

Phonon Scattering in Semiconductors From Thermal Conductivity Studies

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The lattice thermal conductivity of a number of semiconductors including InSb, GaAs, GaSb, CdTe, and CdS has been measured between 1.7 and 300°K. This, together with previous work on Si and Ge, is used to investigate the validity of the relaxation time expressions for scattering of phonons by boundaries, atomic impurities and electrons, and to discuss phonon-phonon interactions and resonance scattering effects. The results indicate that the boundary scattering and isotope scattering relaxation times lead to accurate calculated values of thermal conductivity only when the materials are exceptionally pure. Structure, which has been identified as due to resonance scattering, has been observed in the data for most of the materials. Electron-phonon scattering has been noted in GaSb but the complexity of the problems make the analysis only qualitative. The maximum transverse acoustical phonon frequency may be of more significance than the Debye temperature for thermal conductivity calculations.

I. INTRODUCTION

THE lattice thermal conductivity of a number of semiconductors has been investigated in the range 1.7 to 300°K in order to study phonon scattering.^{1,2} In this temperature range the phonons are subjected to a number of interactions. The phonons can be scattered by crystallite boundaries,³ by other phonons,⁴⁻⁶ and by imperfections and impurities of all types⁷ including dislocations, isotopes, and strain fields.⁸ In addition there is recent evidence of electron-phonon scattering,⁹⁻¹¹ and resonance scattering by localized modes due to impurities.¹²⁻¹⁴

Almost every known phonon scattering process that has been found in other materials in this temperature range below room temperature has been found in the various semiconductors. Mass-difference scattering has been investigated in isotopically pure germanium¹⁵ and in germanium-silicon alloys.^{16,17} Impurity scattering which is stronger than that expected due to the mass difference of the impurity atoms has also been studied in silicon,^{9,18,19} germanium,⁹ and gallium arsenide.²⁰ A

scattering process which has the same frequency and temperature dependence as boundary scattering but which depends on the concentration of certain impurities has been found in silicon.²¹ Boundary scattering has also been investigated in silicon.²¹ The possibility of optical mode scattering and transport has been noted in some of the III-V compounds.²² Electron-phonon effects have been studied in germanium⁹⁻¹¹ as have strain-induced electron-phonon scattering.^{23,24} The resonance scattering mechanism first discussed by Pohl¹² and by Klein²⁵ was probably first evidenced in measurements on samples of oxygen-doped silicon in which structure was noted in the data near 50°K.²⁶

The value of semiconductor studies is that the phonon effects are all present and it is possible to isolate certain scattering mechanisms. Many of the materials can be prepared in extremely pure and perfect form²⁷ so that impurity scattering effects can be minimized, and such intrinsic properties as phonon-phonon scattering can be investigated.²⁸ The materials can then be carefully doped with certain impurities and the number and nature of these impurity centers can be accurately determined by well-known electrical and optical techniques.²⁷ In this way, scattering of phonons due to specific impurities or imperfections can be studied.

¹ P. G. Klemens in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 7.

² P. Carruthers, *Rev. Mod. Phys.* **33**, 92 (1961).

³ H. B. G. Casimir, *Physica* **5**, 595 (1938).

⁴ R. Peierls, *Quantum Theory of Solids* (The Clarendon Press, Oxford, 1955).

⁵ P. G. Klemens, *Proc. Roy. Soc. (London)* **A208**, 108 (1951).

⁶ C. Herring, *Phys. Rev.* **95**, 954 (1954).

⁷ P. G. Klemens, *Proc. Phys. Soc. (London)* **68**, 1113 (1955).

⁸ P. Carruthers, *Phys. Rev.* **114**, 995 (1959).

⁹ J. A. Carruthers, T. H. Geballe, H. M. Rosenberg, and J. M. Ziman, *Proc. Roy. Soc. (London)* **A238**, 502 (1957).

¹⁰ J. F. Goff and N. Pearlman, *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, Canada, 1961), p. 284.

¹¹ J. A. Carruthers, J. F. Cochran, and K. Mendelssohn, *Cryogenics* **2**, 160 (1962).

¹² R. O. Pohl, *Phys. Rev. Letters* **8**, 481 (1962).

¹³ C. T. Walker and R. O. Pohl, *Phys. Rev.* **131**, 1433 (1963).

¹⁴ M. Wagner, *Phys. Rev.* **131**, 1443 (1963).

¹⁵ T. H. Geballe and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).

¹⁶ B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, *Phys. Rev.* **125**, 44 (1962).

¹⁷ A. M. Toxen, *Phys. Rev.* **122**, 450 (1961).

¹⁸ M. G. Holland in *Proceedings of the International Conference*

on *Semiconductor Physics, Prague, 1960* (Publishing House of the Czechoslovakian Academy of Sciences, Prague, 1961), p. 633.

¹⁹ J. C. Thompson and B. A. Younglove, *Phys. Chem. Solids* **20**, 146 (1961).

²⁰ G. A. Slack (to be published).

²¹ M. G. Holland and L. J. Neuringer, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 475.

²² E. F. Steigmeier and I. Kudman, *Phys. Rev.* **132**, 508 (1963).

²³ R. W. Keyes and R. J. Sladek, *Phys. Rev.* **125**, 478 (1962).

²⁴ R. J. Sladek, *Proceedings of the International Conference on the Physics of Semiconductors, Exeter 1962* (The Institute of Physics and the Physical Society, London, 1962), p. 35.

²⁵ M. V. Klein, thesis, Cornell University, 1960 (unpublished).

²⁶ M. G. Holland, *Proceedings of the Seventh International Conference on Low Temperature Physics* (The University of Toronto Press, Toronto, Canada, 1961), p. 280.

²⁷ R. A. Smith, *Semiconductors* (Cambridge University Press, Cambridge, England, 1959).

²⁸ M. G. Holland, *Phys. Rev.* **132**, 2461 (1963). This paper will henceforth be referred to as I.

TABLE I. Sample properties. The symbols are defined in Ref. 28.

Sample	v_l	$\times 10^5 v_t$ cm/sec	v_s	$\theta_D^\circ K$	$A \times 10^{-44}$ sec ³	L cm	F^a	$\tau_b \times 10^{-6}$ sec	N cm ⁻³
InSb	3.77 ^b	2.28 ^b	2.3	208 ^b	0.923	0.554	0.83	2.00	7×10^{18}
GaAs-1	5.24 ^c	1.625 ^b	3.3	345 ^d	0.465	0.729	0.75	1.66	7×10^{16}
-2		2.48 ^e				0.534	0.80	1.30	7×10^{15}
-3		3.35 ^e				0.367	0.85	0.905	$\sim 10^{18}$
GaSb- <i>n</i> -1	3.97 ^e	2.78 ^e	3.09	270 ^f	0.813	0.294	0.82	0.78	4.0×10^{18}
- <i>n</i> -2						0.588	0.73	1.39	1.4×10^{18}
- <i>p</i> -1						0.294	0.82	0.78	1.0×10^{17}
- <i>p</i> -2						0.336	0.78	0.85	2.0×10^{17}
CdS	4.42 ^g	1.76 ^g	2.20	286 ^h	6.43	0.587	0.84	2.24	$\geq 10^{16}$
CdTe	2.97 ⁱ	1.81 ⁱ	2.08	252 ^j	9.80	0.726	0.80	2.80	$\sim 5 \times 10^{17}$

