THERMAL CONDUCTIVITY OF NATURAL DIAMOND BETWEEN 320 AND 450 K

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Thermal-conductivity experiments with linear heat flow and radiation thermometry were done on one hundred selected natural diamonds. The results were found to correlate with the infrared absorptions and thus with the nitrogen impurity concentrations. A few results for synthetic diamonds are also reported.

1. Introduction

Various workers [1–11] have reported measurements of the thermal conductivity of diamond at temperatures well below 300 K. Up to 300 K (the Debye temperature of diamond is about 2000 K) various phonon scattering mechanisms are dominant [12]; above room temperature it is mainly phonon scattering by point defects which determines the diamond conductivity. Since most diamonds contain relatively large amounts of nitrogen (of the order of 0.1 atomic percent [13–18]) the conductivity above room temperature varies greatly amongst diamonds. Because of its supreme conductivity diamond has been used for the last decade as a heat-dissipating substrate for semiconductor microwave devices working at temperatures up to about 450 K [19–22]. Knowledge of the diamond conductivity at such temperatures is needed for this application. However, extrapolations of earlier work and the very few recent results around 400 K [23–26] do not give a clear picture and therefore the present experiments were made.

The published results up to 300 K were obtained with linear heat-flow experiments and measurements of temperature differences mostly by means of thermocouples [1–11]. The samples were about 8 mm long. Decker and Schorr used linear heat-flow and radiation thermometry [23,24]. Using thermocouples they also measured the spreading resistances in irregularly shaped diamonds. The present experiments are an extension of their work with radiation thermometry. This kind of thermometry has the advantages that possible large inhomogeneities in samples would be observable, that the samples can be much shorter than 8 mm and that experiments are relatively fast (since, for instance, mounting thermocouples on diamond is not involved). Large numbers of samples can thus be investigated. On the other hand, experiments below 300 K which are often made in vacuum would be much more complicated with radiation thermometry than with thermocouples. For this reason the present measurements were only made above room temperature.

One hundred samples of natural diamond with various infrared absorptions [27,28] were investigated. Such absorptions correlate with the impurity concentrations and are the basis of classification of the diamonds (see section 2.1). The possible effect of hydrogen on diamond conductivity has not yet been studied, neither have the effects of inclusions and cracks. Although some anisotropy might arise from mechanical strain or distortion of the perfect crystal lattice, crystallographic orientation of the samples was not considered as diamond has cubic symmetry and thus the second-rank conductivity tensor reduces to a scalar.

Section 2 of this paper describes the experiment: samples, thermal conductivity measurements, infrared absorption measurements and measurements of other properties. The results for diamonds without absorptions at 7–10 μm are discussed in section 3 and those for diamonds with absorptions at 7–10 μm in section 4. In section 5 the results are compared with other thermal conductivity work, with the results of nitro-

gen measurements for some samples, and with a few results for synthetic diamond. The conclusions are summarized in section 6.

2. Experiments

2.1. Samples

The samples are rectangular bars, sawn and polished from selected natural diamonds at the Drukker factory in Cuijk, The Netherlands. Serial numbers were assigned for reference. The cross sections are 1×1 mm^2, except for bar 13 (2.3 mm^2) and bars 14 and 15 (0.23 mm^2). Their lengths range from 1.9 to 8.4 mm with an average of 4 mm. Occasionally two bars were cut from one rough stone, and this is either indicated with braces in table III or the data for the two bars were combined. All the bars are of gem quality i.e. with no inclusions, cracks or flaws observable at 10X magnification. Unless stated otherwise, the bars are light brown or light grey.

