evidence indicates that both loops and submicroscopic defect clusters exist in these neutron irradiated specimens.

SUMMARY

Copper crystals irradiated with neutrons between 50 and 70°C show the following characteristics when isothermally annealed between 75 and 350°C:

(1) A decrease in volume is detected and is proportional to the neutron exposure. The maximum specific volume changes for 1.14×10^{18} (*nvt* total epicadmium flux) and 0.532×10^{18} (*nvt* total epicadmium flux) are -3.93×10^{-5} and -2.46×10^{-5}, respectively.

(2) Measurable shrinkage of the single crystals takes place between 225 and 325°C, and the temperature where the maximum shrinkage rate occurs appears to be higher for the lower neutron dose.

(3) The change in size distribution of prismatic dislocation loops can be predicted by Eq. (1).

(4) The activation energy for the annealing process corresponds to the activation energy for self-diffusion.

(5) Dislocation loops and submicroscopic point-defect clusters are present in neutron irradiated copper.

ACKNOWLEDGMENTS

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Thermal Conductivity of Silicon and Germanium from 3°K to the Melting Point*

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The thermal conductivity K of single crystals of silicon has been measured from 3 to 1580°K and of single crystals of germanium from 3 to 1190°K. These measurements have been made using a steady-state, radial heat flow apparatus for $T>300$°K and a steady-state, longitudinal flow apparatus for $T<300$°K to give absolute K values. This radial flow technique eliminates thermal radiation losses at high temperatures. The accuracy of both the low-temperature apparatus and the high-temperature apparatus is approximately $\pm5\%$. Some special experimental techniques in using the high-temperature apparatus are briefly considered. At all temperatures the major contribution to K in Si and Ge is produced by phonons. The phonon thermal conductivity has been calculated from a combination of the relaxation times for boundary, isotope, three-phonon, and four-phonon scattering, and was found to agree with the experimental measurements. Above 700°K for Ge and 1000°K for Si an electronic contribution to K occurs, which agrees quite well with the theoretical estimates. At the respective melting points of Si and Ge, electrons and holes are responsible for 40% of the total K and phonons are responsible for 60%. The measured electronic K yields values for the thermal band gap at the melting point of 0.6 ± 0.1 eV for Si and 0.26 ± 0.08 eV for Ge.

INTRODUCTION

In a semiconductor, various carriers can contribute to the thermal conductivity. These are phonons, photons, electron-hole pairs, and the separate electron and holes. The problem of sorting out the contributions from these processes has been handicapped by the lack of accurate high-temperature measurements. In this paper, we report on measurements of the thermal conductivity K of single crystals of germanium and silicon between 300 and 1580°K taken with an improved cylindrical heat flow apparatus. The measurements of K of silicon below 300°K have been taken with an existing longitudinal heat flow apparatus.[1] Germanium and silicon were measured because they are easily obtained with high purity and known electrical characteristics. As a consequence of this investigation, they could serve as standard materials for K measurements.

The purpose of this investigation was to measure and analyze the K of these materials up to the melting point and, in particular, to unravel the magnitude of the contributions from the various carriers of heat. It was found that the phonon or lattice thermal conductivity is dominant and decreases faster than $1/T$ at high temperatures. The bipolar thermal conductivity, i.e., from electron-hole pairs, is significant at high temperatures and agrees with a simple theory. The polar thermal conductivity, i.e., from the separate electrons and holes, is small, and the photon thermal conductivity is not detectable.

* This work is part of a thesis submitted by C. J. Glassbrenner to the Physics Department of the University of Connecticut in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[1] G. A. Slack, Phys. Rev. 122, 1451 (1961).

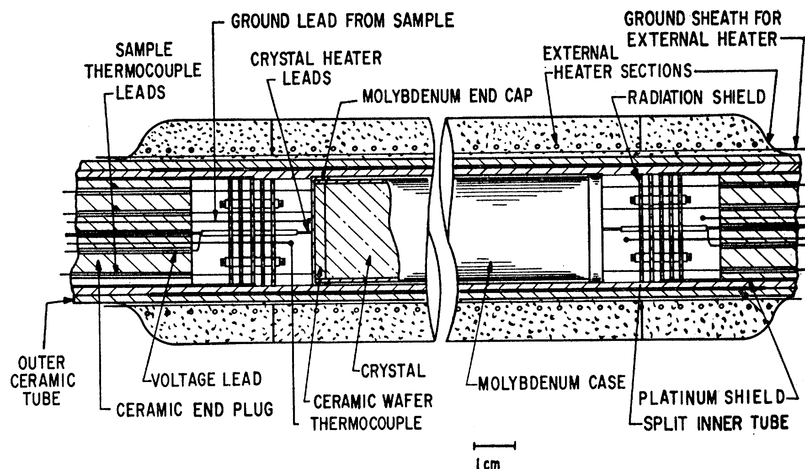

FIG. 1. The high-temperature radial heat flow apparatus showing the crystal sample, heater, thermocouples, and shields.

CRYSTAL SPECIFICATIONS AND PREPARATIONS

A. Low-Temperature Silicon Crystal

The silicon single crystal used for the low-temperature measurements was grown by the pedestal method from a bar of high-purity silicon by W. C. Dash of this laboratory. The growth direction was [111]. It was made with care in order to be oxygen and dislocation free.[2–4] Any vacancy clusters were less than one micron in diameter as determined by etchpit and copper decoration techniques. The pedestal method prevents the silicon from coming in contact with quartz, usually the chief source of oxygen. The crystal was 2 cm long with a geometrical average diameter of 0.44 cm. The diameter varied slightly along the length of the sample. The cross section could be best described as an equilateral triangle with rounded corners, typical of [111] oriented crystals. The room-temperature resistivity was approximately 2000 Ω-cm, and the sample was p type.

B. Crystals Used at High Temperatures

The silicon and germanium samples were both single crystals, cylindrically shaped, approximately 13 cm long by 2.6 cm in diameter. They had on the order of 10^5 dislocations[5] per cm^2. The Ge crystal was grown by the Čzochralski method with a [100] axis from a charge of zone-refined germanium. The room-temperature resistivity of the charge material was greater than 40 Ω-cm which indicates that it was basically intrinsic. The dominant impurity in the charge was specified as antimony. The single crystal of silicon was produced by the floating zone process. The atmosphere was argon and the axis of the cylinder was [111]. The diameter of the "as-received" crystals varied slightly along the axis. Their crystal faces were clearly visible.

[2] W. C. Dash, J. Appl. Phys. **29**, 736 (1958).
[3] W. C. Dash, J. Appl. Phys. **30**, 459 (1959).
[4] W. C. Dash, J. Appl. Phys. **31**, 736 (1960).
[5] W. C. Dash (private communication).

A rather elaborate machining operation was used on the crystals in order to insure that the axial heater was exactly in the center of the sample and that the thermocouples were at exactly known positions along the radii. These physical conditions imposed on the heater and thermocouples were solved by cutting the sample into two exactly equal half-cylinders. For this purpose, the original single crystal was centerless, ground to a uniform diameter and carefully cut lengthwise into two approximately equal halves. The flat side of each half-cylinder was given an optically flat polish so that the halves would fit tightly together. Thermocouple grooves were then cut in one of the halves. The nominal radial distances of the center line of the three thermocouple grooves from the axis were: 2.5 and 10 mm on one side of the heater groove, and 6.5 mm on the other side. A heater groove was cut along the axis of each half so that the heater would be in the center of the assembled cylinder. After the grooves were cut, the two halves were temporarily cemented together, but were offset slightly along the longitudinal axis. They were centerless ground a second time so that the interfacial plane and heater wire passed through the center of the cylinder.