^a See Ref. 40.^b R. F. Potter, Phys. Rev. **103**, 47 (1956).^c T. B. Bateman, H. J. McSkimin, and J. M. Whelan, J. Appl. Phys. **30**, 544 (1959).^d C. W. Garland and K. C. Parks, J. Appl. Phys. **33**, 759 (1962).^e H. J. McSkimin, W. L. Bond, G. L. Pearson, and H. J. Hrostowski, Bull. Am. Phys. Soc. **10**, 111 (1956).^f P. V. Gul'tyaev and A. V. Petrov, Fiz. Tver. Tela. **1**, 368 (1959) [English transl.: Soviet Phys.—Solid State **1**, 330 (1959)].^g See A. R. Hutson, J. Appl. Phys. **32**, 2287 (1961).^h Calculated from data of M. Balkanski and J. M. Besson, J. Appl. Phys. **32**, 2292 (1961).ⁱ Reported by D. G. Thomas, J. Appl. Phys. **32**, 2298 (1961).^j S. Yamada, J. Phys. Soc. Japan **15**, 1940 (1960).

In this work data on several III-V compounds, including InSb, GaAs, and GaSb, as well as the II-VI compounds CdS and CdTe, will be presented and analyzed. This, together with previous data and analyses on Ge and Si²⁸ will be used to investigate the validity of the relaxation time expressions for scattering of phonons by boundaries, atomic impurities, and electrons, and to discuss phonon-phonon interactions and resonance scattering effects.

The data will be analyzed for the most part using the phenomenological theory developed by Callaway.²⁹ In I it was shown that a more complicated type of analysis, in which separate heat transport by transverse and longitudinal phonons is considered, gives an excellent fit to the data on germanium and silicon over a very wide range of temperature. It was also shown, however, that this two-mode conduction analysis, and the Callaway analysis give approximately the same results in the boundary scattering and impurity scattering regions. Thus, because of ease of calculation, the Callaway form will be used where applicable.

II. EXPERIMENTAL PROCEDURES AND RESULTS

The thermal conductivity was measured in the apparatus described previously.³⁰ The samples were rectangular parallelepipeds usually $\frac{1}{8} \times \frac{1}{8}$ in. or larger in cross section and from $\frac{1}{2}$ to 1-in. long. The sample surfaces were roughened with 280-grit silicon carbide powder and the ends coated with indium. A differential thermocouple and carbon resistance thermometers were attached to the sample by means of spring loaded clamps.

For samples with very low thermal conductivity, such as GaSb, the accuracy of the low-temperature data was checked by minimizing the heat leaks to and

from the sample. Long lengths of superconducting niobium wire were used for the four-heater lead wires, and long lead wires were also used for the carbon resistors and the thermocouples. The results remained the same under these conditions.

Sample Properties

Hall effect and resistivity were measured as a function of temperature, and the donor and acceptor densities were deduced from these measurements.²⁷ Table I lists the parameters of the samples studied. For all the samples except CdS and GaSb, the number of impurities is assumed equal to $|1/Re|$, the reciprocal of the product of Hall coefficient and electronic charge at room temperature. This assumes that there is little compensation in the samples, and that the Hall coefficient proportionality factor is approximately equal to 1.³¹ For CdS the density of impurities is taken from spectroscopic analysis so that electrically inactive as well as the electrically active impurities are included.

For *n*- and *p*-type GaSb the interpretation of the Hall and resistivity data is complicated. In the case of *n*-type material there are three conduction band minima which are very close in energy.³² The values of *N* given in Table I for GaSb-*n*-1 and GaSb-*n*-2 are deduced from a comparison of our Hall and resistivity with the results and analysis of Sagar.³³ The Hall and resistivity data for the two *p*-type GaSb samples are shown in Fig. 1. Comparing these data with measurements on Ge interpreted by Fritzsche,^{34,35} leads to the conclusion that there is impurity conduction in the

³¹ See for example: H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7.

³² H. Ehrenreich, J. Appl. Phys. **32**, 2155 (1961).

³³ A. Sagar, Phys. Rev. **117**, 93 (1960).

³⁴ H. Fritzsche, Phys. Rev. **99**, 406 (1955).

³⁵ H. Fritzsche, Phys. Chem. Solids **6**, 69 (1958).

²⁹ J. Callaway, Phys. Rev. **113**, 1046 (1959).

³⁰ M. G. Holland and L. G. Rubin, Rev. Sci. Instr. **33**, 923 (1962).

GaSb samples. Analysis of the number of impurities and the compensation (relative number of minority centers) is usually complicated in these cases, so that we have simply used $N=1/Re$ at room temperature. The values of the densities for the GaSb are probably correct to better than an order of magnitude. The one n -type sample has about three times greater a density of impurities than the other, and the one p -type sample has about twice the density of the other, as indicated in Table I.

Thermal Conductivity Measurements

Thermal conductivity data for the III-V compounds InSb, GaAs, and GaSb are shown in Figs. 2, 3, and 4.

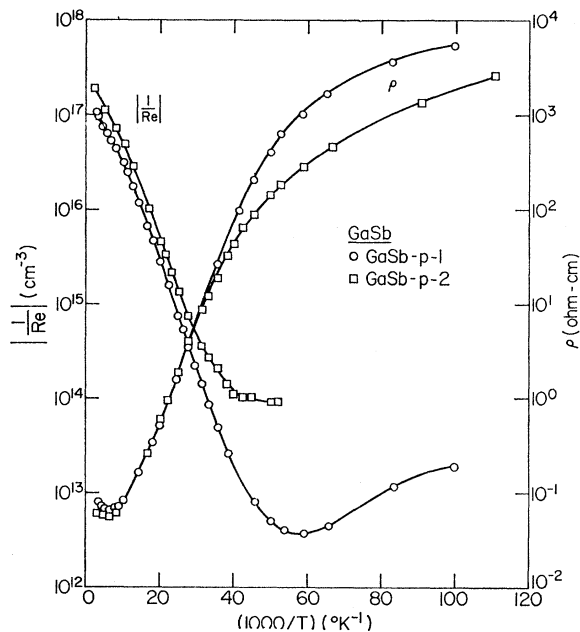


FIG. 1. Hall coefficient and resistivity versus temperature for p -type GaSb.

The solid lines on these figures came from theory and will be discussed in Sec. III. The InSb data are in reasonable agreement with those of Mielczarek and Frederikse³⁶ who took data from 15 to 45°K, and with the 200 to 300°K part of the high-temperature measurements of Busch and Steigmeier.³⁷ The GaAs data are in reasonable agreement with those of Slack.²⁰ We know of no other low-temperature data on GaSb.