Infrared spectra (see section 2.3) and also electrical resistivities (see section 2.4) were measured to classify the diamonds. Pre-selection was carried out in the ultraviolet. Thirty bars are of type IIa diamond with absorptions at $7-10~\mu$m lower than about 0.6 cm^{-1} and with resistivities above 10^{10} Ω.cm. The birefringence differs among these bars (see section 2.4). Bars 1–5 are colourless and bars 28–30 are brown to dark brown. Eighteen bars were characterized as type IIb diamonds, although only bars 45–48 are blue and follow Custers' characterization [29]. Bars 31–44 are thus less pronounced type IIb's. Bars 49–97 are of type Ia diamond with absorptions in the $7-10~\mu$m interval. Only bar 85 shows weakly the sharp absorption peaks at 3.22 and 7.12 μm; diamonds with more pronounced peaks at these wavelengths will be the subject of a later study. These peaks are attributed to hydrogen in diamond [30,31]. Bars 98–100 are yellow and have slight absorptions at 8.85 μm, indicating type Ib diamond. The division in the various types does not at all represent the mining percentages (probably less than 1 weight-percent of the total mine production is type IIa diamond).

Most bars were cut from diamonds of the company's stock (with unknown mine origin). Berman and Mar-

tinez loaned me bars 12, 73 and 98. Raal gave two rough diamonds which were cut to bars 47 and 48 and to 99 and 100. The classification of bars 98, 99 and 100 as Ib's was done by them.

2.2. Thermal conductivity measurements

A diamond bar was clamped between two identical metal probes (with a pressure of 20 N/mm^2 and use of heat transfer grease). The metal probes were high-purity gold, silver or copper, with cross-sectional areas about equal to that of the diamond bar. The top surfaces of the bar and probes were blackened with a thin ($\approx 20~\mu$m) uniform layer of paint. Part of the radiation from a circle (0.04 mm in diameter) on the blackened surface was focussed by a mirror objective on the indium antimonide cell of a modified Barnes microscope (model RM 2A). The temperature response was made linear electronically. The metal–diamond–metal
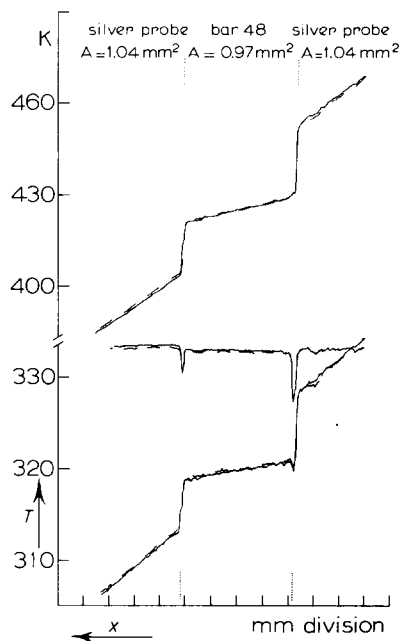

Fig. 1. Two measurement curves of bar 48. Full and broken curves were recorded at different times to check if the heat flow was steady. Imperfections in the paint, especially at the edges of the bar and probes caused irregularities in the temperature record. These can be seen also in the calibration curve with zero heat flow, at 334 K. The measurements give by means of eq. (1): $k(320) = 20.9$ and $k(428) = 13.7$ Wcm^{-1} K^{-1}.

Table I
Type IIa diamond

Bar	$k(320)$ (Wcm^{-1}K^{-1})	$k(450)$ (Wcm^{-1}K^{-1})
1 and 2	20.2	12.3
3 and 4	19.0	12.5
5	19.2	12.9
6 and 7	19.1	12.6
9 and 8	19.8	11.8
10 and 11	18.4	12.5
12	19.4	12.5
13	19.7	12.2
14 and 15	19.6	13.0
16 and 17	18.0	12.3
18 and 19	19.2	12.7
20 and 21	20.1	13.1
22 and 23	18.7	12.6
24 and 25	19.4	12.5
26 and 27	18.3	12.2
28	17.5	11.3
29 and 30	17.9	12.4

system was movable underneath the objective in the x direction. A heat flow was set up in this direction and the corresponding temperature gradients were measured when the heat flow was steady. The measurements were carried out in air (with gold shielding to reduce convection and to prevent stray radiation).