After the machining, the sample was assembled and encapsulated in a molybdenum case with a high-purity Al_2O_3 ceramic wafer placed at each end. See Fig. 1. Molybdenum was used because it does not form any low melting alloys with either Si or Ge. Neither the Mo nor the Al_2O_3 contributes electrically active impurities to the Si or Ge in significant amounts during the lengthy, high-temperature runs.

The intrinsic electronic K could be suppressed if, inadvertently, the material became highly doped to a level of about 10^{18} carriers/cc. As a check on the impurity concentration, the electrical conductivity and Hall coefficient of the germanium and silicon samples were measured before and after the high-temperature measurements. Before use the room-temperature resistivity of the germanium crystal was 46.6 Ω-cm, and the

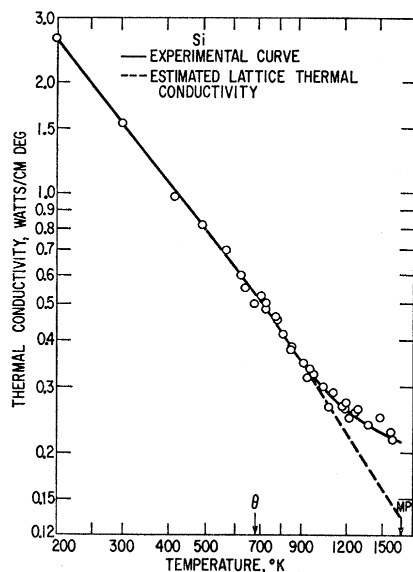

FIG. 2. K versus T for Si showing the experimental points and the extrapolated lattice component K_g. The Debye and melting temperatures are θ and MP, respectively.

net carrier concentration was $2\times10^{12}/\text{cm}^3$. The crystal was so lightly doped that it could not be well characterized as either n- or p-type. After the K had been measured to near the melting point, the electrical resistivity dropped to 4.6 Ω-cm and the crystal was now doped with 8×10^{15} acceptors/cm^3. These acceptors were identified as copper. The copper was probably introduced during the machining of the germanium sample prior to the measurements.

The room-temperature resistivity of the high-temperature silicon sample was 440 Ω-cm with a carrier concentration of $1.27\times10^{13}/\text{cm}^3$ and it was n type. After the K had been measured to near the melting point of silicon, the room-temperature resistivity dropped to 177 Ω-cm, the carrier concentration rose to 2.46×10^{13}, and it was still n type. The specific impurities could not be identified. The important conclusion from these measurements is that neither the germanium nor silicon contained enough electrically active impurities to affect the intrinsic polar or bipolar thermal conductivity in any way.

APPARATUS

The low-temperature measurements were made with a steady-state, longitudinal heat flow apparatus designed by Slack.[1] The final form of the high-temperature, cylindrical-flow thermal conductivity apparatus was obtained after several modifications. Figure 1 shows the details of the sample in the final version of the high-temperature apparatus. A more detailed description of the entire method and apparatus will be published elsewhere later. The central section of the apparatus is shown in Fig. 1. The vacuum plumbing was designed so that the sample chamber could be evacuated to 10^{-6} Torr and then filled with ultra-pure helium. The outer ceramic tube serves as the wall of the vacuum chamber for the sample. The external, 3-section electric heater is wound on this tube, and serves to control the average temperature of the sample. The split inner tube holds the sample and all of the removable parts, i.e., thermocouples, heaters, shields, etc., in place.

The cylindrical geometry for measuring the high-temperature thermal conductivity was chosen for reasons previously stated.[6] In the present, more thorough measurements, certain experimental problems arose which will now be given a cursory examination. Ultrapure helium gas was used for the atmosphere, because it contained a low oxygen content,[7] and thus there were no oxidation problems at high temperatures. The gas served to provide good thermal contact between the sample and the heater and thermocouple wires. The gas also partially helped to suppress the vapor transport of Si and Ge, which would be appreciable at high temperatures in a vacuum. The molybdenum jacket which encased the germanium and silicon reduced the exposed surface area of the samples and hence further reduced the evaporation. This case also held the halves together. Molybdenum was employed for the jacket, axial heater wire, voltage leads, and heater leads because of its previously mentioned chemical stability. The temperature gradients were measured with platinum versus platinum-10% rhodium because these thermocouples are very stable with time and possess well-

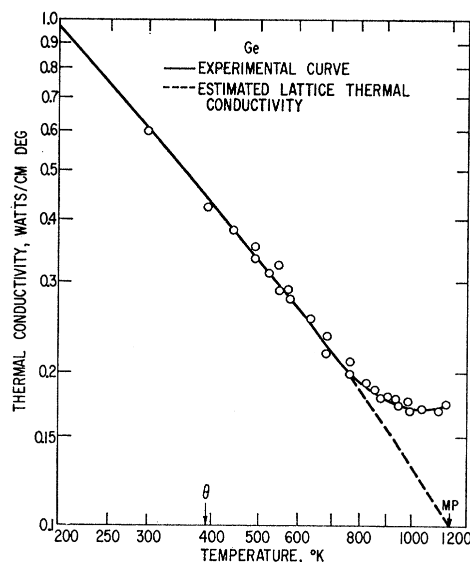

FIG. 3. K versus T for Ge showing the experimental points and the extrapolated lattice component K_g. The Debye and melting temperatures are θ and MP, respectively.

[6] G. A. Slack and C. J. Glassbrenner, Phys. Rev. **120**, 782 (1960).
[7] J. R. Young and N. R. Whetten, Rev. Sci. Instr. **32**, 453 (1961).

known calibration curves. However, they have a very small emf output and are subject to contamination problems unless carefully used. The thermocouples and axial crystal heater were insulated from the sample by Degussit[8] alumina tubing because it is a very pure ceramic, and is available in very small diameters. It does contain a small amount of iron and silicon, i.e., about 300 ppm. The radiation shields were made from platinum -40% rhodium. These served to keep heat losses from the end of the sample low. They also served as vapor barriers for germanium and silicon vapor coming from the sample. The external heater winding was made in three sections so that both the temperature gradient along the axis of the apparatus near the ends of the sample and the average temperature of the sample could both be controlled. A ground sheath was placed under the external heater to reduce stray electrical leakage currents. The ceramic end plugs were installed to hold the electrical wires in place and to reduce axial heat conduction by the gas. They also helped to protect the thermocouple wires in the temperature gradient from the silicon and germanium vapors.

The electrical heater power to the sample was furnished by either dc or ac. Direct current was used below about 750°K and ac was used (about 435 cycles/sec) at higher temperatures. Due to the lower electrical resistance of the Si, the Ge, and the Al_2O_3 at high temperatures, a small leakage voltage from the crystal heater always appeared in the thermocouples above about 850°K. This leakage was rendered harmless by use of ac since any small 435-cycle ac voltage was not recorded by the thermocouple galvanometer. To insure that the temperature gradient was measured accurately, a few

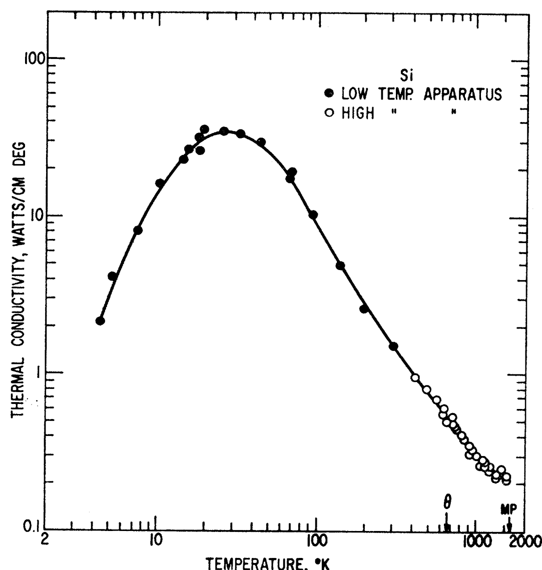

FIG. 4. The low- and high-temperature K versus T results for Si.