The two sets of data for InSb at low temperatures were taken about one year apart on the same sample. The GaAs results were derived from two samples, GaAs-2 being the same sample as GaAs-1 but with reduced cross section. GaAs-3, the second sample, is a

³⁶ E. V. Mielczarek and H. P. R. Frederikse, Phys. Rev. **115**, 888 (1959).

³⁷ G. Busch and E. Steigmeier, Helv. Phys. Acta **34**, 1 (1961).

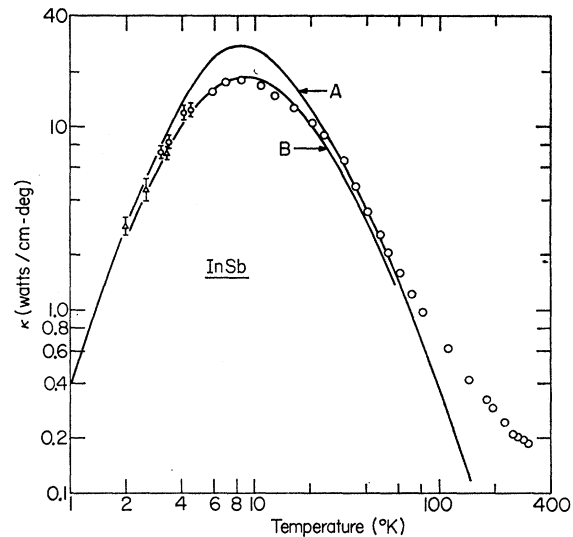


FIG. 2. Thermal conductivity of InSb. Curve A=Callaway equation with $\tau_b=2.0 \times 10^{-6}$ sec, $A=0.923 \times 10^{-44}$ sec³, $B_1+B_2=1.92 \times 10^{-22}$ sec/deg³. Curve B=same but $A=2.8 \times 10^{-44}$ sec³.

less pure sample from a crystal grown in this laboratory several years ago. Four separate samples of GaSb were measured.

A dip in the data should be noted for InSb near 15°K and for GaAs near 30°K. The thermal conductivity was investigated carefully in these regions to ensure that the dips are real effects and not merely scatter.

The thermal conductivity results for the II-VI compounds CdTe and CdS are shown in Figs. 5 and 6. The solid lines again represent theoretical results which

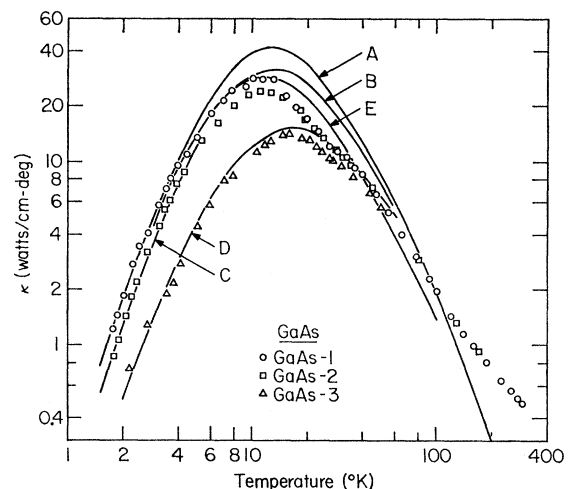


FIG. 3. Thermal conductivity of GaAs. Curve A=Callaway equation with $\tau_b=1.66 \times 10^{-6}$ sec, $A=0.466 \times 10^{-44}$ sec³, $B_1+B_2=3.6 \times 10^{-23}$ sec/deg³. Curve B=same as curve A but $A=0.93 \times 10^{-44}$ sec. Curve C same as curve A but $\tau_b=1.30 \times 10^{-6}$ sec. Curve D has $\tau_b=0.53 \times 10^{-6}$ sec, $A=2.0 \times 10^{-44}$ sec³, $B_1+B_2=3.6 \times 10^{-23}$ sec/deg³. Curve E has $\tau_b=1.66 \times 10^{-6}$ sec, $A=0.46 \times 10^{-44}$ sec³, $B_1+B_2=5 \times 10^{-22}$ sec/deg³.

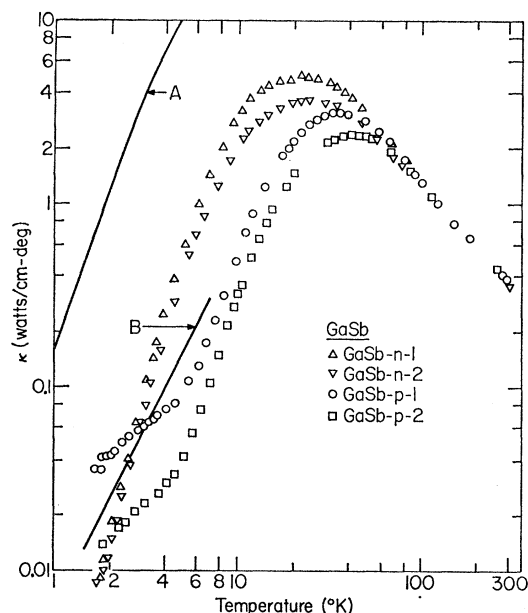


FIG. 4. Thermal conductivity of GaSb. Curve A=Callaway equation with $\tau_b \approx 1 \times 10^{-6}$ sec, $A = 0.813 \times 10^{-44}$ sec³. Curve B is from Ziman's theory of electron-phonon interactions, Eq. (9).

will be discussed in Sec. III. The CdTe data are in good agreement with those of Slack.³⁸ We know of no other thermal conductivity data on CdS.

There is more scatter in the low-temperature region of the CdTe data than is usual with our equipment. This might be attributed to inability to make good thermal contact to the specimen. To keep the brittle samples from breaking, the clamps were not tightened

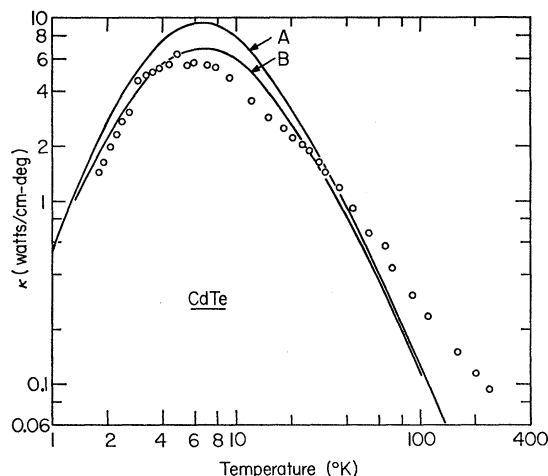


FIG. 5. Thermal conductivity of CdTe. Curve A: Callaway equation with $\tau_b = 2.80 \times 10^{-6}$ sec, $A = 9.80 \times 10^{-44}$ sec³, $B_1 + B_2 = 7.4 \times 10^{-22}$ sec/deg³. Curve B same as curve A but with $A = 29.4 \times 10^{-44}$ sec³.

³⁸ G. A. Slack, Bull. Am. Phys. Soc. 8, 208 (1963); G. A. Slack and S. Galginitis, Phys. Rev. 133, A253 (1964).

as much as usual and the resulting thermal resistance at the clamps might give rise to more error in the data than is normal.