Two typical measurement curves T versus x are shown in fig. 1. The temperature gradients on the hot and cold probes were found to be always the same to within 7 percent. This indicates that the heat flow was

one-dimensional with negligible loss. The temperature gradients on the painted surfaces were thus equal to those in the bulk. Direct determination of the heat flow was not necessary because the thermal conductivity of diamond follows from

$$k_d(T_d) = k_m(T_d)\frac{A_m}{A_d}\frac{(dT/dx)_m}{(dT/dx)_d} \, , \tag{1}$$

where A is the cross section and the subscripts d and m refer to diamond and metal, respectively. T_d is the mean diamond temperature. The mean of the temperature gradients on the hot and cold probes was used.

In no case did the measurement curve T versus x show significant curvature. Thus all hundred bars are homogeneous conductors. For each bar measurement curves T versus x were run in at least four different temperature intervals. The $k(T)$ results were plotted double logarithmically (some results are shown in fig. 8). Linear regression (see also section 3.1) in these plots led to derived values $k(320)$ and $k(450)$ for each bar (or two bars cut from the same diamond). If the correlation of the data was too low, as occasionally found for shorter bars, more conductivity measurements were made. The coefficient of correlation between ln k and ln T data is -0.93 ± 0.04 averaged over the results of all bars. The derived conductivity results at 320 and 450 K are given in the tables I, II, III and IV.

Systematic error due to non-uniform paint is excluded since the metal–diamond–metal system was also investigated with the heat flow in the opposite

Table II
Type IIb diamond

Bar	$k(320)$ (Wcm^{-1}K^{-1})	$k(450)$ (Wcm^{-1}K^{-1})	Peak at 3.56 μm (cm^{-1})	Resistivity (Ω.cm)
31 and 32	19.6	13.5	0	10^7
33	18.4	13.3	0	10^8
34	18.8	13.3	1.2	10^4
35 and 36	19.4	11.4	1.2	3.10^4
37 and 38	19.5	11.5	2.4	3.10^3
39	19.3	12.9	4.7	3.10^3
40	20.1	12.4	3–5.5	10^6–10^3
41 and 42	19.6	12.2	4.7	10^3
43 and 44	18.6	12.3	5.4	10^3
45 and 46	20.2	13.2	4.0	10^2
47 and 48	20.1	11.7	6.1	10^2

Table III
Type Ia diamond

Bar	k(320) (Wcm⁻¹K⁻¹)	k(450) (Wcm⁻¹K⁻¹)	a(7.3) (cm⁻¹)	a(7.8) (cm⁻¹)	a(≈8.4) (cm⁻¹)
49	17.6	11.8	0.3	1.4	1.1
50	17.0	11.6	0.4	1.3	1.2
51	17.6	11.4	3.2	3.2	3.7
52	16.0	11.0	3.0	4.4	4.5
53	17.8	11.8	1.1	1.2	1.5
54	13.9	10.3	6.0	5.5	7.5
55	18.0	11.2	1.7	2.2	3.8
56	16.5	11.0	1.6	2.1	3.2
57	16.0	11.0	2.2	2.5	3.3
58	14.0	10.2	2.3	3.5	5.3
59	15.5	10.8	0.3	8.7	4.3
60	14.8	10.2	0.6	11.6	6.0
61	14.5	10.2	0.5	3.0	7.2
62	13.5	9.6	0.5	3.0	7.3
63	13.1	10.0	2.0	4.5	10.7
64	11.9	9.3	0.8	5.0	12.2
65	11.3	8.7	14.6	15.6	13.6
66	11.0	8.4	15.0	15.6	13.6
67	15.5	11.3	1.3	2.2	2.6
68	14.2	10.2	2.2	2.9	4.8
69	14.0	10.3	2.7	8.4	5.0
70	14.2	9.8	4.7	5.7	5.2
71	13.1	9.5	5.0	16.5	10.5
72	12.2	9.2	19.3	13.3	13.1
73	10.9	8.2	14.0	15.0	13.5