[8] Degussit A123, Liasson Company, New York, New York.

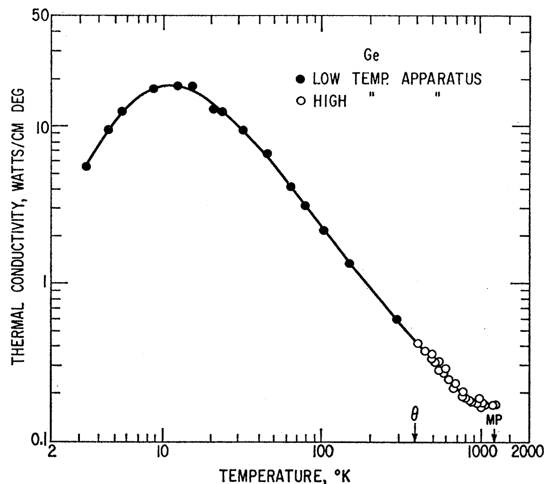

FIG. 5. The low- and high-temperature K versus T results for Ge.

special measuring techniques were employed. Since no two thermocouples are exactly alike, two of the three thermocouples inside the sample were always calibrated in terms of the third when the sample was in an isothermal condition. Checks on the presence of possible thermocouple contamination were made in two ways. First the high-temperature K data points were always followed by a reconfirmation of lower temperature K points at about 400°K. Secondly, variations in the axial temperature gradients in the apparatus at and beyond the radiation shields were intentionally produced by the end windings on the external heater. These variations should not affect the measured K. Any apparent effect meant contaminated thermocouples. Discrepancies of these types resulted in rejection of the high-temperature data, and a reassembly of the entire apparatus with new thermocouples. The final results for both Si and Ge each involved several such reassemblies.

Under steady-state operating conditions between 30 and 50 W of electrical power was furnished to the crystal heater. This is equivalent to about 4 W/cm of sample length. The average temperature differences between the center and surface of the sample ran between 1 and 3°K. The heater wire temperature usually operated between 50 and 100°K above the sample temperature.

RESULTS

The results of the present investigation of the high-temperature K of Si and Ge are shown in Figs. 2 and 3. The composite results for single crystal Si are shown in Fig. 4. Notice that the low-temperature results (solid circles) join on smoothly to the high-temperature results (open circles). Both sets of data were obtained in their respective apparatuses as absolute thermal conductivity values, and neither set of data has been adjusted to match the other. The actual data points in the low-temperature set span the temperature range from 4.3 to 304°K, while the high-temperature points cover the

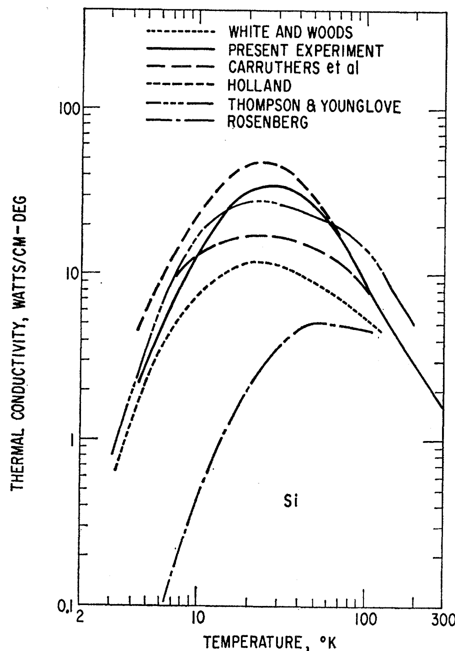

FIG. 6. Comparison of present and previous low-temperature K versus T results for Si.

418 to 1577°K range. The Debye temperature of Si at 674°K is shown for scaling purposes. The melting point, MP, of silicon at 1681°K is only 104°K above the highest point measured.

The results for single crystal Ge are shown in Fig. 5. The points for temperatures between 3.2 and 300°K have been taken from Slack and Glassbrenner.[6] The high-temperature data points between 398 and 1194°K were measured in the present high-temperature apparatus. Neither set of data was adjusted, and again the agreement between the low-temperature and high-temperature data is very good. The Debye temperature θ of Ge is 395°K. These results approach to within 16°K of the melting point, MP, of Ge at 1210°K. The absolute accuracy of both the high- and low-temperature results is computed to be $\pm 5\%$, while the relative accuracy of any two points measured on the same sample is $\pm 2\%$. Table I gives smoothed values for the K of Si and Ge. The low-temperature region where K depends on sample size has been excluded.

TABLE I. Representative values of the thermal conductivity K for high-purity single crystals of silicon and germanium (accuracy $\pm 5\%$).

	K, W/cm deg			K, W/cm deg	
T°K	Si	Ge	T°K	Si	Ge
20		15.	400	1.05	0.44
30		10.5	500	0.80	0.33$\bar{8}$
40		7.7	600	0.64	0.26$\bar{9}$
50	26.	5.9	700	0.52	0.21$\bar{9}$
60	21.	4.7	800	0.43	0.193
70	17.0	3.7	900	0.35$\bar{6}$	0.177
80	13.9	3.1	1000	0.31$\bar{0}$	0.171
90	11.4	2.5$\bar{5}$[a]	1100	0.28$\bar{0}$	0.169
100	9.5	2.2$\bar{5}$	1200	0.26$\bar{1}$	0.173
125	6.0	1.66	1210		0.173
150	4.2$\bar{0}$[a]	1.30	1300	0.24$\bar{8}$	
175	3.2$\bar{5}$	1.10	1400	0.23$\bar{7}$	
200	2.6$\bar{6}$	0.95	1500	0.22$\bar{7}$	
250	1.95	0.73	1600	0.21$\bar{9}$	
300	1.56	0.60	1681	0.21$\bar{6}$	

[a] The bar over the last digit indicates that it is rather uncertain.

PREVIOUS DATA

A. Silicon Below 300°K

A comparison of the present and previous low-temperature K measurements of silicon below 300°K is shown in Fig. 6. Except for the measurements by Thompson and Younglove, all of the measurements agree quite well above 100°K. Some of the variation in K below 100°K is accounted for by boundary scattering in different size samples. However most of the variation in Fig. 6 is caused by phonon scattering from impurities and other crystalline defects. The earliest report of thermal conductivity measurements of silicon at low temperatures of which the authors are aware was made by Rosenberg.[9] He measured a polycrystalline silicon sample over the temperature range 2 to 100°K, and employed gas thermometers to measure the temperature gradient during steady-state heat flow. Scattering by the grain boundaries in his polycrystalline sample is probably the reason that Rosenberg's K results are much lower than any of the others. White and Woods[10] have measured a single crystal silicon sample (room-temperature resistivity 6.7 Ω-cm) over a temperature range of 2 to 100°K. The impurities present in this sample were not stated. Thompson and Younglove,[11] in the temperature interval 2 to 200°K, have measured several samples of silicon doped with boron or arsenic. Figure 6 shows their measurement of their most highly doped silicon sample (boron doped with a room-temperature resistivity of 2000 Ω-cm). Carruthers *et al.*[12] have measured the thermal conductivity of a high-purity single crystal silicon sample, n type from 2 to 300°K. The net carrier concentration was 5×10^{14} at 300°K. Holland[13] measured the thermal conductivity of several silicon samples containing different amounts of oxygen and has discussed the effect of oxygen as a scatterer of phonons to reduce the thermal conductivity. His measurements of an n-type sample with the least amount of oxygen ($<10^{16}$ cm^{-3}) and a room-temperature resistivity of 260 Ω-cm agree very closely with the present experiment.