Anisotropic values of thermal conductivity might be expected for CdS because of the crystal structure.³⁹ Unfortunately, the shape of the samples available allowed an accurate measurement of the conductivity only along the c axis. Dips are also evident in this data, near 20°K for both CdTe and CdS.

III. DISCUSSION

Most of the thermal conductivity data will be analyzed using the phenomenological equation due to Callaway.²⁹

$$\kappa = CT^3 \int_0^{\theta_D/T} \frac{x^4 e^x (e^x - 1)^{-2} dx}{\tau^{-1}}. \quad (1)$$

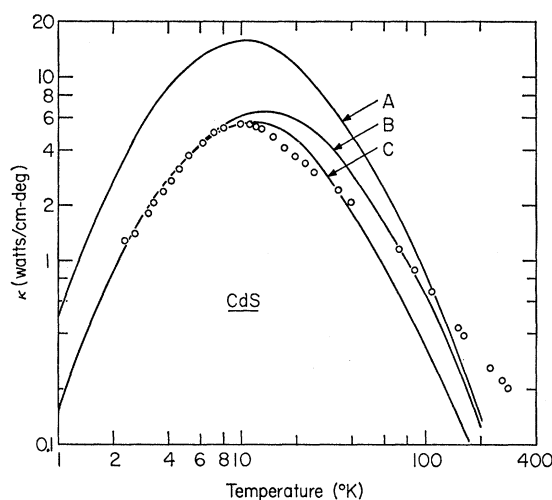


FIG. 6. Thermal conductivity of CdS. Curve A=Callaway equation with $\tau_b = 2.24 \times 10^{-6}$ sec, $A = 6.4 \times 10^{-44}$ sec³, $B_1 + B_2 = 2.74 \times 10^{-22}$ sec/deg³. Curve B: $\tau_b = 6.4 \times 10^{-7}$ sec, $A = 25.7 \times 10^{-44}$ sec³, $B_1 + B_2 = 2.74 \times 10^{-22}$ sec/deg³. Curve C: $\tau_b = 6.4 \times 10^{-7}$ sec, $A = 25.7 \times 10^{-44}$ sec³, $B_1 + B_2 = 5.5 \times 10^{-22}$ sec/deg³.

This equation has been discussed and the symbols defined in I. The total relaxation time τ will include boundary scattering, isotope scattering, and phonon-phonon scattering.

The Casimir expression³ for the boundary scattering relaxation time $\tau_b^{-1} = v/L$, $L = 1.21(l_1 l_2)^{1/2}$, where $l_1 l_2$ is the sample cross section, has been shown many times to give good agreement, normally in the range 10 to 50%, with the experimental results at low temperatures. However, in pure semiconductors the agreement between theory and experiment is better than five percent if the correction for finite sample length is taken into account.^{40,41} This was used in I for fitting

³⁹ See for example: R. H. Bube, Proc. IRE 43, 1836 (1955).

⁴⁰ R. Berman, F. E. Simon, and J. M. Ziman, Proc. Roy. Soc. (London) A220, 171 (1953).

⁴¹ R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) A231, 130 (1955).

the data on germanium and silicon. In the present work the relaxation time τ_b is calculated from the Casimir formula and then is corrected by the factor F which is taken directly from the curve, due to Ziman,⁴⁰ which considers the effect of finite sample length. Completely diffused scattering is assumed so that $f=1$ in Fig. 4 of Ref. 40.

The impurity scattering (mass-difference) relaxation time must be modified for compounds.^{7,42}

$$\tau_I^{-1} = A\omega^4 = V\omega^4\Gamma/4\pi v^3 \quad (2)$$

$$\Gamma = \sum_{x,y,\dots} \frac{x}{(x+y+z+\dots)} \left(\frac{M_A}{\bar{M}} \right)^2 \Gamma(A) + \frac{y}{(x+y+z+\dots)} \left(\frac{M_B}{\bar{M}} \right)^2 \Gamma(B) + \dots \quad (3)$$

$$\Gamma(A) = \sum_i f_i \left(\frac{\Delta M_i}{\bar{M}_A} \right)^2. \quad (4)$$

The compound is $A_xB_yC_z\cdots$, V is the molecular volume, and

$$\bar{M} = \frac{xM_A + yM_B + zM_C + \dots}{(x+y+z+\dots)}. \quad (5)$$

The remaining symbols are defined in I.

The phonon-phonon term $\tau_p^{-1} = (B_1+B_2)\omega^2T^3$ employed by Callaway²⁹ will be used here. The inadequacy of this term was discussed in I, but since we will be interested, for the most part, in the region from the lowest temperature to just above the maximum in κ , the form of τ_p is not of vital importance.

Thus, the total scattering probability, or the inverse relaxation time, will be given by

$$\tau^{-1} = (v/LF) + A\omega^4 + (B_1+B_2)\omega^2T^3. \quad (6)$$

The values of several of the parameters calculated for the various specimens used are listed in Table I.

The solid lines in Figs. 2 through 6 are fits using Eq. (1) with the relaxation time of Eq. 6. In each case curve A is obtained using the theoretical value of the boundary scattering and impurity (isotope) scattering relaxation time. The parameters used are indicated in the figure captions.

Boundary Scattering

The theoretical value of τ_b leads to an excellent fit to the low-temperature data for InSb and pure GaAs, as well as for the Si and Ge previously studied. This is true only if the length to width correction is applied.

The dependence of τ_b on sample size was investigated in GaAs. As mentioned earlier, sample GaAs-2 is sample GaAs-1 reduced in size. The τ_b calculated in

TABLE II. Relaxation time ratios.

Sample	$\frac{\tau_b \text{ theory}}{\tau_b \text{ exp}}$	$\frac{\tau_I \text{ theory}}{\tau_I \text{ exp}}$	B_1+B_2 sec/deg ³	θ_{TA} (°K)	n
Ge	1	1	2.8×10^{-23}	100 ^a	1.2 ^f
Si	1	1	3.8×10^{-24}	210 ^b	1.2 ^f
O-Si	~ 1	~ 5	3.8×10^{-24}	210 ^b	...
InSb	1	~ 3	1.9×10^{-22}	68 ^c	1.1 ^g
GaAs-1	1	~ 2	3.6×10^{-23}	118 ^d	1.1 ^h
GaAs-3	1.7	~ 4	3.6×10^{-23}	118 ^d	1.1 ^h
GaSb	> 50	...	...	?	1 ^h
CdS	~ 3.5	~ 4	2.7×10^{-22}	240 ^e	1 ^h
CdTe	~ 1.5	~ 3	7.4×10^{-22}	?	1 ^{h,i}

^a See Ref. 58.

^b See Ref. 59.

^c F. A. Johnson, S. J. Fray, and R. H. Jones, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Publishing House of Czechoslovak Academy of Sciences, Prague, 1960), p. 349.

^d W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, *J. Appl. Phys.* **32**, 2102 (1961); see also Ref. 60.

^e Estimated from data on M. Balkanski and J. M. Besson, *J. Appl. Phys.* **32**, 2292 (1961).

^f G. A. Slack and C. Glassbrenner (to be published).

