

# Thermal Conductivity of Pure and Impure Silicon, Silicon Carbide, and Diamond

GLEN A. SLACK

General Electric Research Laboratory, Schenectady, New York

(Received 24 February 1964)

Thermal conductivity measurements on high-purity SiC and impure Si and SiC have been made over the temperature range from 3° to 300°K. These results show that the thermal conductivity  $K$ , of the highest purity SiC is intermediate between those of pure Si and pure diamond, and at 300°K is greater than that of copper. The heat transport in SiC is produced by phonons and these are scattered by other phonons, isotopes, and the crystal boundaries in the pure material.

In impure SiC the phonons are also scattered by the electrically active impurities Al and N. These impurities reduce the  $K$  of SiC in much the same way that B and P impurities do in Si. The N impurities in natural diamonds also reduce their  $K$  below that of ideally pure diamond, but the effect is rather different since N is not electrically active.

## INTRODUCTION

THE thermal conductivities  $K$  of the adamantine semiconductors germanium, silicon, silicon carbide, and diamond are rather high compared to other solids, and can be lowered considerably by various impurities. The present paper shows how the  $K$  vs temperature  $T$  curves for these adamantine materials are related, and shows how rather high concentrations of impurities affect the  $K$  of Si, SiC, and diamond. The  $K$  of the crystals can be understood in terms of a theory of heat transport by phonons. The reduction in  $K$  caused by the impurities is appreciable at 300°K and becomes even larger at lower temperatures for Si and SiC. In contrast to this the effect of impurities on the  $K$  of diamond appears to decrease at the lower temperatures.

Data on the  $K$  of pure Ge and Si have been published,<sup>1</sup> as have measurements of the effect of various impurities on the  $K$  of both Ge<sup>2</sup> and Si.<sup>3,4</sup> Table I lists the samples of Si studied in the present experiments, and also some pertinent ones from the literature. A number of scattered measurements on the  $K$  of impure SiC have been published,<sup>5-10</sup> and are listed in Table I. All except one of these SiC samples were polycrystalline, and only Ref. 10 gives approximate  $K$  values for a single crystal.

All of the  $K$  values for the polycrystalline samples in Table I have been corrected<sup>6</sup> to give effective  $K$  values for zero porosity, i.e., a sample density of 3.21 g/cm<sup>3</sup>. Much of the data on the  $K$  of commercial SiC brick have been omitted, a summary of which can be found in Vasilos and Kingery.<sup>6</sup> The  $K$  measurements on SiC brick bonded with foreign materials have been summarized by Baumann and Swentzel,<sup>11</sup> and will not be discussed here.

The  $K$  curves for several natural crystals of diamond of unknown impurity content have been given in the literature,<sup>12-17</sup> and these samples are also listed in Table I.

## SAMPLES

The samples that were measured in the present experiments were synthetic single crystals of Si and SiC, except for sample R3 of Si which was polycrystalline. The impurity content of the doped Si samples was determined from the measured electrical conductivity. The doping levels were high and approached the maximum solid solubility limits for Si to within a factor of 2.

The samples of SiC were all synthetic, and were grown from the vapor phase by methods previously described.<sup>18-20</sup> These samples, listed in Table I, tended to be rather small, particularly sample R66. In fact R66 was smaller than any of the diamond samples whose  $K$  has been reported. Thermocouples<sup>21</sup> were used for measuring the temperature differences, and it was this

<sup>1</sup> C. J. Glassbrenner and G. A. Slack, Phys. Rev. **134A**, 1058 (1964).

<sup>2</sup> A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

<sup>3</sup> M. G. Holland, *Proceedings of the International Conference on Semiconductor Physics, Prague 1960* (Academic Press Inc., New York, 1962), p. 633.

<sup>4</sup> M. G. Holland and L. J. Neuringer, *Proceedings of the International Conference on Semiconductor Physics, Exeter, 1962* (Institute of Physics and the Physical Society, London, 1962), p. 474.

<sup>5</sup> J. L. Weeks and R. L. Seifert, Rev. Sci. Instr. **24**, 1054 (1953).

<sup>6</sup> T. Vasilos and W. D. Kingery, J. Am. Ceram. Soc. **37**, 409 (1954).

<sup>7</sup> E. J. Smoke and J. H. Koenig, Rutgers University, New Brunswick, New Jersey, College of Engineering Research Bulletin No. 40 (1958).

<sup>8</sup> I. B. Fieldhouse, J. C. Hedge, I. J. Lang, and T. E. Waterman; W.A.D.C. Tech. Report 57-487, ASTIA Document 150954 (February 1958), P.B. 131718.

<sup>9</sup> I. B. Fieldhouse, *Thermodynamic and Transport Properties of Gases, Liquids, and Solids* (McGraw-Hill Book Company, Inc., New York, 1959), p. 391.

<sup>10</sup> G. Bosch, Philips Res. Rept. **16**, 455 (1961).

<sup>11</sup> H. N. Baumann and J. P. Swentzel, Bull. Am. Ceram. Soc. **16**, 419 (1937).

<sup>12</sup> A. Eucken, Physik. Z. **12**, 1005 (1911).

<sup>13</sup> W. J. deHaas and T. Biermasz, Physica **5**, 47 (1938).