Bar	k(320) (Wcm⁻¹K⁻¹)	k(450) (Wcm⁻¹K⁻¹)	a(7.3) (cm⁻¹)	a(7.8) (cm⁻¹)	a(≈8.4) (cm⁻¹)
74	10.8	7.8	10.5	27	17.5
75	10.7	8.3	0.8	29	15.7
76	10.6	7.7	18.5	15.2	15.5
77	9.9	7.4	0.6	31	16.5
78	9.9	7.5	8.5	26	18.0
79	9.6	7.6	6.8	27	15.5
80	9.3	7.3	5.0	43	23
81	9.3	7.4	28	18.5	19.0
82	8.6	6.7	30	26	26
83	8.5	6.3	10.0	33	20
84	8.3	6.3	2.0	51	29
85	8.2	6.3	13.0	35	24
86	7.6	5.9	37	30	33
87	7.6	5.9	27	30	29
88	7.6	5.9	6.3	64	37
89	7.3	6.1	35	29	30
90	7.0	5.3	11.0	74	45
91	6.9	5.5	29	54	44
92	6.8	5.5	15.0	45	31
93	6.6	5.1	36	55	47
94	6.4	5.0	14.0	72	43
95	6.1	4.9	15.5	69	42
96	5.6	4.7	35	60	51
97	5.3	4.2	30	95	67

Table IV
Type Ib diamond

Bar	$k(320)$ $(\text{Wcm}^{-1}\text{K}^{-1})$	$k(450)$ $(\text{Wcm}^{-1}\text{K}^{-1})$	$a(7.8)$ (cm^{-1})	$a(8.85)$ (cm^{-1})
98	17.5	12.5	1.6	1.7
99 and 100	17.5	11.9	1.6	1.6

direction in each series of measurements. As expected the values of k did not depend on the kind of probe used, the cross section of the bars (compare results of bar 13 with those of 14 and 15), or the heat flow used (up to 4 watts). The cross sections of the bars and probes were measured to 2 percent accuracy and checked against the densities and weights. The determination of the temperature gradients on diamond was accurate to within 5–10 percent depending on the paint quality and length of the bar. The derived $k(320)$ values have an estimated accuracy of about 4 percent, and the $k(450)$ values are slightly less accurate since there were fewer experimental $k(T)$ results at the high temperature end.

Similar measurements were carried out on a few 3/4 mm diamond cubes, giving results accurate within 10–15 percent [25]. The equipment is also suitable for the study of thermal resistance at metal/diamond interfaces [32].

2.3. Infrared absorption measurements

The transmission was recorded from 3 to 9.5 μm (the grating limit) with the beam normal to a long surface of each bar, through about 80 percent of its volume. The spectra were run on a double beam Leitz spectrophotometer (model IIIG with micro attachment). The equipment was at room temperature, but the beam heats the diamond and its holder raising the temperature by 20–30 K. The spectra thus refer to about 320 K. If the absorptions in the 7–10 μm interval were large, the bar was polished thinner and a new spectrum recorded. This happened for most of the bars 75–97. A typical spectrum is shown in fig. 2.

Spectra were also made with small aperture ($<$1 mm^2), with the beam going through the middle and/or the ends of each bar to check homogeneity. The absorptions varied less than 15% in each of the hundred bars, except for bar 40 which is a very inhomogeneous
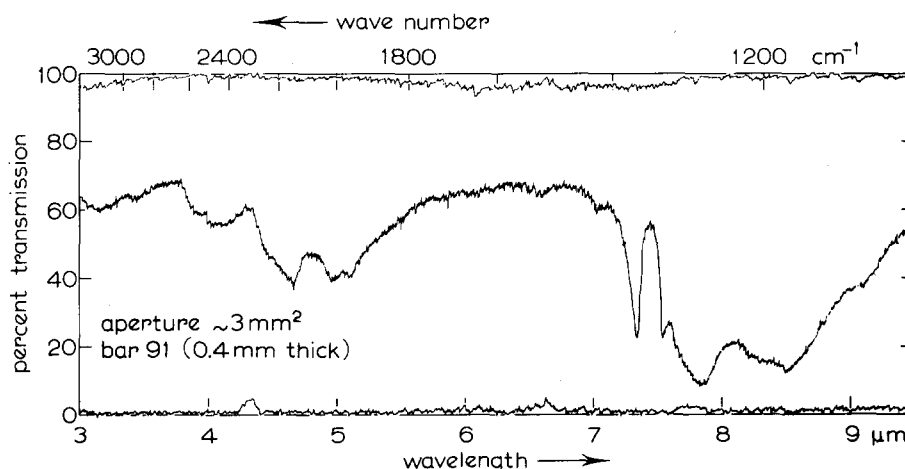