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B. Above 300°K

Various previous authors have measured the K of Si and Ge over part of the high-temperature range studied here. Consider Si first. Figure 7 shows how the present results on Si for $T>300$°K compare with some of the better previous data. The earliest K data on Si that has been reported is that of Koenigsberger and Weiss[14] in 1911 who found 0.84 W/cm deg at 290°K for an impure sample. Later authors,[13–24] who have measured K as a function of temperature for $T>300$°K, are listed in Table II. The recent values of K determined by Shanks *et al.*[23] from thermal diffusivity measurements are about 10% lower than the present ones between 300 and 900°K, and 20% higher at 1400°K. The absolute accuracy of the K values in the present experiment is ±5%, and this same limit of error seems to be present in the data of Shanks *et al.*, as judged from the scatter of the points and the size of the samples used. Thus the 10% difference is just within the combined limit of error. The almost temperature-independent K found by Shanks *et al.* for $T>1000$°K, however, is not confirmed. The K of Si continues to decrease with increasing temperature up to 1580°K, The high-temperature heat-capacity data used by Shanks *et al.* is in reasonably good (±2%) agreement with that given by Kelley,[25] so the conversion from thermal diffusivity to K should be accurate. The reason for the discrepancy in K determined by these two different methods is not as yet understood. The K results of Abeles *et al.*[21,22] from 310 to 1200°K, also determined from thermal diffusivity measurements, fall between the present curve and that of Shanks *et al.*

In reviewing the literature on the K of Ge it can be seen that the early measurements on Ge by Greico and Montgomery[26] gave $K=0.59$ W/cm deg at 298°K, in good agreement with the present value of 0.60 W/cm deg at 300°K. The temperature variation of K of Ge for temperatures near or above room temperature has been measured by many investigators. These are listed[6,21,22,26–36] in Table II. Some of these K versus T curves for Ge are shown along with the present results in Fig. 8. The agreement of the older results with the present ones is to within ±20% at 300°K, but becomes increasingly poor at the higher temperatures. The very abrupt rise in K suggested by the authors[6] in 1960 is not confirmed. The change in slope is much more gradual. The large range of values for K of Ge above 700°K found in the other curves in Fig. 8 can be attributed to experimental difficulties in measuring and controlling the thermal radiation losses. The K values deduced from thermal diffusivity measurements by Abeles *et al.*[21,22] are not subject to this source of error, and the agreement of these results with the present ones between 500 and 1070°K is very good. The 10% discrepancy between the present results and those of Abeles *et al.* at 300°K is about at the outer limits of accuracy

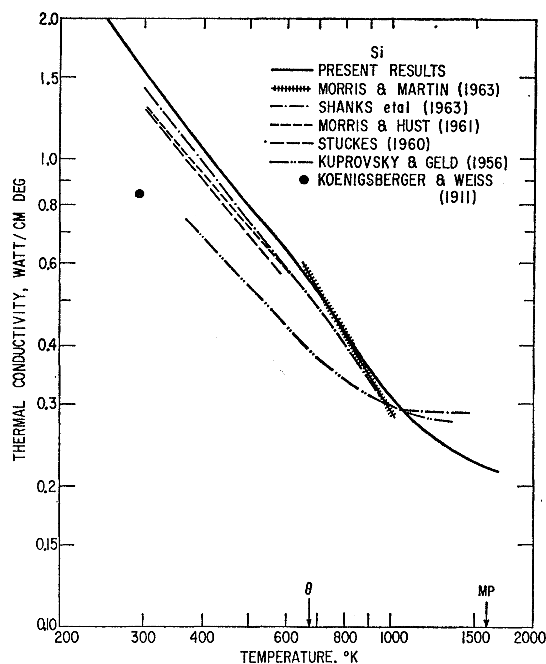

FIG. 7. Comparison of present and previous high-temperature K versus T results for Si.

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[35] E. D. Devyatkova and I. A. Smirnov, Fiz. Tverd. Tela **2**, 561 (1960) [English transl.: Soviet Phys.—Solid State **2**, 527 (1960)].
[36] E. D. Devyatkova and I. A. Smirnov, Fiz. Tverd. Tela **4**, 1669 (1962) [English transl.: Soviet Phys.—Solid State **4**, 1227 (1962)].

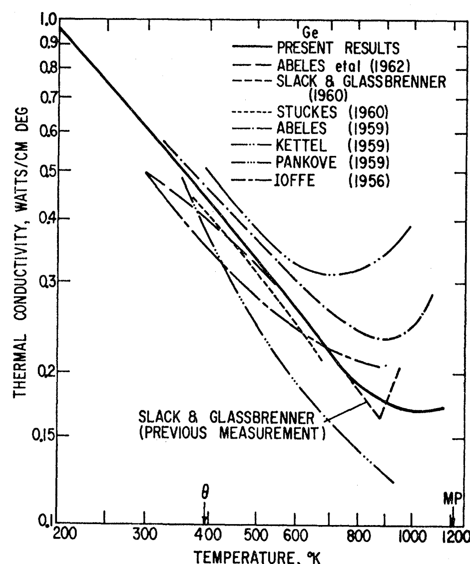

FIG. 8. Comparison of present and previous high-temperature K versus T results for Ge.

of the two experiments. The reason for this probably real discrepancy is not completely understood.

INTERPRETATION OF LOW-TEMPERATURE MEASUREMENTS

In the temperature range below 300°K, the K results on Si and Ge can be interpreted using Callaway's formalism.[37–39] The K due to heat transport by phonons is given by

$$K=\frac{k}{2\pi^2 v}\left(\frac{kT}{\hbar}\right)^3\int_0^{\theta/T}\tau_C(x,T)\frac{x^4e^x}{(e^x-1)^2}dx\,, \tag{1}$$

where k=Boltzmann's constant, v=average sound velocity, T=absolute temperature, h=Planck's constant, θ=Debye temperature, $x=(\hbar\omega/kT)$, ω=phonon frequency, and τ_C is a combined relaxation time. The complicating effects[37] of normal phonon scattering have been neglected. The combined relaxation time is thus taken as

$$\tau_C^{-1}=\tau_B^{-1}+\tau_I^{-1}+\tau_U^{-1}\,, \tag{2}$$

where τ_B, τ_I, τ_U are the relaxation times for boundary, isotope, and umklapp scattering of the phonons.

The particular form of the relaxation times shall now be examined. Klemens[40,41] has derived a relaxation time for scattering by point imperfections. His results are valid for isotope scattering.

$$\tau_I^{-1}(\omega)=3V_0\Gamma\omega^4/\pi v^3\,, \tag{3}$$

where V_0= average volume per atom in the crystal, and Γ=point impurity scattering parameter.[42] For umklapp scattering the following semiempirical expression[43] will be used:

$$\tau_U^{-1}=B_U\omega^2T\,. \tag{4}$$

TABLE II. Literature references to the thermal conductivity of Si and Ge for $T\geq 300$°K.