<sup>14</sup> R. Berman, F. E. Simon, J. Wilks, Nature **168**, 277 (1951).

<sup>15</sup> R. Berman, F. E. Simon, and J. M. Ziman, Proc. Roy. Soc. (London) **A220**, 171 (1953).

<sup>16</sup> R. Berman, E. L. Foster, and H. M. Rosenberg, *Report of the Conference on Defects in Crystalline Solids, Bristol, 1954* (The Physical Society, London, 1955), p. 321.

<sup>17</sup> R. Berman, E. L. Foster, and J. M. Ziman, Proc. Roy. Soc. (London) **A237**, 344 (1956).

<sup>18</sup> O. Muhlhauser, Z. Anorg. Chem. **5**, 105 (1894).

<sup>19</sup> J. A. Lely, Ber. Deutschen Keram. Ges. **32**, 229 (1955).

<sup>20</sup> D. R. Hamilton, J. Electrochem. Soc. **105**, 735 (1958).

<sup>21</sup> G. A. Slack, Phys. Rev. **122**, 1451 (1961).

TABLE I. Properties of the samples of silicon, silicon carbide, and diamond.<sup>a</sup>

Material	Sample	Physical structure	Size <i>L</i>	cm <i>d</i>	Major impurities atom/cm <sup>3</sup>	Electrical type	$\sigma$ at 300°K $\Omega^{-1} \text{ cm}^{-1}$	Reference
Si	Pure	S.C.	2.0	0.44	Cu?	P	$5 \times 10^{-4}$	1
	12M	S.C.	3.2	0.70	B, $4.0 \times 10^{16}$	P	?	4
	R5	S.C.	2.6	0.56	B, $3 \times 10^{20}$	P	$2.2 \times 10^3$	
	R3	P.	3.2	1.24	B, $5 \times 10^{20}$	P	$3.8 \times 10^3$	
	R6	S.C.	3.2	1.20	P, $2.0 \times 10^{19}$	N	$3.6 \times 10^2$	
	R55	S.C.	1.7	0.55	P, $1.7 \times 10^{20}$	N	$1.5 \times 10^3$	
SiC	R66 <sup>b</sup>	S.C.	0.35	0.12	N, $\sim 1 \times 10^{17}$	N	$9 \times 10^{-2}$	
	R43 <sup>b</sup>	S.C.	0.70	0.14	N, Al, $\sim 10^{18}$	N	$4.5 \times 10^{-1}$	
	R52 <sup>b</sup>	S.C.	0.67	0.16	Al, $4 \times 10^{19}$	P	1.6	
	10 $\alpha$ <sup>b</sup>	S.C.	0.8	0.21	N, $\sim 10^{18}$	N	?	10
	10 $\beta$ <sup>b</sup>	P.	1.0	0.11	? ?	?	?	10
	5	P.	4.4	0.56	?	?	?	5
	6	P.	2.5	2.9	?	?	?	6
	7	P? <sup>c</sup>	1.3	1.4	?	?	?	7
	8	P.	3.8	17.2	?	?	?	8,9
Diamond	12	S.C.	0.13	0.35	N?	?	?	12
	13a	S.C.	0.6	0.09	N?	?	?	13
	13b	S.C.	0.9	0.10	N?	?	?	13
	I	S.C.	1.1	0.39	N?	type I	?	14, 15, 17
	I+n	S.C.	1.1	0.1	neutrons <sup>d</sup>	type I	?	16
	IIa	S.C.	1.0	0.10	?	type IIa	?	17
	IIb	S.C.	0.7	0.13	?	type IIb	?	17

<sup>a</sup> S.C. = single crystal, P. = polycrystalline, *L* = length of the sample, *d* = effective diameter of sample,  $\sigma$  = electrical conductivity.

<sup>b</sup> Sample R66 was colorless and was a 6H polytype, R43 was light green and 6H polytype, and R52 was dark blue and a mixture of 6H and 15R polytypes. Sample 10 $\alpha$  was 6H while sample 10 $\beta$  was cubic. The other SiC samples were of unspecified polytype.

<sup>c</sup> Reference 7 states that the sample was a single crystal, but this seems unlikely in view of the size samples required by the apparatus.

<sup>d</sup> K measured after neutron irradiation.

technique that permitted the study of such small samples. Crystals R43 and R52 were produced in large, commercial, electric-arc furnaces,<sup>18,22</sup> and were selected from the core material. Crystal R66 was prepared in a special laboratory furnace,<sup>20</sup> and was kindly supplied by Dr. D. R. Hamilton.

The impurities in the SiC are known with much less certainty than those in the Si, since the SiC was not intentionally doped. The dominant impurity in the purest sample, R66, was estimated<sup>23</sup> to be nitrogen at a concentration of the order of magnitude of  $10^{16}$  to  $10^{17} \text{ cm}^{-3}$ . In addition there are probably some deep level impurities such as Fe-group elements at comparable concentrations. This crystal was a 6H polytype, and was cut so that the heat flow was perpendicular to the *c* axis. The electrical conductivity  $\sigma$  of this crystal was measured as  $\sigma = 9 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$  at 300°K, and it was *n* type. The major metallic impurities in R52 and R43 were determined by means of an emission spectrograph, and are listed in Table II. Aluminum is the dominant metallic impurity in both. The one common nonmetallic impurity in such commercial SiC crystals is generally nitrogen, and its concentration was estimated from the electrical measurements. An x-ray study showed that sample R52 was a mixture of 6H and 15R polytypes while R43 was a 6H polytype. In both cases the heat flow was perpendicular to the *c* axis.