Fig. 2. A transmission spectrum of bar 91, thinned (after the conductivity measurements) to 0.4 mm. The spectrum shows clearly the three main absorptions at 7.3, 7.8 and $\approx$8.4 μm and the values of a are given in table III. The curve at the bottom was obtained with blocked aperture and the one at the top with open aperture.

type IIb diamond. Two type Ia bars were excluded
from the present series of diamonds because of inho-
mogeneity. Additional spectra of most bars were run
with the beam parallel to the length of the bar. The
aperture was then limited by the 1 mm² cross section.

The absorption values $a(\lambda)$ were derived from the
spectra, with correction for reflections as described
for diamond by Clark, Ditchburn and Dyer [33]. The
refractive index of diamond at 7–10 µm was taken as
2.33 [34]. An interpolated curve a versus λ was
obtained for each type Ia diamond from about thirty
well-chosen readings of its spectrum between 7.0 and
9.5 µm. This curve was extrapolated to 10 µm. The
values $\int_7^{10} a d\lambda$ with λ in µm and $\int_7^{10} a\lambda^{-2} d\lambda = \int_{1000}^{1430} a d\sigma$
with the wave number σ in cm^{-1} were calculated.

The relative strengths of the most pronounced type
IIb peak [35] are listed in table II. The most charac-
teristic type Ia absorptions are the sharp peak at
7.29 $<\lambda<$ 7.36 µm, the value of a at 7.80 µm and
the maximum value of a at 8.30 $<\lambda<$ 8.55 µm. These
are listed in table III for each bar. The values of a at
8.85 µm (indicative of type Ib diamond) are listed in
table IV. Even the weakest type Ia diamonds and the
type Ib's have significant absorptions at 7–10 µm with
respect to $a(6.75)$. Here type Ia diamond is about as
transparent as the other types and it was found that
$a(6.75) = 0.6 \pm 0.4$ cm^{-1}. This large uncertainty gives
also an error in the values of a above 7 µm and in the
integral values. Small values of a are therefore not too
accurate, but for larger values this uncertainty is
negligible since the random error in the spectra is
5–10 percent.

2.4. Measurements of other properties

Each bar was examined at 100 × magnification
between crossed polarizers and a classification of the
birefringence according to strength and uniformity
was made.

Electrical contacts were made on well cleaned bars
with silver paint. Resistivity measurements were carried
out at room temperature in darkness. Direct currents
were measured with applied voltage gradients of 30
V/mm (not all diamonds behave ohmically). The resis-
tivities of some of the type IIa diamonds are $\approx 10^{14}$
Ω.cm. A parallel type IIa plate was used to remove
the Joule heat during measurement of type IIb dia-
monds. The resistivities of type IIb bars are given in

table II: they are accurate to within a factor of 2. Bar
40 is very inhomogeneous, the two values refer to the
two ends of this bar.

3. Diamonds without absorption at 7–10 µm

3.1. Type IIa results

The derived thermal conductivity values are given
in table I. The three brown bars 28, 29 and 30 have
slightly lower than average conductivity at 320 K
(more than two standard deviations). This needs
further study, for instance by investigating the impur-
ities in these bars. Possibly lattice distortion corre-
sponding to birefringence causes a reduction in con-
ductivity. However, a correlation between birefringence
and conductivity was not found. Therefore further
quantitative analysis of the birefringence in the bars
has not been made.