Mtrl	Author	Method	Temp. range °K	Year	Ref.
Si	Koenigsberger and Weiss	c	293	1911	14
	Kuprovski and Geld	b	380–1190	1956	15, 16
	Kingery	c	370–540	1959	17
	Mette *et al.*	e	550–770	1960	18
	Stuckes	c	300–580	1960	19
	Morris and Hust	c	300–700	1961	20
	Abeles *et al.*	d	310–1200	1962	21, 22
	Shanks *et al.*	d	300–1400	1963	23
	Morris and Martin	c	680–1000	1963	24
Ge	Greico and Montgomery	c	298	1952	26
	McCarthy and Ballard	c	280–370	1955	27
	Ioffe	a	300–870	1956	28
	Shtenbeck and Baranskii	a	200–370	1957	29
	Baranskii and Konopliasova	a	80–370	1958	30
	Abeles	a	320–1070	1959	31
	Kettel	a	390–1000	1959	32
	Pankove	e	370–970	1959	33
	Stuckes	c	310–680	1960	34
	Devyatkova and Smirnov	a	80–440	1960, 62	35, 36
	Slack and Glassbrenner	a, b	3–1020	1960	6
	Abeles *et al.*	d	310–1070	1962	21, 22

[a] Absolute, steady-state, longitudinal heat flow.
[b] Absolute, steady-state, radial heat flow.
[c] Comparative, steady-state longitudinal heat flow.
[d] Variable state, thermal diffusivity.
[e] Other.

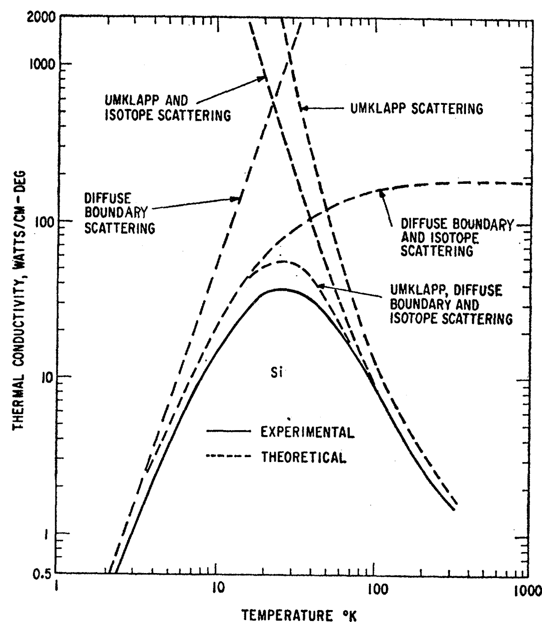

FIG. 9. Comparison of the low-temperature K results for Si with the theory in which various phonon scattering mechanisms are considered.

[37] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[38] J. Callaway and H. C. von Baeyer, Phys. Rev. **120**, 1149 (1960).
[39] J. Callaway, Phys. Rev. **122**, 787 (1961).
[40] P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.
[41] P. G. Klemens, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 14, p. 198.
[42] G. A. Slack, Phys. Rev. **126**, 427 (1962).
[43] G. A. Slack and S. Galginaitis, Phys. Rev. **133**, A253 (1964).

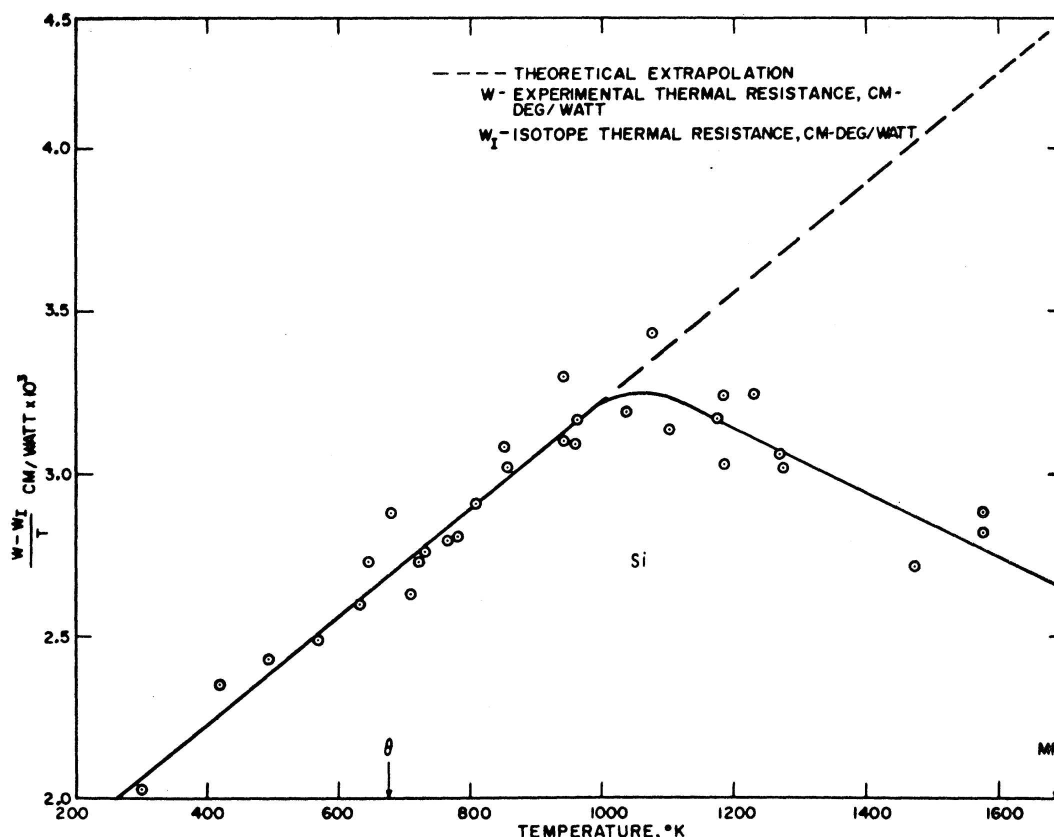

FIG. 10. The function $(W-W_I)T^{-1}$ versus T for Si as a means of determining the extrapolated lattice thermal resistivity at high temperatures.

Here B_U has the approximate value[43] of

$$B_U \sim (h\gamma^2/2\pi m\theta v^2)\exp(-\theta/3T), \tag{5}$$

where γ = Grüneisen's constant assumed to be equal to 2, and m = average mass of a single atom. For boundary scattering the relaxation time for diffuse scattering of the phonons off the walls of the crystal is simply

$$\tau_B^{-1} = v/L, \tag{6}$$

where L is the average diameter of the crystal. For Si these various relaxation times have been included in the K expression given in Eq. (1) using the following values: $v=6.4\times10^5$ cm/sec, $\theta=674$°K, $V_0=1.99\times10^{-23}$ cm^3, $\Gamma=1.65\times10^{-5}$, and $L=0.44$ cm. The results of the calculations for various combinations of relaxation times are shown in Fig. 9 for Si. It can be seen that all three relaxation times must be used in order to obtain agreement between theory and experiment. The theoretical curve with all three scattering processes included gives a maximum K of 56 W/cm deg at 28°K for Si compared to the observed maximum of 39 W/cm deg at 25°K. The fit at lower K values is rather better. In view of the simple model used for deriving Eq. (1) such agreement is considered reasonable. A similar sort of analysis has been carried out by other authors[6,37] for Ge at low temperatures, where the agreement is even better. Some improvement in the fitting of the theory to experiment can be made by including the effects of both the transverse and longitudinal phonon branches and the effects of phonon dispersion.[44] These added complications will not be considered here. The primary conclusion to be drawn from the low-temperature results for $T<300$°K is that phonons are the only significant carriers of the thermal energy, and they are scattered by other phonons, isotopes, and the crystal boundaries. Other carriers of thermal energy do, however, become important for $T>300$°K.