The crystal of 6H SiC whose K was measured by

Bosch<sup>10</sup> had N as the dominant impurity at an estimated concentration of about  $10^{18} \text{ cm}^{-3}$ . In terms of the net concentration of impurities this places it between samples R52 and R43. The cubic SiC studied by Bosch<sup>10</sup> is of unstated purity, as are the various samples<sup>5-9</sup> that have been measured at  $T \geq 300^\circ \text{K}$ .

The samples of diamond that have been studied are listed in Table I. They are all small size natural crystals of unstated and generally unknown purity. The three samples measured by Berman *et al.*<sup>14-17</sup> were, however, specified as to the type of diamond. The type designations tell something about the impurity content. Kaiser and Bond<sup>24</sup> have shown that type I diamonds possess considerable quantities of nitrogen, generally in the range from  $10^{19}$  to  $10^{20} \text{ cm}^{-3}$ , and sometimes as much as  $4 \times 10^{20} \text{ cm}^{-3}$ . The type IIa and IIb diamonds, on the other hand, have very little nitrogen (i.e.,  $10^{18}$  to

TABLE II. Major metallic impurities in the SiC samples as determined by emission spectrography.

Element	Concentration (a)	
	R43	R52
Al	7	40
B	<2	<2
Fe	<0.4	<0.4
Na	2	2

<sup>a</sup> Concentration given in units of  $10^{18} \text{ atoms/cm}^3$ . The concentrations of Ca, Cu, K, Mg, Ti, V, Zn, Zr were all less than  $10^{18} \text{ cm}^{-3}$ .

<sup>24</sup> W. Kaiser and W. L. Bond, Phys. Rev. **115**, 857 (1959).

<sup>22</sup> The Norton Company, Worcester, Massachusetts.

<sup>23</sup> W. J. Choyke and L. Patrick, Phys. Rev. **127**, 1868 (1962).

$10^{19} \text{ cm}^{-3}$ ). Kaiser and Bond make the plausible speculation that the incorporated N may be responsible for the rather low  $K$  of the type I compared to that of the type II diamonds found by Berman *et al.* Natural diamonds also contain many other trace impurities<sup>25</sup> such as Al, Si, and Mg in the range of  $10^{17}$  to  $10^{19} \text{ cm}^{-3}$ . Even the purest natural type IIa diamonds generally have an aggregate impurity content of about  $10^{18} \text{ cm}^{-3}$  of metallic elements. Whether these are substitutional impurities or precipitated phases is not always clear. For example, the electron-spin-resonance studies<sup>26</sup> and x-ray studies<sup>27</sup> of nitrogen in diamond indicate that most of the nitrogen is not in the form of isolated, substitutional atoms.

Nitrogen appears to be the most common impurity in natural diamonds. From 95%<sup>24</sup> to 99%<sup>28</sup> of natural, gem-quality diamonds are type I, which probably means that the N concentration is  $> 10^{19} \text{ cm}^{-3}$ . Therefore, it is reasonable to assume that the diamonds whose  $K$  was measured by DeHaas and Biermasz<sup>13</sup> and Eucken<sup>12</sup> were also type I, and contained nitrogen as a major impurity. The variability in the N content of natural diamonds may well be responsible for the variability in  $K$  found by the various authors. It does not seem likely that any of the diamonds so far measured have

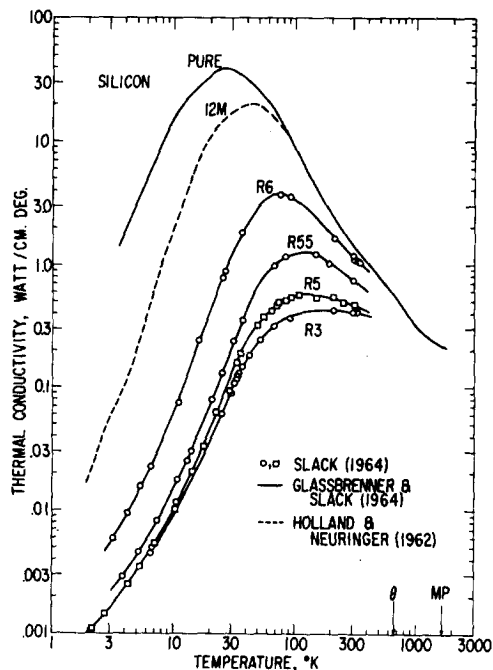


FIG. 1. The thermal conductivity vs temperature of pure Si and of impure Si doped with P (R6, R55), and with B (12M, R5, R3). The Debye temperature and melting point of Si are  $\theta$  and MP, respectively.

<sup>25</sup> F. A. Raai, *Am. Mineralogist* **42**, 354 (1947).

<sup>26</sup> W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, *Phys. Rev.* **115**, 1546 (1959).

<sup>27</sup> R. J. Elliott, *Proc. Phys. Soc. (London)* **76**, 787 (1960).

<sup>28</sup> E. N. Bunting and A. Van Valkenburg, *Am. Mineralogist* **43**, 102 (1958).