The type IIa conductivity values agree with extra-
polation of the results in refs. 5, 7, 9 and 10, and also
with Decker and Schorr's values [23,24]. The slope s
of the regression line ln k versus ln T was calculated
for each bar or pair of bars. The mean value is −1.26.
Within the accuracy (given by one standard deviation
of 15 percent) it was found that s did not depend on
temperature in the relatively narrow interval of the
experiments. However, the value of s is slightly higher
than obtained between 150 and 300 K [5,7,9,10]. In
other words, ln k versus ln T is slightly convex between
150 and 450 K. This behaviour agrees with experiments
on other kinds of crystals and also with theory [12].
Apart from U-processes, there is the effect of 1.1
atomic percent carbon 13 which causes considerable
phonon scattering. This isotope scattering should be
the same in all diamond types.

3.2. Type IIb results

Table II does not give any "low" conductivity value,
not even for the strongest type IIb bars. This is in
accordance with the observation that the measurement
curves T versus x of the inhomogeneous bar 40 did not
show curvature. Two conductivity measurements of a
strong type IIb bar are shown in fig. 1.

The results do not agree with a published extra-
polation of the conductivity of type IIb diamond to

above 300 K [36]. This extrapolation was based on only one experimental $k(T)$ value above 140 K [4].

The impurities which make type IIb diamonds p-type semiconductors were thought to be boron or aluminium. These would cause point defect scattering additional to the isotope scattering. The conductivities of type IIb and type IIa bars are nearly the same and thus significant phonon scattering due to these impurities is not observed. This implies (eq. (5), section 4.3) that concentrations of boron or aluminium in dispersed ("point defect") form would be less than ≈200 and ≈1 atomic ppm, respectively. Impurity analyses of natural type IIb diamonds have shown that boron is always below this concentration and that aluminium can be well above 1 ppm [37,38]. This supports the recent idea that boron is the acceptor centre in semi-conducting diamond [38–40]. However, correlation of analyses by spectrographic or nuclear methods with impurity concentrations inferred from thermal conductivity measurements is made difficult by the known presence of clouds of micro-inclusions in gem-quality diamonds [41].

The combined results for type IIb and type IIa diamond (omitting bars 28, 29 and 30) give mean values with one standard deviation: $k(320) = 19.3 \pm 0.6$ and $k(450) = 12.5 \pm 0.6$ Wcm^{-1}K^{-1}. These values will be referred to as the type II result. Possible phonon scatterers do not give a significant variation in conductivity amongst the 45 type II bars. The results may be generalized that diamonds without absorptions at 7–10 μm additional to $a(6.75)$ (see section 2.3) have high conductivities.

4. Diamonds with absorptions at 7–10 μm

4.1. Type Ia results

These are given in table III. Values of s (see section 3.1) given by

$$k \propto T^s \qquad (2)$$

have been derived for all 49 bars and are given in fig. 3. Values for the type Ia bars with the highest conductivities agree well with the type II result. It is obvious from these data that the lower the conductivity the smaller the value of s. The conductivities of type Ia diamonds converge thus to that of type II diamond,
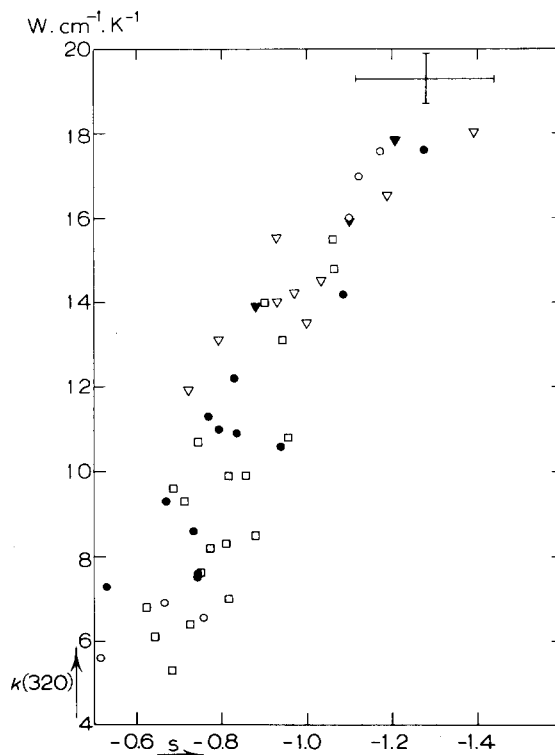