^g See Ref. 37.

^h Present work.

ⁱ See Ref. 57.

Table I for this smaller sample also leads to an excellent fit to the data as indicated by curve C of Fig. 3.

For the less pure sample of gallium arsenide, GaAs-3, and for GaSb, CdTe, and CdS, the theoretical value of τ_b did not lead to a good fit to the data at low temperatures. For GaAs-3, the value of τ_b^{-1} must be increased by a factor of 3.5 over the theoretical value, in order to fit the data at low temperature (see curve D of Fig. 3). For the GaSb samples the theoretical value of τ_b^{-1} leads to an overestimation of the low-temperature thermal conductivity by at least a factor of 50. For CdTe and CdS the theoretical value of τ_b^{-1} overestimates the thermal conductivity by factors of about 1.5 and 3.5, respectively. A comparison between the theoretical values of τ_b and the values needed to fit the data at low temperatures is given in Table II.

Increased boundary scattering, that is an increase in τ_b^{-1} , may be related to impurities. In boron-doped silicon²¹ it was found that an apparent increase in boundary scattering could be correlated with an increase in boron content. This same type of behavior has also been noted in germanium,^{9,11} gallium arsenide,²⁰ several doped alkali halides,^{43,44} and neutron-irradiated Al_2O_3 .⁴⁵ In the calculations for boron-doped silicon²¹ a new relaxation time, independent of temperature and frequency, was postulated but no theoretical justification of this scattering mechanism has been found. There is always the possibility that increased boundary scattering is due to large scale crystal defects such as impurity clusters⁴⁴ or grain boundaries,¹¹ but these have seldom been detected.

⁴³ R. O. Pohl, *Phys. Rev.* **118**, 1499 (1960).

⁴⁴ G. A. Slack, *Phys. Rev.* **105**, 832 (1960).

⁴⁵ R. Berman, E. L. Foster, B. Schneidmeyer, and S. M. A. Tirmizi, *J. Appl. Phys.* **31**, 2156 (1960).

⁴² See for example: G. A. Slack, *Phys. Rev.* **126**, 427 (1962).

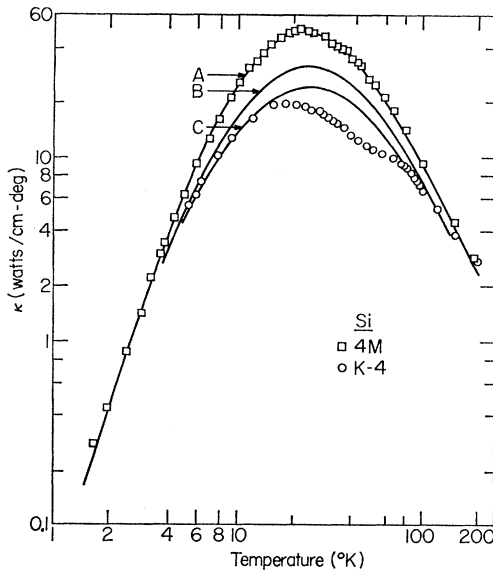


FIG. 7. Thermal conductivity of Si. 4-M data from Ref. 21, K-4 data from Ref. 18. Curve A: Callaway equation with $\tau_b = 0.86 \times 10^{-6}$ sec, $A = 1.32 \times 10^{-44}$ sec³, $B_1 + B_2 = 3.8 \times 10^{-24}$ sec/deg³. Curve B same as curve A but $A = 3.96 \times 10^{-44}$ sec³. Curve C same as curve A but $A = 6.60 \times 10^{-44}$ sec³. Sample K-4 contains $\sim 10^{18}$ oxygen/cm³ and 4-M contains less than 10^{16} oxygen/cm³.

Impurity Effects

Of all the semiconductors studied, we have found that only in Si and Ge could the maximum in the thermal conductivity be fitted by using the isotopic contribution to the impurity scattering relaxation time. For the materials studied here, the amount of impurity scattering calculated from the impurity concentrations listed in Table I, even assuming a mass difference $(\Delta M/M)^2 \sim 1$, is orders of magnitude less than the isotope scattering. Nevertheless, the impurity scattering must be increased by factors of 2 to 4 over the values calculated due to the isotopes for all the materials except GaSb, and for GaSb the impurity effects are even larger. One point of importance is that the number of impurities indicated in Table I is, except for CdS, the number of electrically active impurities. It is quite possible that other electrically inactive impurities, for example, dissolved gases, are responsible for these large impurity effects.¹⁸ Structural defects^{1,8} could also be a cause of impurity scattering.

In each of Figs. 2, 3, and 5, curve B is an attempt to fit the data by increasing τ_I^{-1} . A comparison between the theoretical isotope scattering values of τ_I , and the values needed to fit the data near the maximum are given in Table II. For CdS, curve B in Fig. 6 includes an increase in boundary scattering as well as impurity scattering. Curve D of Fig. 3 is a fit to GaAs-3 also using an increase in both τ_I^{-1} and τ_b^{-1} . An attempt to fit the data on GaSb using Eq. (1) and theoretical values of τ_I and τ_b resulted in values several orders of magnitude higher than the experimental points, so

that no further fitting was attempted using this formalism.

Even with increased values for τ_I^{-1} and, in some cases τ_b^{-1} , the fits are, in general, good only in the region from the lowest temperatures to just above the thermal conductivity maximum. In all cases except GaSb, this is partly due to the presence of dips in the data in this region.

Resonance Scattering

The results of Pohl and Walker^{12,13} on resonance scattering mechanisms indicate that the dips present in the data at temperatures just above the maximum in κ are also associated with impurities. In fact if one examines the older data on Si,²¹ a similar dip can be noted. It was only when the oxygen was removed from the Si that the dip disappeared from the data and the isotope scattering could be used to obtain a good fit. This effect of oxygen on the thermal conductivity of silicon can be seen more clearly in Fig. 7. Curve A is an attempt to fit the data on the oxygen-doped silicon using the theoretical values of boundary scattering and isotope scattering and the phonon-phonon parameter $B_1 + B_2 = 3.8 \times 10^{-24}$ sec deg⁻³. This curve can be seen to fit the data on oxygen-free silicon very closely. Curves B and C are obtained by increasing the impurity scattering term by factors of three and five, respectively. From this figure it appears that once the dip was eliminated, by removing about 10^{17} oxygen/cm³, the problem of an unaccountably large amount of impurity scattering disappeared. Curves B and C are similar to the curves obtained using increased impurity scattering for GaAs, InSb, CdTe, and CdS. Since the data on each of these samples also show a dip, we deduce that the increased impurity scattering is probably associated with resonance scattering.

Data which can be characterized as having a bump or dip can often be fitted by using a resonance-type relaxation time of the form first used by Pohl.¹²

$$\tau_R^{-1} = \frac{R\omega^2 T^n}{(\omega_0^2 - \omega^2)^2 + (\Omega/\pi)^2 \omega^2 \omega_0^2}, \quad (7)$$

where R is a proportionality constant containing the concentration of impurities causing the resonance scattering, ω_0 is the resonance frequency, and Ω describes damping of the resonance.