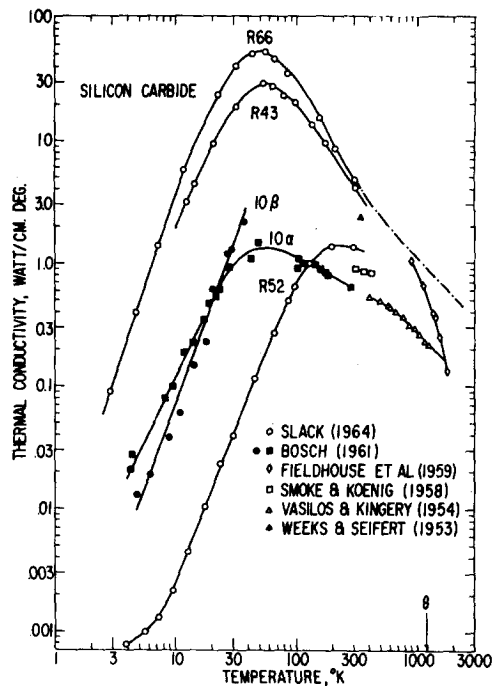


FIG. 2. The thermal conductivity  $K$  vs temperature of high-purity SiC (R66) and various less pure samples. The dot-dash curve is the estimated extrapolation of  $K$  to the Debye temperature  $\theta$ .

had N concentrations near  $4 \times 10^{20} \text{ cm}^{-3}$ . Thus even lower  $K$  values than those already reported may be found for some gem-quality natural diamonds.

## EXPERIMENTAL TECHNIQUE

The  $K$  measurements were made over the temperature range from  $3^\circ$  to  $300^\circ \text{K}$  using a steady-state, longitudinal heat flow in an apparatus previously described.<sup>21</sup> The absolute accuracy of the  $K$  values is believed to be  $\pm 5\%$  for the large size samples of Si, and  $\pm 10\%$  for the smallest samples of SiC, R66.

## EXPERIMENTAL RESULTS AND ANALYSIS

### Pure Crystals

The experimental  $K$  vs  $T$  curves for Si, SiC, and diamond are collected together in Figs. 1, 2, and 3. From these curves it is apparent that the  $K$  is quite variable, and that the purer the crystal is the higher is its  $K$ . The purest Si has an impurity concentration of about  $10^{14} \text{ cm}^{-3}$ , the purest SiC about  $10^{17} \text{ cm}^{-3}$ , and the purest diamond about  $10^{18} \text{ cm}^{-3}$ . The ideal behavior of the  $K$  vs  $T$  curve for the pure Si has been calculated<sup>1,29</sup> by assuming that phonons are the only carriers of heat, and that they are scattered by other phonons, the Si isotopes, and the crystal boundaries. The agreement between the calculation and the theory is satisfactory for Si. This same theory can be applied to the results

<sup>29</sup> B. K. Agrawal and G. S. Verma, *Phys. Rev.* **127**, 24 (1962).

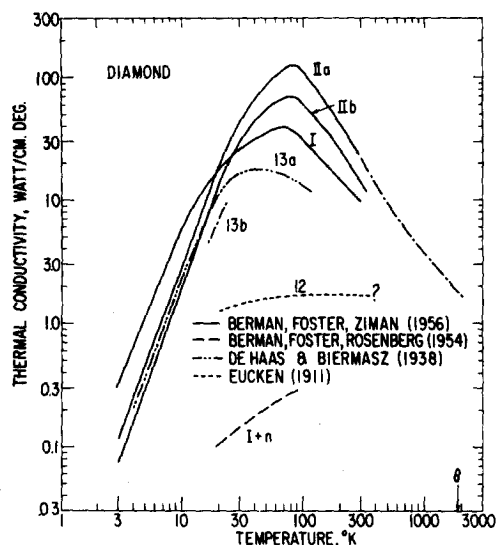


FIG. 3. The thermal conductivity  $K$  vs temperature of several samples of natural diamond. The dot-dash curve is the estimated extrapolation of  $K$  to the Debye temperature  $\theta$ . The sample labelled I- $n$  is a type I diamond that has been neutron irradiated. Sample 12 has a ? because the  $K$  measurements are of questionable accuracy.

for SiC and diamond. However, the agreement between theory and experiment is not expected to be as good because the crystals are not as pure.

The  $K$  vs  $T$  curves for the purest available samples of Si, SiC, and diamond together with a curve for pure Ge<sup>1</sup> are shown plotted together as solid lines in Fig. 4. The predicted theoretical behavior for the pure Ge and Si crystals nearly coincides<sup>1</sup> with the experimental curves, and is not shown in Fig. 4. However the theoretical  $K$  curves for SiC and diamond have rather higher  $K$  values than the observed ones. These two theoretical curves are shown as dashed lines in Fig. 5. They have been computed by the method used in Ref. 1 for Ge and Si for a crystal diameter of 0.1 cm. The general shape of the experimental and theoretical curves is the same, but the theoretical  $K$  values for  $T < 300^\circ\text{K}$  are about twice as large as the experimental ones. The theoretical curves have been matched to the extrapolated experimental values at  $T = \theta$ . Since there is some uncertainty in this extrapolation, there is uncertainty in the actual numbers predicted by the theory. However these dashed theoretical curves shown in Fig. 4 probably represent an upper limit on  $K$  that will not be exceeded even by pure crystals. The difference between the theoretical and experimental curve is, at least in part, caused by the residual impurities in the SiC and the diamond. The theoretical upper limits on the  $K$  of SiC and diamond at  $300^\circ\text{K}$  are 7 and 35 W/cm-deg, respectively. These are both higher than the corresponding value for pure copper which is 4 W/cm-deg. The  $K$  results for SiC sample R66 are sufficiently close to the theoretical curve that it is worthwhile tabulating them. Table III gives some smoothed values for the  $K$  of R66 in the temperature range from  $50^\circ$  to  $300^\circ\text{K}$ . Below