Fig. 3. Plot of conductivities at 320 K versus s (defined by $k \propto T^s$) for 49 type Ia diamonds. The significance of the symbols is given in table VI. The mean value for type II diamond is shown with one standard deviation.

but the intercept may be well above 1000 K for strong type Ia diamonds.

Bar 97 has "record" absorption values for diamond. Bars 53 and 54, cut from one rough stone, show that type Ia diamond can be very inhomogeneous. As for type IIa diamond, it was found that birefringence has no effect on the conductivity of type Ia diamond.

Fig. 4 is a semilogarithmic plot of data of all 49 bars. A good linear regression was found. Random sampling showed that the second decimal of the coefficient of correlation between $k(320)$ and $\ln a(7.8)$ is significant (table V). The 7.8 μm absorption may be used for prediction of the conductivity at 320 K with a standard error of ± 1.3 Wcm^{-1}K^{-1}. This error is slightly larger than expected from the combined accuracies of the conductivity and absorption data (see also section 4.2). Since according to Kaiser and Bond
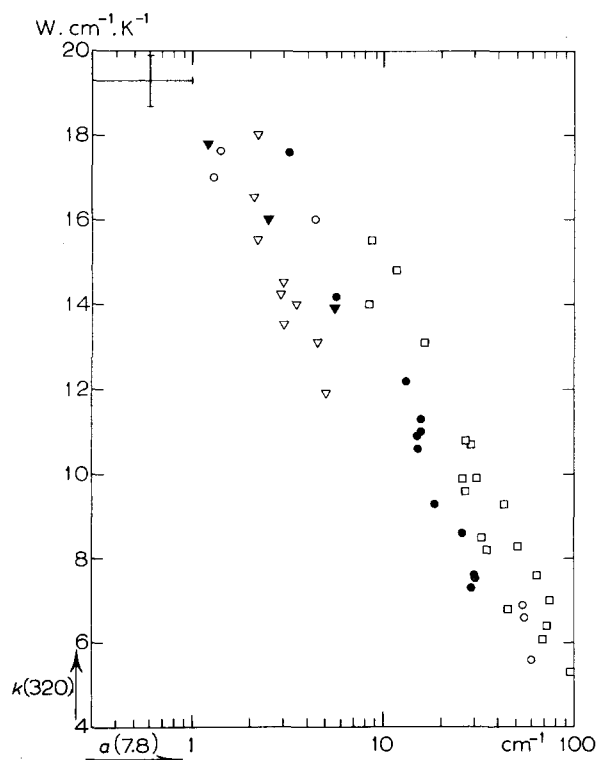
Fig. 4. Plot of conductivities at 320 K versus the absorptions at 7.8 μm for 49 type Ia diamonds. Table VI gives the significance of the symbols. The type II result is shown.

the value of $a(7.8)$ correlates with the nitrogen impurity content, the abscissa in fig. 4 could also have been given in atomic percent nitrogen (see also section 4.3).

The spectra were run at 320 K only, but earlier optical work has shown that the 7–10 μm absorptions are almost independent of temperature [28]. Therefore, meaningful correlations between $k(450)$ and absorption data could be made as well.