For KCl containing KNO₂, dips were found near 4°K and the curves could be fitted using $n=0$ in Eq. (7). For KCl containing KI, NaCl, CaCl₂, etc., the dips appeared above the conductivity maximum and the curves could be fitted using $n=2$.¹³

Wagner¹⁴ has shown that the form of Eq. (7) with $n=0$ can be obtained by considering inelastic scattering of phonons by localized modes, in which the impurity centers are polyatomic. For monatomic impurities the form of the relaxation time is more complicated than

Eq. (7), but does show a similar temperature dependence to that obtained using $n=2$. This latter process is a three-quantum process in which two phonons combine to excite the localized mode, and, thus the effect appears in the same temperature region, above the maximum, in which the umklapp three-phonon processes are important. Since it was shown in I that the applicability of the Callaway formalism is questionable in this temperature region, and since incorporating the relaxation time given by Eq. (7) into the equations for two-mode conduction cannot be done with any accuracy, no attempts have been made to fit the data presented here with this resonance scattering mechanism.

Electron-Phonon Scattering

Attempts to fit the data on GaSb, using the formalism of Eq. (1) with the theoretical values of boundary scattering and impurity scattering gave poor results. Any scattering process used in fitting these data must take into account several important differences between the results on the n -type samples and the p -type samples. (1) The two n -type samples differ in impurity content by about a factor of three but the thermal conductivity is almost the same at 2°K and differs by less than 50% at the maximum. (2) The two p -type samples have a change in slope near 5°K. The thermal conductivity of the samples at 2°K differs by about a factor of two, which is about the difference in the estimated impurity concentration. (3) The p -type samples, which have a factor of ten fewer impurities than the n -type samples, have a much lower thermal conductivity over most of the range 3 to 30°K.

The actual density of impurities is difficult to calculate in these GaSb samples, because of the presence of three nearby conduction band minima in n -type material, and because of the impurity band in each of the p -type samples. Nevertheless, the densities as determined in Table I, are so large ($\gtrsim 10^{17}$) that electron-phonon scattering is suggested.

The possibility of electrons carrying heat as well as acting as scatterers should also be considered. However, if the resistivity is used in the normal Wiedemann-Franz¹ relation for the electron thermal conductivity κ_e , this contribution turns out to be orders of magnitude too small. On the other hand, there are several electron-phonon scattering mechanisms which may account for the low values of thermal conductivity.

First consider electron-phonon scattering due to electrons in an impurity band. Ziman^{46,9} has derived the relaxation time for the case in which the electrons are contained in a parabolic band, and the number of electrons is large enough so that the degeneracy temperature is comparable to the lattice temperature near

4°K.

$$\tau_z^{-1} = \frac{C^2 m^{*3} v}{4\pi \hbar^4 \rho} \left(\frac{T}{T_s} \right) \left(\frac{x}{1 - e^{-x}} \right) \left(1 - \frac{1}{x} \ln w \right), \quad (8)$$

where $T_s = \frac{1}{2} m v^2$, and w is a complicated function of T , T_s , x , and T_F (the fermi temperature). The constant C measures the strength of the electron-phonon interaction in electron volts, m^* is the effective electron mass, and ρ the density.

For GaSb with $m^*/m \lesssim 1$ and $N \sim 10^{17}$ we find $T_s < T < T_F$ in the temperature range $T < 20^\circ\text{K}$, so that the factor $w \sim 1$ in Eq. (8). In this case the electron gas is degenerate, the relaxation time becomes independent of the number of impurities, and the thermal conductivity integral can be solved exactly giving

$$\kappa_z = \left(\frac{k}{\hbar} \right)^3 \frac{\hbar^4}{\pi} \frac{\rho}{m^{*2} C^2} T^2 \int_0^\infty x^3 (e^x - 1)^{-1} dx. \quad (9)$$

Now, if one assumes $(Cm^*/m) = 0.5$, curve B of Fig. 4 is obtained. m^*/m is about⁴⁷ 0.2 for the heavy-hole band in GaSb; it is not clear what the value would be in the impurity band. A value of $C=2$ was used by Ziman for p -type germanium. The valence bands of GaSb and Ge are similar,^{32,48} so that a similar value of C may be reasonable. The conduction bands in GaSb and Ge, however, are different in that the 000 minimum has the lowest energy in GaSb with the 111 minima (the lowest in Ge) and the 100 minima nearby. If the constant C is related to the deformation potential,⁴⁹ which may be related to the change in energy gap E_g with pressure³² by

$$E_C \sim \frac{dE_g}{d \ln V} = - \frac{1}{k} \frac{dE_g}{dP}, \quad (10)$$

where E_C is the deformation potential, k is the compressibility, and V the volume, then C would be several times higher for GaSb than for Ge.

These questions about the electron-phonon interaction constant are quite complex⁴⁹ and the arguments are intended to indicate only the order of magnitude. It is clear from Fig. 4 that the Ziman equation gives the correct magnitude of thermal conductivity, but it does not give the correct slope. Furthermore, Eq. (9) cannot account for the dependence of κ on impurity concentration, or the change in slope found in the data for the p -type samples. Variations in the parameter $C(m^*/m)$ will change the magnitude of τ_z . Also, if $m^* > m$, the condition $T_s < T < T_F$ no longer holds and Eq. (9) must be replaced by a more complete expression obtained by using $w \neq 1$ in Eq. (8). In this case it may be possible to obtain a dependence of κ on impurity

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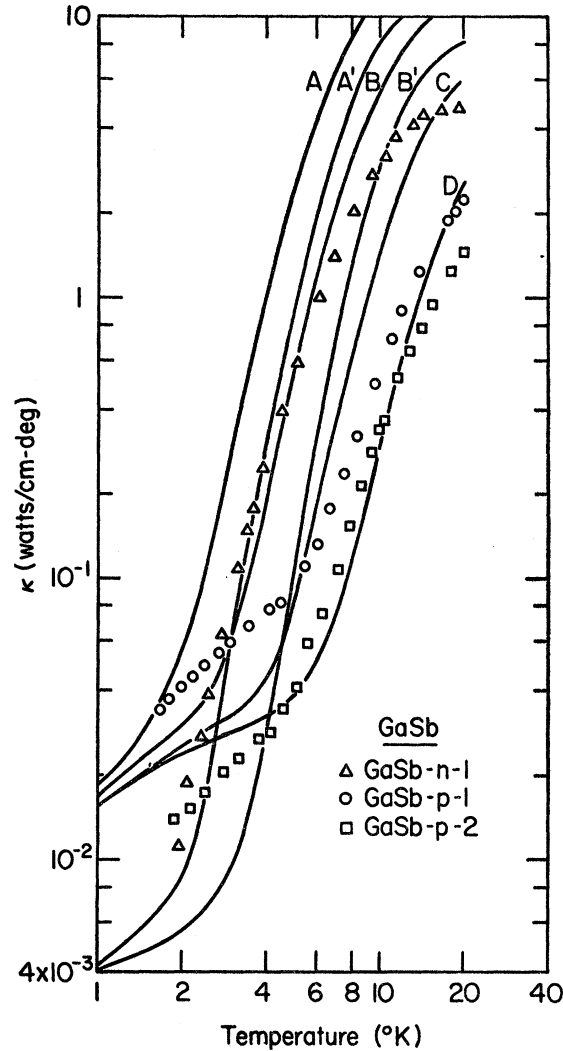


FIG. 8. Thermal conductivity of GaSb. Curves are from Keyes theory [Eq. (12)]. A: $\gamma=0.1$, $\delta=4 \times 10^{-3}$; B: $\gamma=0.1$, $\delta=2 \times 10^{-3}$; C: $\gamma=0.1$, $\delta=1 \times 10^{-3}$; D: $\gamma=0.1$, $\delta=0.5 \times 10^{-3}$; A': $\gamma=1.0$, $\delta=4 \times 10^{-3}$; B': $\gamma=1.0$, $\delta=2 \times 10^{-3}$.

concentration and a change in the slope of κ versus T at 5°K. Similar arguments were used in explaining the Ge data.