TABLE III. Representative values for the thermal conductivity of high-purity SiC sample R66.

$T$ $^\circ\text{K}$	$K$ W/cm deg
50	52
70	43
100	28
150	15
200	9.5
300	4.9
500	2.4 (e) <sup>a</sup>
1000	1.1 (e) <sup>a</sup>
1200	0.9 (e) <sup>a</sup>

<sup>a</sup> (e) = extrapolated.

$50^\circ\text{K}$  the measured  $K$  is not an intrinsic property of pure SiC.

An expression for the theoretical value of the thermal conductivity  $K_\theta'$  at  $T = \theta$  has been given by Leibfried and Schlömann.<sup>30</sup> Table IV shows how these  $K_\theta'$  values, calculated assuming a value for Grüneisen's constant of  $\gamma = 2.0$ , compare with the experimental numbers  $K_\theta$  at  $T = \theta$ . Figure 5 shows a plot of  $K$  vs  $K'$ , the straight line is  $K/K' = 1.15$ . This ratio would be unity if the agreement between experiment and theory were perfect. A disagreement of only 15% is, really, quite good, and shows that the behavior of all four materials, Ge, Si, SiC, and diamond is equally well treated by the theory. The  $K$  of pure SiC is roughly a geometric mean between that of Si and diamond for all  $T \geq 100^\circ\text{K}$ . This is a

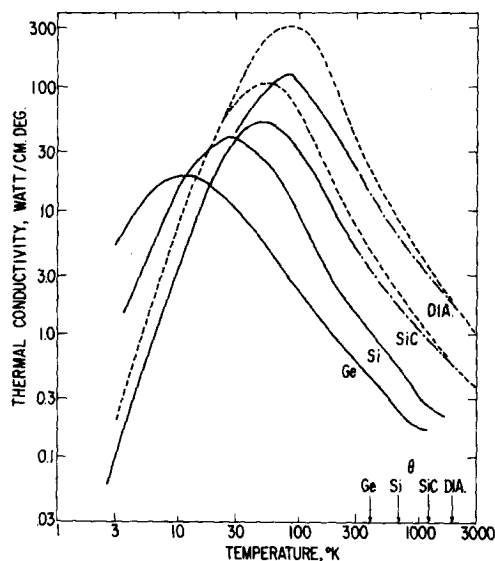


FIG. 4. An intercomparison of the thermal conductivity  $K$  vs temperature curves of Ge (pure), Si (pure), SiC (R66), and diamond (IIa). The general increase of  $K$  with increasing Debye temperature  $\theta$  should be noted. The dashed curves for SiC and diamond are theoretical estimates for the pure crystals with a diameter of 0.1 cm. The Ge and Si crystals shown have diameters of 1.06 and 0.44 cm, respectively.

<sup>30</sup> G. Leibfried and E. Schlömann, *Nachr. Akad. Wiss. Göttingen, Math. Physik. Kl.* 4, 71 (1954).

TABLE IV. Parameters for calculating the thermal conductivity of Ge, Si, SiC, and diamond.<sup>a</sup>

Material	$\rho$ g/cm <sup>3</sup>	$\bar{M}$ g	$V_0$ Å <sup>3</sup>	$c_{44}$ 10 <sup>12</sup> dyn/cm <sup>2</sup>	$\bar{v}$ 10 <sup>6</sup> cm/sec	$\theta$ °K	$\Gamma \times 10^5$	$K_\theta'$ W/cm deg	$K_\theta$ W/cm deg
Ge	5.32	72.60	22.6	0.67	0.40	395	4.90	0.41	0.45
Si	2.33	28.09	19.9	0.80	0.67	674	1.65	0.46	0.54
SiC	3.21	20.05	10.4	2.5	1.0	1200	1.73	0.90	0.9±0.1
Diamond	3.51	12.01	5.64	5.76	1.44	1900	0.63	1.50	1.8±0.1

<sup>a</sup>  $\rho$ =density,  $\bar{M}$ =average atomic mass,  $V_0$ =average volume per atom,  $c_{44}$ =elastic constant,  $\bar{v}$ =average sound velocity  $=[2(c_{44}/\rho)^{1/2} + (c_{11}/\rho)^{1/2}]/3$ ,  $\theta$ =Debye temperature for  $T > 300^\circ\text{K}$ ,  $\Gamma$ =isotope scattering parameter,  $K_\theta'$ =theoretical value of  $K$  at  $T=\theta$ , and  $K_\theta$ =experimental value of  $K$  at  $T=\theta$ .

useful result, but would not have been at all apparent if the  $K$  results in the previous literature<sup>5-10</sup> for impure SiC had been used.