INTERPRETATION OF HIGH-TEMPERATURE MEASUREMENTS

Lattice Thermal Conductivity

In the present context high temperature means $T>300$°K. In this region it is necessary to consider photons and electrons and holes as well as phonons as possible carriers of thermal energy. We shall assume that these various carriers interact only weakly so that their contributions to the thermal conductivity are additive.

[44] M. G. Holland, Phys. Rev. **132**, 2461 (1963).

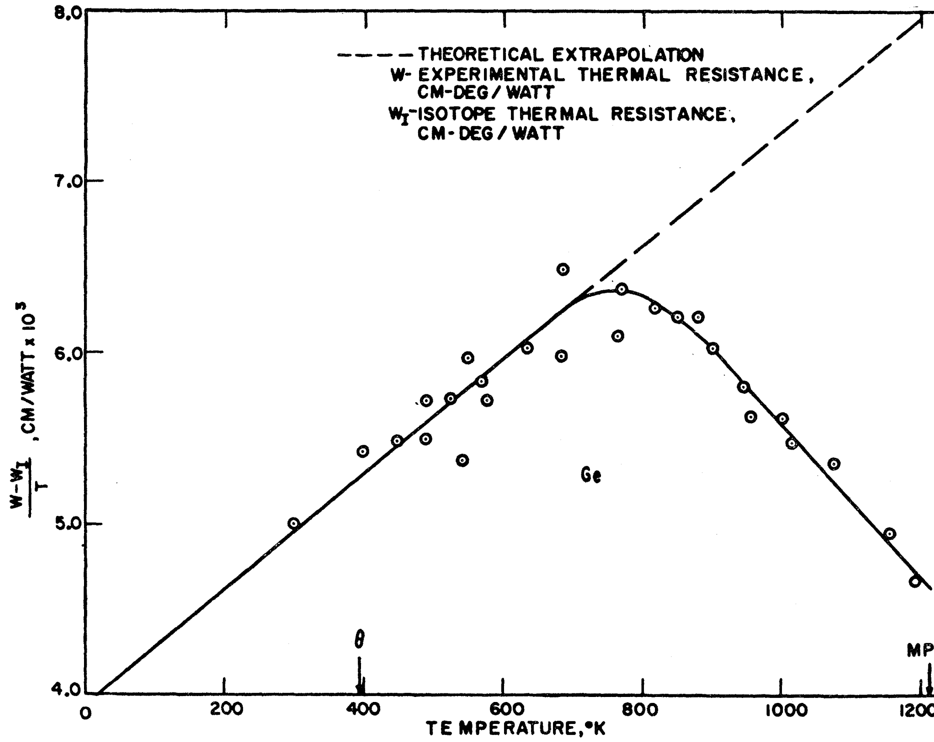

FIG. 11. The function $(W-W_I)T^{-1}$ versus T for Ge as a means of determining the extrapolated lattice thermal resistivity at high temperatures.

Thus

$$K=K_g+K_e+K_r, \tag{7}$$

where K_g is the phonon, K_e is the electronic, and K_r is the radiative or photon contribution to K.

Let us first consider the lattice thermal conductivity K_g. At high temperatures we have to consider the relaxation times τ_I and τ_U given in Eqs. (3) and (4), but we can neglect τ_B in Eq. (6). Equation (4) gives the relaxation time for 3-phonon umklapp processes. However, for $300°\text{K}<T<1681°\text{K}$, we are in the range of T comparable to or greater than the Debye temperature θ for both Si and Ge. In this range, it may be necessary to consider the relaxation times for four-phonon processes, as Pomeranchuck[45–47] has pointed out. He gives a relaxation time for these higher order (H) processes as:

$$\tau_H^{-1}=B_H\omega^2T^2, \tag{8}$$

with B_H a constant. K_g can be evaluated for $T>\theta$ from Eqs. (1), (3), (4), and (8) if τ_C^{-1} is taken as

$$\tau_C^{-1}=\tau_U^{-1}+\tau_H^{-1}+\tau_I^{-1}.$$

In the region where $T>\theta$ the quantity x in Eq. (1) is small, and the integral simplifies to

$$K=\frac{k}{2\pi^2 v}\left(\frac{kT}{\hbar}\right)^3\int_0^{\theta/T}\tau_C x^2dx. \tag{9}$$

Also the exponential factor in B_U disappears to make B_U temperature-independent. Thus

$$\tau_C^{-1}=(B_UT+B_HT^2)\omega^2+A\omega^4. \tag{10}$$

For $T\geq\theta$ the isotope scattering is much less important than the phonon-phonon scattering. In this limit Eqs. (9) and (10) can be reduced by the method used by Ambegaokar,[48] to

$$K_g^{-1}\equiv W_g=W_U+W_H+W_I,$$

where

$$\begin{aligned}W_U&=\pi vhB_UT/\theta k^2,\\ W_H&=\pi vhB_HT^2/\theta k^2,\\ W_I&=4\pi^2V_0\theta\Gamma/hv^2.\end{aligned} \tag{11}$$

This reduction requires $W_g\gg W_I$. This condition is fulfilled for Si and Ge at high temperatures. The only really unknown quantity in Eq. (11) is B_H. The quantities B_U and B_H can be evaluated experimentally from a plot of $(W_g-W_I)T^{-1}$ versus T. The quantity W_I is, except for a difference of a factor of 12 in the definition of Γ, the same as that given by Ambegaokar.[48] For Si one obtains $W_I=0.033$ cm deg/W. For Ge the value is $W_I=0.17$ cm deg/W using $V_0=2.26\times10^{-23}$ cm^3, $\theta=395°\text{K}$,[49] $\Gamma=4.90\times10^{-5}$,[50] and $v=3.94\times10^5$ cm/sec.

[45] I. Pomeranchuk, Phys. Rev. **60**, 820 (1941).
[46] I. Pomeranchuk, J. Phys. USSR **4**, 259 (1941).
[47] I. Pomeranchuk, J. Phys. USSR **7**, 197 (1943).
[48] V. Ambegaokar, Phys. Rev. **114**, 488 (1959).
[49] P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).
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The determination of W_g is the next problem. Consider Eq. (7). As has been shown,[6] K_r is negligible at all temperatures for Ge. The measurements of Ukhanov[51] on the optical absorption of Si and Ge at elevated temperatures were employed to calculate K_r. This calculation shows that K_r is also negligible (i.e., less than 2% of total K) for Si at all temperatures. The K_e term in Eq. (7) becomes important only at the very highest temperatures when the number of thermally generated carriers becomes very large. This term is responsible for the upturn in the K results shown in Figs. 2 and 3 above 800°K. Thus K_g is the only significant term in Eq. (7) for $T<800$°K in Si and Ge. Therefore, the total measured thermal conductivity is $K=W_g^{-1}$ for $T<800$°K. Figures 10 and 11 show the plots of $(W-W_I)T^{-1}$ versus T for Si and Ge. The linear approximation predicted by Eq. (11) is satisfactory for $T\geq 0.5\theta$ until at high temperatures the K_e term becomes important. The dashed extrapolations in Figs. 10 and 11 show what the behavior would be if only the lattice thermal conductivity K_g were present.