Next consider the electron-phonon scattering mechanism first proposed by Keyes,⁵⁰ which states that the scattering of phonons by donors, for example, at low temperatures results from the large effect of strain on the energy of an electron in a hydrogen-like donor state. Griffin and Carruthers⁵¹ showed that resonance scattering is associated with this effect and they obtained the approximate relaxation time,

$$\tau_{pe}^{-1} = \frac{G\omega^4}{[\omega^2 - (4\Delta/\hbar)^2]^2} \frac{1}{[1 + r_0^2\omega^2/4v^2]^8}, \quad (11)$$

⁵⁰ R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

⁵¹ A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

where G is a proportionality constant containing the number of scattering centers, 4Δ is the chemical shift, which is related to the splitting of electronic states, and r_0 is the mean radius of the localized state. (Note added in proof. 4Δ is the "valley orbit" splitting of the four-fold degenerate ground-state donor energy in Ge. For acceptor states, or donors with different ground state degeneracies, 4Δ should be changed appropriately.⁵¹) This approximate equation does not take the longitudinal and transverse modes into account properly, but gives essentially the correct frequency dependence.

Unfortunately, many of the parameters in Eq. (11) are not known for GaSb.⁵² Since little is known about the impurity ionization energies, let alone the energies of the excited states, we make the assumption $\omega \ll 4\Delta/\hbar$ so that the resonance term is eliminated and we are left with the equation in the form used by Keyes.

Now, the thermal conductivity can be expressed as

$$\kappa = CT^3 \times \int_0^{\theta/T} \frac{x^4 e^x (e^x - 1)^{-2} dx}{\tau_b^{-1} + \alpha x^4 T^4 + \beta x^2 T^5 + \gamma x^4 T^4 (1 + \delta x^2 T^2)^{-\delta}}, \quad (12)$$

where

$$\gamma = Gk^4/(4\Delta)^4$$

$$\delta = r_0^2 k^2 / 4\hbar^2 v_s^2,$$

and the remaining terms are defined in I.

Equation (12) can be used to obtain an empirical fit to the data. The results using the theoretical values of τ_b^{-1} and α , and several values of γ and δ are shown in Fig. 8. Since the fit only extends to 20°K, the β term does not contribute to the integral.

Even though none of the curves actually fits the data, the appearance of a slope change between 2 and 6°K is highly encouraging. This change is due to the "cutoff" term $(1 + \delta x^2 T^2)^{-\delta}$. A value of δ between 0.5 and 1×10^{-3} , which appears to be needed to fit the data on the p -type samples, corresponds to an effective hole radius of 10 to 15 Å. A value of $\delta > 4 \times 10^{-3}$, which appears necessary to fit the data on the n -type samples, corresponds to an effective electron radius of greater than 30 Å.⁵²

The value of γ can be expressed in terms of several parameters, and for GaSb we obtain

$$\gamma \sim 2.5 \times 10^{-29} N (E_d^2/\Delta)^2, \quad (13)$$

where N is the concentration of scattering centers, and E_d is the shear deformation potential. That is, for $N = 10^{18}$ and $\gamma = 1$, we obtain $(E_d^2/\Delta) = 2 \times 10^5$ eV. Keyes has indicated that for an antimony atom in germanium $E_d^2/\Delta \sim 2.5 \times 10^6$ eV.

It appears from the limited curve fitting attempts

⁵² This would suggest that the energy, which is usually inversely proportional to the radius, would be small for the electrons and large for the holes; that is, that the acceptor states are deep and the donor states shallow.

that use of Eq. (12) will lead to an overestimation of the data near the maximum in κ . Griffin and Carruthers found the same effect in their attempts to fit germanium data. This can come from neglect of the resonance term, but is more likely because of some additional scattering mechanism. For example, large numbers of impurities can easily introduce strains in the lattice, and these strains can act as scattering centers.⁸ Furthermore, the mass-difference scattering term $\alpha\alpha^4T^4$ has been seen to lead to an overestimation of the data for the other III-V compounds, and additional scattering is suggested in each case.

The experimental results on GaSb are very similar to those previously obtained by Carruthers *et al.* for germanium.⁹ The germanium results were explained qualitatively by Ziman with a relaxation time indicated by Eq. (8). It appears that the Keyes scattering mechanism could be equally useful in explaining these germanium results even at temperatures below 1°K.¹¹ The data for GaSb can also be better explained using the Keyes mechanism than the Ziman approach.

One additional point can be made concerning the Griffin and Carruthers equation (Eq. 11). For the case $\omega \gg 4\Delta/\hbar$ and the r_0 cutoff term reasonably small, the reciprocal relaxation time τ_{pe}^{-1} would be almost frequency-independent over some ranges of frequency. The τ_{pe}^{-1} would then behave like a boundary scattering term which depends on the impurity content. However, the combined conditions, small Δ , small r_0 , and large electron-phonon coupling would be necessary in each of the many different materials where anomalously large boundary scattering has been observed.

Phonon-Phonon Interactions

The values of the phonon-phonon interaction constant B_1+B_2 used in the curve fits of the data are listed in Table II. The effects of varying this term can be seen by a comparison of curves B and E in Fig. 3 for GaAs and of curves B and C in Fig. 6 for CdS. It is possibly of significance that the high-temperature fit obtained using $\tau_p^{-1} = (B_1+B_2)\omega^2T^3$ gives particularly poor results for CdS.⁵³

In I it was shown that the relaxation time $\tau_p^{-1} = B\omega^2T^3$ is valid only for N processes, for longitudinal modes, and for certain crystal classes. It was also shown that the term $(B_1+B_2)\omega^2T^3$ could be used with B_1+B_2 as an adjustable parameter to fit the data on Si and Ge to temperatures above the maximum in κ , but that this term does not take all of the three-phonon processes into account correctly. Thus, it seems that a comparison of the parameters B_1+B_2 used to obtain the fits in Figs. 2 to 8 would not be very meaningful.