The calculation of the theoretical upper limit on the  $K$  of the SiC and diamond requires a knowledge of various physical parameters of these materials. These parameters are listed in Table IV together with those for Ge, Si, and diamond. Most of these parameters are readily obtainable from the literature, and no further mention of them will be made. However, some discussion of  $\theta$  and  $\bar{v}$  for SiC is necessary. Since the following arguments will be approximate, SiC will be treated as if all of the numbers referred to the cubic or  $\beta$ -phase of SiC. The elastic constants,  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ , have apparently not yet been measured. They can be estimated from the measured<sup>31</sup> value of Young's modulus,  $Y=4.5 \times 10^{12}$  dyn/cm<sup>2</sup>, and the estimated values for Poisson's ratio,  $\nu=0.25$  and anisotropy constant  $A=1.4$ . These are

based on a comparison with  $c_{ij}$  data<sup>32</sup> for Si, Ge, GaAs, and InSb. The result is:  $c_{11}=5.4 \times 10^{12}$  dyn/cm<sup>2</sup>,  $c_{12}=1.8 \times 10^{12}$  dyn/cm<sup>2</sup>, and  $c_{44}=2.5 \times 10^{12}$  dyn/cm<sup>2</sup>. These  $c_{ij}$  values are in passable agreement with those estimated by Tolpygo,<sup>33</sup> and yield an average sound velocity of  $\bar{v}=1.0 \times 10^6$  cm/sec. The Debye temperature at  $0^\circ\text{K}$ ,  $\theta_0$ , calculated from the  $c_{ij}$  values is  $1200^\circ\text{K}$ , in good agreement with both the low- and high-temperature heat capacity data.<sup>34,35</sup>

### Impure Crystals

The discussion of impurity effects will be qualitative because the detailed nature of the impurities in SiC and diamond is not well understood at present.

#### A. Silicon

We are interested in the effects of electrically active impurities on the  $K$  of Si crystals. The presence of electrically inactive impurities such as C, Ge, and O will affect  $K$ , but these effects, per atom of impurity, are much smaller.<sup>3,36,37</sup> Our concern is with the most highly soluble III-V impurities As, B, and P, since of all the various trace impurities possible it is believed that these will produce the largest effects on  $K$ . The  $K$  results for pure and intentionally doped Si are shown in Fig. 1. For all temperatures  $3^\circ \leq T \leq 300^\circ\text{K}$  the  $K$  decreases with increasing impurity content of B or P. The decrease is substantial at  $300^\circ\text{K}$  and becomes larger and larger as  $T$  decreases. A comparison of the results for R5 and R55 show that for a concentration of B or P at a level of  $2 \times 10^{20}$  cm<sup>-3</sup> the  $K$  would be about the same. Therefore, these two electrically active elements have about the same effect in decreasing  $K$ , although one is a donor and one an acceptor. Measurements of the electrical conductivity indicate that almost all of the heat transport in these heavily doped samples is caused by phonons, as it is in pure Si. From the extra-

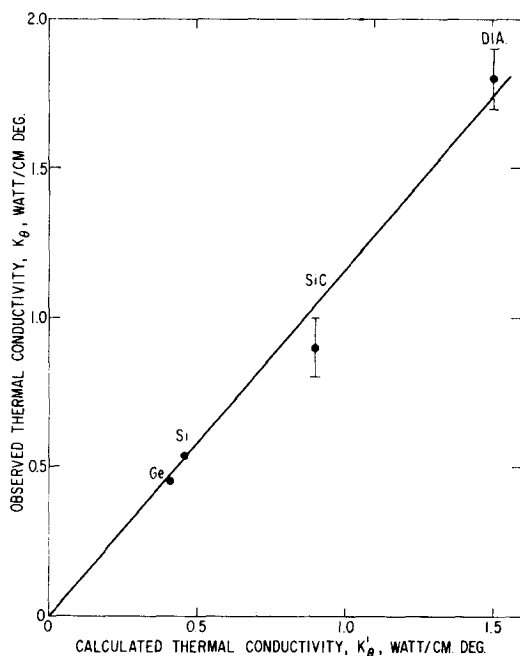


FIG. 5. A comparison of the observed  $K_\theta$  and computed  $K_\theta'$  thermal conductivities at the Debye temperature  $\theta$ . The straight line shown is given by  $K_\theta = 1.15 K_\theta'$ .

<sup>31</sup> D. P. H. Hasselman and H. D. Batha, Appl. Phys. Letters 2, 111 (1963).

<sup>32</sup> K. S. Aleksandrov and T. V. Ryzhova, Kristallografiya 6, 289 (1961) [English transl.: Soviet Phys.—Cryst. 6, 228 (1961)].

<sup>33</sup> K. B. Tolpygo, Fiz. Tverd. Tela 2, 2655 (1960) [English transl.: Soviet Phys.—Solid State 2, 2367 (1961)].

<sup>34</sup> G. E. Humphrey, S. S. Todd, J. P. Coughlin, and E. G. King, U. S. Bureau of Mines Report No. 4888 (July 1952).

<sup>35</sup> A. Magnus, Ann. Physik 70, 303 (1923).