The linear portions of the curves in Figs. 10 and 11 yield the following empirical expressions for W_g:

$$\begin{aligned}\text{Ge:}\quad & W_g=(3.95\times10^{-3}T+3.38\times10^{-6}T^2+0.17)\ \text{cm deg/W},\\ \text{Si:}\quad & W_g=(1.56\times10^{-3}T+1.65\times10^{-6}T^2+0.03)\ \text{cm deg/W}.\end{aligned}\tag{12}$$

The first term in these equations yields an experimental value of B_U which agrees with that estimated from Eq. (5) to within a factor of two for both Si and Ge. Such agreement is quite satisfactory. If the very approximate theory used in obtaining Eq. (11) is taken at face value, the results in Eq. (12) for B_H show that the ratio τ_H/τ_U is 3 for Ge and 1 for Si at $T=\theta$. This ratio becomes smaller at higher temperatures. Notice that we have chosen to interpret the observation that K_g for Si and Ge at high temperatures decreases faster than T^{-1} as a sign that 4-phonon processes are taking place. A similar conclusion has been arrived at by Stuckes[19] and by Steigmeier and Kudman[52] for various IV and III-V semiconductors. The result that the 3-phonon and 4-phonon relaxation times, τ_H and τ_U, are nearly equal at $T=\theta$ should, however, be greeted with some caution. The main purpose of the plots in Figs. 10 and 11 is to allow one to make a reasonable extrapolation of K_g in the temperature region where K_e is appreciable.

This extrapolation of K_g from Figs. 10 and 11 has been replotted as the dashed curve in Figs. 2 and 3. The difference between this curve and the experimental results is, from Eq. (7), just K_e. These experimental values of K_e for Si and Ge are plotted in Figs. 12 and 13.

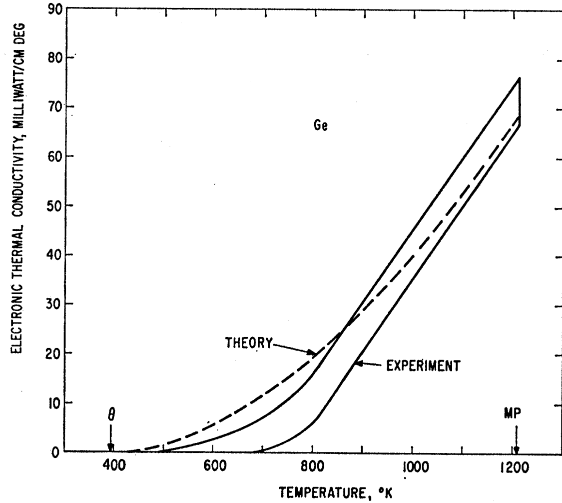

FIG. 13. Comparison of the experimental and theoretical electronic thermal conductivity, K_e versus T, for Ge.

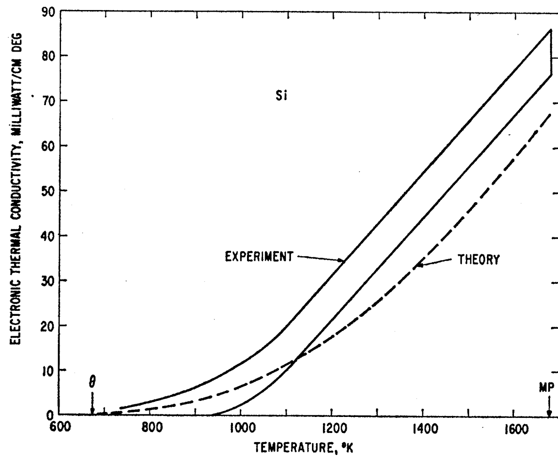

FIG. 12. Comparison of the experimental and theoretical electronic thermal conductivity, K_e versus T, for Si.

Electronic Thermal Conductivity

The experimental results for K_e can be compared with the theory that has been developed by Davydov and Shmushkevitch,[53] by Price,[54] and by Drabble and Goldsmid.[55] Their results for K_e can be written as the sum of an electronic polar contribution K_{ep}, and an electronic bipolar part K_{eb}.

$$K_e=K_{ep}+K_{eb},$$

where

$$\begin{aligned}K_{ep}&=2\left[\frac{k}{e}\right]^2\sigma T,\\ K_{eb}&=\frac{b}{(1+b)^2}\left[\frac{E_G}{kT}+4\right]^2\left[\frac{k}{e}\right]^2\sigma T.\end{aligned}\tag{13}$$

[51] Yu. I. Ukhanov, Fiz. Tverd. Tela **3**, 2105 (1961) [English transl.: Soviet Phys.—Solid State **3**, 1529 (1962)].

[52] E. F. Steigmeier and I. Kudman, Phys. Rev. **132**, 508 (1963).

[53] B. Davydov and I. Shmushkevitch, Uspekhi Fiz. Nauk USSR **24**, 21 (1940).

[54] P. J. Price, Phil. Mag. **46**, 1252 (1955).

[55] J. R. Drabble and H. J. Goldsmid, *Thermal Conduction in Semiconductors* (Pergamon Press, Inc., London, 1961), pp. 104–119.

TABLE III. The theoretical electronic thermal conductivity of Si and Ge versus temperature.

Crystal	T °K	$b/(1+b)^2$	E_G eV	σ ohm^{-1} cm^{-1}	K_{ep} mW/cm deg	K_{eb} mW/cm deg	K_e mW/cm deg
Si	800	0.21	0.92	3.9	0.0	1.4	1.4
	1000	0.21	0.85	22.	0.3	6.2	6.5
	1200	0.21	0.78	73.	1.3	16.4	17.7
	1400	0.21	0.71	170.	3.5	31.9	35.4
	1600	0.21	0.55	315.	7.5	50.5	58.0
	1681	0.21	0.52	385.	9.6	58.2	67.8
Ge	400	0.20	0.61	0.9	0.0	0.3	0.3
	600	0.19	0.52	30.	0.3	5.0	5.3
	800	0.18	0.43	160.	1.9	18.0	19.9
	1000	0.16	0.34	440.	6.5	33.4	39.9
	1200	0.16	0.26	870.	15.5	51.9	67.4
	1210	0.16	0.25	890.	16.0	52.5	68.5

The various quantities are defined as k=Boltzmann's constant, e=electronic charge, σ=total electrical conductivity at T, b=mobility ratio at T, and E_G=indirect energy gap at T. The polar part K_{ep} is the usual Wiedemann-Franz-Lorenz contribution present in metals. The bipolar part K_{eb} is a property of semiconductors, and is caused by electron-hole pairs with energy E_G diffusing down the temperature gradient. Equation (13) has been derived for a very idealized semiconductor which is assumed to be intrinsic, to possess simple parabolic valence and conduction bands, and in which the charge carriers suffer only acoustic mode lattice scattering where the scattering probability varies with the carrier energy e as $\sqrt{e}$. Neither Si nor Ge can be said to fit this model very well since they have multiple minima conduction bands, multiple valence bands, and since both acoustic mode and intervalley scattering occur. An exact calculation of K_e in which all of these effects are considered is not undertaken here. However, as will be seen, Eq. (13) yields predictions which are in reasonable agreement with the experiment.