It was also suggested in I that the Debye frequency was not necessarily the important parameter in the thermal conductivity integral since the zone-boundary

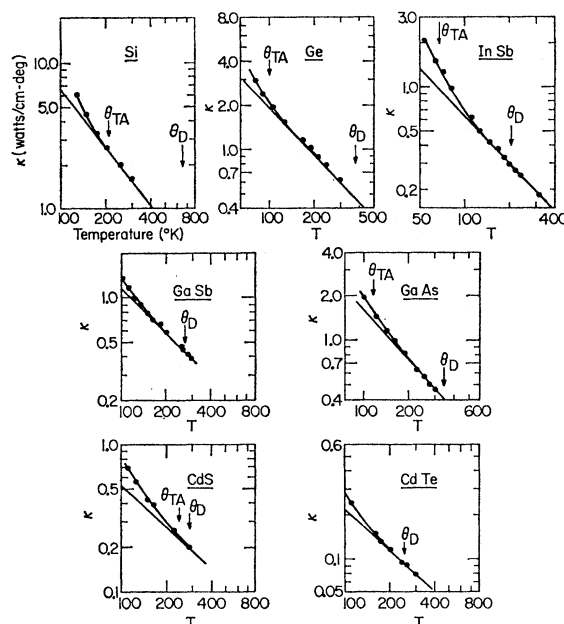


FIG. 9. Thermal conductivity near room temperature for various semiconductors. The straight lines are $\kappa = AT^{-n}$ where n is given in Table II. The values of θ_D and θ_{TA} are shown where known.

frequency of the transverse acoustical phonon, which can be as much as a factor of three lower than the Debye frequency, is most important for limiting U processes.

The results obtained here can be used to illustrate this point in the following way: Most theories indicate that for $T > \theta_D$, the thermal conductivity should vary as T^{-n} , $n \sim 1$.⁵⁴⁻⁵⁶ There should be some slight effect due to impurity scattering,^{54,56} but that will be neglected here. The results of I indicate that for certain materials with a flat TA phonon branch, the T^{-n} dependence should begin at $T > \theta_{TA}$ where θ_{TA} is the temperature corresponding to the zone boundary frequency of the TA phonon. Figure 9 shows the data above the maximum for Ge, Si, and the III-V and II-VI compounds studies here. A straight line of slope $-n$ has been drawn on each of the curves. The values of θ_{TA} and θ_D are indicated for those cases in which they are known. The values of n given in Table II have been obtained from high-temperature data where available.

For Si, Ge, GaAs, and CdTe it is clear that the T^{-n} dependence begins at $T < \theta_D$. For CdS, θ_D and θ_{TA} are almost equal, indicating little dispersion in the TA branch. For InSb, θ_D is low and the effect is not clear since impurity scattering is becoming important for $\theta_{TA} < T < \theta_D$. However, Fig. 9 still shows $\kappa \propto T^{-1.1}$ for $T < \theta_D$. In no case is θ_D the temperature at which the thermal conductivity becomes proportional to T^{-n} .

⁵⁴ J. Callaway and H. C. von Baeyer, Phys. Rev. **120**, 1149 (1960).

⁵⁵ P. G. Klemens, G. K. White, and R. J. Tainsh, Phil. Mag. **7**, 1323 (1962).

⁵⁶ V. Ambegaokar, Phys. Rev. **114**, 488 (1959).

⁵³ CdS is the only material studied with hexagonal crystal structure.

It may be argued that a change in slope in the thermal conductivity data which occurs near θ_D is due to optical phonons,^{22,57} since in many cases⁵⁸⁻⁶⁰ $\theta_D \sim \theta_0$, where θ_0 is the temperature corresponding to the minimum optical phonon frequency. However, in Ge and Si,^{58,59} $\theta_{TA} \sim \frac{1}{3}\theta_D$ and the change in slope would probably not occur near θ_{TA} if it were due to optical phonons. For GaAs,⁶⁰ $\theta_{TA} \sim \frac{1}{3}\theta_D$ also and the same argument appears to hold, but high-temperature data are needed in order to better determine n and the approximate temperature at which the data deviates from a T^{-n} dependence.

A comparison of all the data of Fig. 9 would suggest a value of $\theta_{TA} \sim 100^\circ\text{K}$ for GaSb and $\theta_{TA} \sim 150^\circ\text{K}$ for CdTe. Although this is a very approximate type of argument, it serves to illustrate the fact that θ_D may not be so vital in calculating κ , and that the relaxation time $\tau_p^{-1} = (B_1 + B_2)\omega^2 T^3$ is not very realistic over much of a temperature range.

IV. CONCLUSIONS

The thermal conductivity of several III-V and II-VI compound semiconductors has been measured. Attempts have been made to fit the data with the Callaway equation, using both the theoretical values of the boundary scattering and impurity scattering relaxation times, as well as by using τ_b and τ_I as adjustable parameters. Two forms of an electron-phonon relaxation time have been examined and the phonon-phonon interaction discussed.

The validity of several of the relaxation mechanisms has been examined here. The interpretation of the Ge, Si, InSb, and GaAs data indicates that the boundary scattering relaxation time, when altered by the length-to-width correction of Ziman, gives calculated values of κ within 10% of the observed value for very pure samples. The impurity scattering relaxation time when calculated from the effect due to isotopes leads to accurate calculated values of κ only when the material is exceptionally pure. When there are impurities present in the samples, both τ_b and τ_I can lead to erroneous values in the calculation of κ .

The indication from this and other work^{13,28,61} is that the simple phonon-phonon relaxation time used by Callaway is insufficient to explain the conductivity

above the maximum. One attempt to solve this problem was presented in I for Si and Ge, but to follow the complicated procedure for the III-V or II-VI samples is impossible because of a lack of sufficient knowledge of the phonon spectrum.

The problem of electron-phonon scattering is complex and the results on GaSb are only qualitative. Again, greater detailed knowledge concerning the electronic energy states, electron orbits, and various deformation potentials is necessary before accurate calculations can be performed. An effective hole radius of 10 to 15 Å and an effective electron radius of greater than 30 Å has been estimated for GaSb containing greater than 10^{17} impurities/cm³.

Information about the imperfections in the samples can also be obtained from this work. A comparison with previous work on Ge, Si, and oxygen-doped Si yields the following conclusions: (1) The samples of InSb and GaAs have few impurities or crystal imperfections, i.e., a low number of electrically active impurities and no crystal faults large enough to alter the thermal conductivity in the boundary scattering region. (2) InSb and GaAs both contain some impurities which are electrically inactive, probably monatomic, and which are responsible for the apparent resonance scattering. These may be dissolved gases, as was found for silicon. (3) The CdTe and CdS are not as perfect in the sense that they contain crystal imperfections or impurities large enough in size or number to alter the thermal conductivity appreciably in the boundary-scattering region. Impurity scattering of a resonance type is also present in these samples and again these electrically inactive impurities are probably monatomic. (4) The perfection of GaSb cannot be judged from the thermal conductivity measurements because of the exceptionally strong electron-phonon scattering. However, these interactions seem to appear at higher temperatures and lower impurity concentrations than in Ge, which could indicate stronger electron-phonon and hole-phonon interactions in GaSb.

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