<sup>36</sup> A. M. Toxen, Phys. Rev. 122, 450 (1961).

<sup>37</sup> B. Abeles, D. S. Beers, G. D. Cody, and J. P. Dismukes, Phys. Rev. 125, 44 (1962).

polation of the results in Fig. 1 to the maximum impurity concentration of  $\sim 10^{21} \text{ cm}^{-3}$ , it is estimated that the lowest  $K$  that could be obtained in Si by doping would be between 0.1 and 0.2 W/cm·deg at 300°K. At 3°K such a sample would probably have a  $K$  of  $\sim 5 \times 10^{-4} \text{ W/cm} \cdot \text{deg}$ .

### B. Silicon Carbide

The main use of the Si results in the present study is to determine the possible range of  $K$  values that are apt to occur in SiC, where neither the knowledge of nor the control over incorporated impurities is very great. Again the impurities of major concern will be the III and V column impurities, Al and N, which are electrically active in SiC. The electrical conductivity of the SiC samples was measured from 300° to 20°K, and the results are shown in Fig. 6. Even for R52 the  $\sigma$  is so small that the electronic contribution to  $K$  is negligible at all temperatures. Therefore, in SiC as in Si the heat transport is produced by phonons. In the impure SiC the  $K$  is determined mainly by the phonon scattering from the electrically active impurities. The results in Fig. 2 show that these impurities decrease the  $K$  of SiC at and above room temperature, but that the effect is most pronounced in the region  $T < 50^\circ\text{K}$ . Qualitatively this is the same situation found in Si. For example, SiC sample R52 ( $4 \times 10^{19} \text{ cm}^{-3}$  of Al) has the same type of behavior as Si sample R55 ( $1.7 \times 10^{20} \text{ cm}^{-3}$  of P), and the impurity concentrations only differ by a factor of 4. Sample R43 has about the same total content of impurities as does sample R52. However, the Al is all compensated by the N yielding a net donor concentration of  $\sim 10^{17} \text{ cm}^{-3}$ .

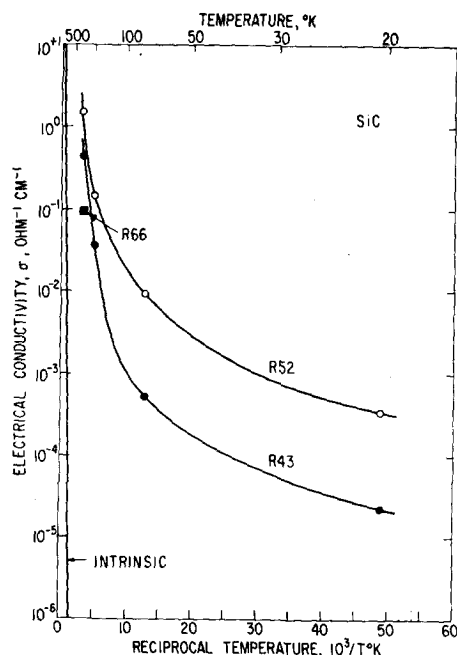


FIG. 6. The electrical conductivity of the SiC samples versus temperature.

Consequently its  $K$  approaches that of the purest sample R66. The data for almost all commercial SiC brick is similar to that of Vasilos and Kingery, and probably represents the behavior of SiC with high concentrations of N. The N content<sup>38</sup> for SiC made in a one atmosphere pressure of N is  $\sim 6 \times 10^{19} \text{ cm}^{-3}$ , which is probably sufficient to give the observed low  $K$  of 0.6 W/cm·deg at 300°K. The N content of SiC can be raised to at least  $3 \times 10^{20} \text{ cm}^{-3}$ .<sup>39</sup> The  $K$  of such SiC at 300°K would probably be about 0.1 or 0.2 W/cm·deg. This is about the same as the minimum value for Si doped with a similar concentration of B.

### C. Diamond

The situation for diamond is somewhat different from that for Si and SiC. The common impurity in natural diamonds is N, but it is not electrically active<sup>24</sup> in diamonds. Therefore, samples I, 13a, and 13b, which probably contain  $10^{19}$  to  $10^{20} \text{ cm}^{-3}$  of N, show no appreciable depression of  $K$  in the region  $T < 50^\circ\text{K}$ . In fact their  $K$  values for  $T < 10^\circ\text{K}$  come close to those predicted from boundary scattering alone. This is distinctly different from the effects in Si and SiC, and is related to the difference in electrical activity.<sup>2</sup> The N does, however, appear to depress the  $K$  in the  $50^\circ \geq T \geq 300^\circ\text{K}$  range, and the variation in N content is undoubtedly responsible for most of the variation in  $K$ . One might estimate that a diamond with  $4 \times 10^{20} \text{ cm}^{-3}$  of N, the maximum amount so far reported,<sup>24</sup> might have a  $K$  as low as say 1 W/cm·deg at 300°K. It is possible that such an impurity concentration rather than experimental difficulties is responsible for the low  $K$  of sample 12 in Fig. 3. If the N atom impurities in the diamond were randomly distributed point impurities, then their effect on  $K$  could be calculated and compared with Fig. 3. However, there is some evidence that the N atom possess a fair degree of ordering in the diamond lattice,<sup>27</sup> and a calculation of  $K$  for impure diamonds would be rather difficult. Such a calculation has been attempted by Agrawal and Verma,<sup>40</sup> who postulated a value of  $\Gamma$  that is 100 times larger than the value in Table IV in order to account for the low  $K$  of the type I diamond. Klemens<sup>41</sup> has attempted to explain this curve by invoking clusters or arrays of defects.