The experimental parameters that are used in Eq. (13) are σ, b, and E_G. Representative values for these parameters and the calculated values for K_{ep} and K_{eb} are given in Table III. For Si, the $\sigma(T)$ values have been taken from Morin and Maita[56] and Mokrovskii and Regel,[57] and the values of b versus T have been estimated from an extrapolation of the mobility curves of Morin and Maita.[56] The $E_G(T)$ values[56] have been corrected for more recent values of the effective mass, and are taken from Hannay.[58] It has been assumed that E_G varies linearly with temperature and the value of $E_G=(1.21-4.1\times10^{-4}T)$ eV was used.

For Ge the $\sigma(T)$ values have been taken from Morin and Maita,[59] from Epstein,[60] and from the recent complication of Hamilton and Seidensticker.[61] The values of b versus T have been estimated from an extrapolation of the data given by Morin and Maita.[59] The $E_G(T)$ values[59] have been corrected for better effective mass values.[58] The equation used for Ge was $E_G=(0.785-4.4\times10^{-4}T)$ eV. The computation of K_{ep} depends only on σ and is probably accurate to ±5%. The computation of K_{eb} depends similarly on σ and is also sensitive to errors in E_G and b. The over-all accuracy in the calculation of K_{eb} is estimated to be ±15%. Figures 12 and 13 show how the calculated theoretical value of K_e compares with the experimental determination, which is judged to be accurate to within ±5 mW/cm deg. This uncertainty is indicated by the broad band in Figs. 12 and 13. Since the theoretical values of K_e are probably accurate to ±15%, the agreement with theory is considered quite adequate. In view of the uncertainties in both the calculated and experimental values of K_e it does not seem worthwhile, at present, to undertake a more exact calculation of K_e in which the details of the band structure of Si and Ge are carefully taken into account.

TABLE IV. The experimentally determined contributions to K in solid Si and Ge at their respective melting points.

Quantity	Si 1681°K	Ge 1210°K
K_{ep}/K	5%	9%
K_{eb}/K	32%	32%
K_g/K	63%	59%
K (W/cm deg)	0.22	0.17

The three contributions to the total thermal conductivity, K_{tot}, at the melting point are K_g, K_{ep}, and K_{eb}. Table IV shows the relative contributions of these three terms for Si and Ge. K_g is estimated from the extrapolated dashed curve in Figs. 2 and 3, K_{ep} is calculated form Eq. (13), and K_{eb} is taken to be equal to $K_{\text{tot}}-K_g-K_{ep}$. For both materials the lattice thermal conductivity is still dominant at the melting point and is 61% of the total, the bipolar electron-hole pair diffusion accounts for 32%, while the usual Wiedemann-Franz-Lorenz contribution is only 7% of the total.

The experimental value of K_{eb} determined from $K_{\text{tot}}-K_g-K_{ep}$ can be used to estimate E_G by means of Eq. (13). The values of b and σ at the melting point are taken from Table III, and the experimental values of K_e are taken from Figs. 12 and 13. The result is that at the melting point the thermal band gap is $E_G=0.6\pm0.1$ eV for Si and $E_G=0.26\pm0.08$ eV for Ge. These values are not very far from the linearly extrapolated values of 0.52 and 0.25 eV given in Table III. The K_e results show that the band gap in the solid at the melting point is nonzero. The gap thus drops discontinuously to zero upon melting, since both liquid Si and Ge are metallic in character.[57,61]

[56] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).
[57] N. P. Mokrovskii and A. R. Regel, Zh. Tekhn. Fiz. **23**, 779 (1953).
[58] N. B. Hannay, *Semiconductors* (Reinhold Publishing Corporation, New York, 1959), p. 332.
[59] F. J. Morin and J. P. Maita, Phys. Rev. **94**, 1525 (1954).
[60] E. A. Epstein, Ph.D. thesis, Purdue University, 1954 (unpublished).
[61] D. R. Hamilton and R. G. Seidensticker, J. Appl. Phys. **34**, 2697 (1963).

MAGNETIC FIELD EFFECTS

The electronic contribution to the K of Ge is about 40% of the total at 1175°K, a temperature 35°K below the melting point. An attempt was made to alter this electronic contribution by applying a moderate magnetic induction in a direction perpendicular to the axis of the K sample. Magnetic induction strengths (MKS units) up to 0.6 Wb/m^2 (6000 G) were applied, but no effect on K was observed to within $\pm 2\%$. Steele[62] found that values up to 1.15 Wb/m^2 had no effect on the K of Ge at 278°K. Here the estimated $K_e = K_{ep} + K_{eb}$ is only $4\times 10^{-4}\%$ of the total K for intrinsic Ge. His experiment was not sufficiently sensitive to see changes this small even if the magnetic induction had been sufficiently strong to suppress K_e. Magnetic effects on K have been seen in HgSe,[63] Bi_2Te_3,[64] and InSb.[65,66] The requirement on the magnetic induction is that it must be large enough so that the charge carriers will make about one cyclotron orbit before being scattered. This minimum value,[65] B_m, is approximately

$$B_m = \pi/\mu,$$

where B is in Wb/m^2, and μ is the carrier mobility in m^2/V-sec. The electron mobility in intrinsic Ge at 1175°K is about 0.03 m^2/V-sec, the hole mobility is even lower. The minimum magnetic induction is thus about 100 Wb/m^2 (10^6 G). It is rather clear why no magnetic effects were seen in Ge. No experiments on Si were tried.

CONCLUSIONS

The thermal conductivity K of silicon has been measured from 3 to 300°K using a steady-state, longitudinal heat flow apparatus. By using the relaxation times for umklapp scattering, isotope scattering and boundary scattering, and Callaway's simple model, a theoretical phonon thermal conductivity was calculated and was found to agree with the experimental measurements.

A high-temperature thermal conductivity apparatus employing steady-state, radial heat flow in a cylindrical sample was designed and was found to give accurate ($\pm 5\%$), absolute, measurements at temperatures from 300 to 1600°K. The method does not require any correction for heat loss by radiation. The K values so obtained agree with those found for both Si and Ge using the low-temperature, longitudinal heat flow apparatus.

The results show that phonons are the dominant carriers of heat in high purity, solid Si and Ge at all temperatures from 3°K to their melting points. The phonon or lattice thermal conductivity K_g decreases faster than the T^{-1} law predicted by three phonon umklapp scattering for $T \geq \theta$, where θ is the Debye temperature. For temperatures $T > \theta$, an approximate theoretical formula has been developed for K_g which agrees with experimental results between $0.5\theta < T < 1.6\theta$. This formula is based on the assumption that three-phonon, four-phonon, and isotope scattering are important at high temperatures, and it predicts that the thermal resistivities of these three processes are additive. It is suggested that the relaxation times for both three- and four-phonon processes are comparable for $T \geq \theta$.

For temperatures above about 1.6θ an electronic thermal conductivity K_e has been found in both Si and Ge. The theoretical and experimental values of K_e agree quite well. The major part of K_e comes from the bipolar term, with some small contribution from the polar term. At the melting point the phonons contribute an average of 61% to the total K while the bipolar and polar contributions are 32% and 7%, respectively.

The thermal band gaps at the melting points are estimated from K_e as 0.6 ± 0.1 eV for Si and 0.26 ± 0.08 eV for Ge. They are in reasonable agreement with the linear extrapolations from lower temperatures.

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[66] R. G. Morris and F. Hornstra, Rev. Sci. Instr. **33**, 1067 (1962).