligible values. At 940°K an abrupt rise in the thermal conductivity was observed. This rise may be due to bipolar diffusion, but

the agreement between experiment and theory is only qualitative.

ACKNOWLEDGMENTS

The authors would like to thank H. Ehrenreich and B. Abeles for helpful discussions concerning the thermal conductivity of germanium.

PHYSICAL REVIEW

VOLUME 120, NUMBER 3

NOVEMBER 1, 1960

New Method for Treating the Antiferromagnetic Ground State*

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(Received January 25, 1960; revised manuscript received June 22, 1960)

A perturbation expansion for the ground-state energy of an antiferromagnetic spin system is obtained in terms of a linked-spin-cluster expansion similar to Goldstone's linked-Feynman-diagram expansion for the interacting Fermion system. From the energy perturbation series, perturbation series for the long- and short-range order may be obtained. Using these perturbation series, the ground-state properties are calculated through seventh order and compared with the results obtained by other investigators. In all cases, the values obtained here for the ground-state energy are lower than those which have been obtained by purely variational means. The results for the long-range order are

radically different from the variational results but agree qualitatively with those obtained by spin-wave theory; however, the method is free of the usual objections which are voiced to spin-wave treatments of antiferromagnetism. The present work is incomplete in that limits on the error introduced by using only a finite number of terms of the perturbation series to calculate the physical properties are not obtained. But the author feels that the merit of the present work is in the method rather than the results since it provides a consistent framework both to settle the convergence question and to treat the antiferromagnetic spin system at finite temperatures.

I. INTRODUCTION

RECENTLY Orbach¹ has examined the ground state of a linear chain of spins one-half coupled together with a combination of the Heisenberg and Ising antiferromagnetic interactions. He was able to obtain exact values for the energy and short-range order of such a spin system by use of an iteration procedure on an IBM 701 computer. By such a method, he showed the variational predictions of Kasteleijn² were in error. That is, Orbach showed that the kink in the curve of short-range order versus relative Ising anisotropy predicted by Kasteleijn was nonexistent. Kasteleijn also predicted the long-range order of such a linear spin system was zero until the relative amount of Ising anisotropy reached the value at which the kink existed in the short-range order curve; thereafter, with an increase of anisotropy, the long-range order was found to rise rapidly to perfect order as the interaction approached the limit of pure Ising coupling. Though Orbach was unable to calculate the long-range order by his exact method, he did point out the dangers of relying on

approximate methods, such as Kasteleijn's, for predicting the long-range order behavior of antiferromagnetic spin systems.

For the two- and three-dimensional antiferromagnetic spin systems, no exact treatment for any of the physical properties of the ground state exists except for the trivial case of the pure Ising interaction. Anderson³ has given an approximate semiclassical spin-wave treatment which predicts an ordered ground state for two- and three-dimensional antiferromagnetic spin systems when the spins are coupled by pure nearest-neighbor isotropic exchange interactions.⁴ Using a hybrid spin-wave variational method, Kubo⁵ has obtained nonzero long-range order predictions for the ground state of one-, two-, and three-dimensional lattices when the spins are coupled by nearest-neighbor isotropic antiferromagnetic exchange interactions. Kubo's prediction of an ordered ground state for the linear chain, as he himself pointed out, cast unfavorable light on his approximation, since Anderson³ had predicted disorder for the linear chain under the same circumstances. However, as has been pointed out by Orbach,¹ the

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‡ This work is based on a thesis submitted to the Graduate School, The Ohio State University, in partial fulfillment of the requirements for the Ph.D. degree, June, 1959.

¹ R. Orbach, *Phys. Rev.* **112**, 309 (1958).

² P. W. Kasteleijn, *Physica* **18**, 104 (1952).

³ P. W. Anderson, *Phys. Rev.* **86**, 694 (1952).

⁴ To be precise, Anderson predicts an ordered ground state when an infinitesimal anisotropy of axial symmetry is present. In the remainder of this paper it is to be understood, when we refer to the isotropic exchange interaction, that an axially symmetric infinitesimal anisotropy is assumed. Such an anisotropy is merely to make the z axis the preferred spatial direction.

⁵ R. Kubo, *Revs. Modern Phys.* **25**, 344 (1953).