### CONCLUSIONS

Measurements have been made of the thermal conductivity  $K$  of some samples of Si with large impurity concentrations and of some pure and impure samples of SiC in the temperature range 3° to 300°K. A comparison of these results with data in the literature on pure Ge,

<sup>38</sup> J. A. Lely and F. A. Kroger, *Semiconductors and Phosphors*, edited by M. Schon and H. Welker (Interscience Publishers, Inc., New York, 1958), pp. 514, 525.

<sup>39</sup> G. A. Slack and R. I. Scace, *J. Chem. Phys.* (to be published).

<sup>40</sup> B. K. Agrawal and G. S. Verma, *Phys. Rev.* **126**, 24 (1962).

<sup>41</sup> P. G. Klemens, *Phys. Rev.* **86**, 1055 (1952).

Si, and on natural diamond shows that the  $K$  of the SiC of the highest purity comes close to the upper limit predicted by theory. The  $K$  of pure SiC lies between the values for pure Si and pure diamond. The heat transport in pure SiC for  $T \leq 300^\circ\text{K}$  is caused by phonons, and these are scattered by other phonons, isotopes, and the crystal boundaries.

In the impure Si and SiC the phonons are further scattered by the electrically active impurities from the III and V columns of the periodic table. For impurity concentrations in the range above  $10^{20} \text{ cm}^{-3}$  the reduction in  $K$  can be as large as a factor of 20 at  $300^\circ\text{K}$ , and becomes larger with decreasing temperature.

The effect of nitrogen, the dominant natural impurity, on the  $K$  of diamond is less severe than the above effects in Si and SiC. It is believed that the effects are smaller because nitrogen is not an electrically active impurity.

#### ACKNOWLEDGMENTS

I would like to thank J. H. McTaggart for his extensive help in making the electrical and thermal conductivity measurements. Thanks are also owed to D. R. Hamilton, G. Busch, and the Norton Company for supplying various samples of SiC, and to F. H. Horn and D. C. Jillson for the Si samples.

## Effect of Temperature on the Mechanical Properties of Solid Pressure-Transmitting Media. I. Talc

R. B. GRAF AND C. O. HULSE

*United Aircraft Corporation Research Laboratories, East Hartford, Connecticut*

(Received 17 June 1964)

High-temperature compression tests have revealed unsuspected high-temperature strength in block talc. Analyses by x-ray diffraction indicate that the increase in strength is associated with the transformation of the talc to protoenstatite, silica, and water. The bulk modulus of elasticity also increases with increasing temperature, reaches a maximum at  $1100^\circ\text{C}$  and then decreases at higher temperatures. These findings suggest that block talc is not as suitable for a solid pressure-transmitting medium at elevated temperatures as is commonly supposed.

#### INTRODUCTION

THE advent of utilizing solid pressure-transmitting media has made available new areas for high-pressure-high-temperature experimentation, even though the data obtained are not as accurate as those measured at lower pressures using other media. Many pressure data which have been reported are based on room-temperature calibration curves constructed by the standard techniques.<sup>1,2</sup> Such measurements are considered to have some validity at high temperatures based on the assumption that the solid pressure-transmitting media decrease in strength with increasing temperatures.<sup>1,3</sup> However, there are apparently few data available concerning the effect of temperature upon the mechanical properties of solid pressure-transmitting media.

The materials which are most widely used as solid pressure transmitting media are talc and pyrophyllite. Talc, which is used principally in piston-cylinder devices, has been preferred over pyrophyllite for this application because it transmits pressure more efficiently,<sup>1,2</sup> and therefore provides more pressure on the

sample for a given applied load. At elevated temperatures the situation is complicated by the transformation of the talc to protoenstatite, silica, and water. Moreover, because of the thermal gradients that exist in high-pressure devices, the extent of the transformation varies throughout the talc cylinder from a maximum at the surface near the heater to no reaction at the outer surface. The confined water vapor may also have some effect on the high-temperature strength of the components in the high-pressure cell.

The present study was undertaken in order to investigate the effect of temperature upon the strength and ductility of block talc, particularly at temperatures where the talc begins to transform to protoenstatite, silica, and water. In addition, the talc was characterized by room-temperature testing of fired samples, volume change, and weight loss measurements. X-ray diffraction, electron microscope, and differential thermal analyses were also utilized in this investigation.

#### EXPERIMENTAL PROCEDURE

The block talc used in this investigation was obtained from the American Lava Corporation and has their designation of Lava Grade 1136. The test specimens were machined into the shape of cylinders 0.500 in.

<sup>1</sup> F. R. Boyd and J. L. England, *J. Geophys. Res.* **65**, 746 (1960).

<sup>2</sup> J. E. Tydings and A. A. Giardini, ASME Preprint 62-WA-307, presented at the Winter Annual Meeting, New York (1962).

<sup>3</sup> F. R. Boyd and J. L. England, *J. Geophys. Res.* **68**, 312 (1963).