The correlation between conductivity and ln $a(7.3)$ is rather low (see table V). It may be non-zero because $a(7.3)$ correlates with other absorptions, for instance with $a(\approx 8.4)$. Results for bars with relatively large $a(7.3)$ values are shown by solid symbols as indicated in table VI. The strength of the 7.3 μm absorption corresponds to the number and/or size of the platelets [42–44]. Platelets have sizes which are large in comparison with the dominant phonon wavelengths at room temperature, and therefore do not reduce effectively the conductivity in these measurements, as can be seen in either figs. 3, 4, etc. where solid and open symbols are at random, or in table V.

4.2. Further study of conductivity and absorption data of type Ia diamond

Two absorption systems at 7–10 μm were found: the so-called A and B features [45,43] both attributed

Table V
Correlations between conductivity and absorption data

	ln $a(7.8)$	ln $a_I(7.8)$	ln $a_{II}(7.8)$	ln $a_{III}(7.8)$	ln $a(7.3)$	ln $a(\approx 8.4)$	ln $\int a\, d\lambda$	ln $\int a\, d\sigma$
$k(320)$	−0.94	−0.96	−0.97	−0.86	−0.75	−0.97	−0.97	−0.97
$k(450)$	−0.94	−0.97	−0.97	−0.83	−0.75	−0.96	−0.97	−0.97

Table VI
Subclassification of the 49 type Ia bars. The symbols in the columns on the right refer to figs. 3–10.

Group	Number of bars	$\dfrac{a(7.8)}{a(\approx 8.4)}$	Ratio A to B nitrogen	$\dfrac{a(7.8)}{a(7.3)}$	
				above 1.3	below 1.3
I	19	above 1.38	above 8	□	
II	18	between 0.85 and 1.38	between 2.1 and 8	○	●
III	12	below 0.85	below 2.1	▽	▼

to nitrogen [13,14] probably present in two forms in the carbon lattice. The ratio of $a(7.8)/a(\approx 8.4)$ gives, following the recipe of Davies and Summersgill [46, 28], a ratio of A to B nitrogen. A subclassification of the 49 type Ia bars was made and is given in table VI. Group I refers to bars with much absorption due to A nitrogen, group III contains bars 61–64 with extreme amounts of B nitrogen. I shall try to find some bars with $a(7.8) < 7$ cm^{-1} for group I and some others with $a(7.8) > 7$ cm^{-1} for group III. Data for such bars would be desirable to complete the picture. Diamonds with much A nitrogen combined with many platelets do not seem to exist; these would have been represented by solid squares.

The squares, circles and triangles are at random in fig. 3 and thus the ratio A to B nitrogen has no effect on the temperature dependence of the conductivity.

Linear regressions through the squares, circles and triangles could have been drawn in fig. 4. They are separated by at least one standard deviation, which has an average value for the three groups of 0.9 Wcm^{-1}K^{-1} and this is about the accuracy inferred from individual experimental errors. Table V gives the coefficients of correlation between conductivity and ln $a(7.8)$ after subclassification. Those of group III are low because the range of results is small.

The absorption at 7.80 μm is mainly due to A nitrogen, but decomposition of $a(7.8)$ into partial absorptions due to A and B nitrogen alone leads to low correlation coefficients between conductivity and ln $a_A(7.8)$ or ln $a_B(7.8)$. This indicates that the type Ia conductivity should be analysed in terms of A + B nitrogen.

The correlation in fig. 5 is high and the regression line has been drawn. The coefficients of correlation between conductivity and ln $a(\approx 8.4)$ are given in table V. Squares, circles and triangles in fig. 5 are at random around the regression line, whereas they were more or less separated in fig. 4. Conductivity at 320 K is predictable from $a(\approx 8.4)$ with a standard error of ± 0.9 Wcm^{-1}K^{-1}. The values $a(\approx 8.4)$ refer to the two nitrogen systems combined, because for bars of group I the maximum absorption value is at 8.31 μm due to A nitrogen and for those of group III it is at 8.54 μm due to B nitrogen [45].

The complicated absorption system was also integrated with respect to λ [47,48] and with respect to σ to study correlations with conductivity. The two inte-
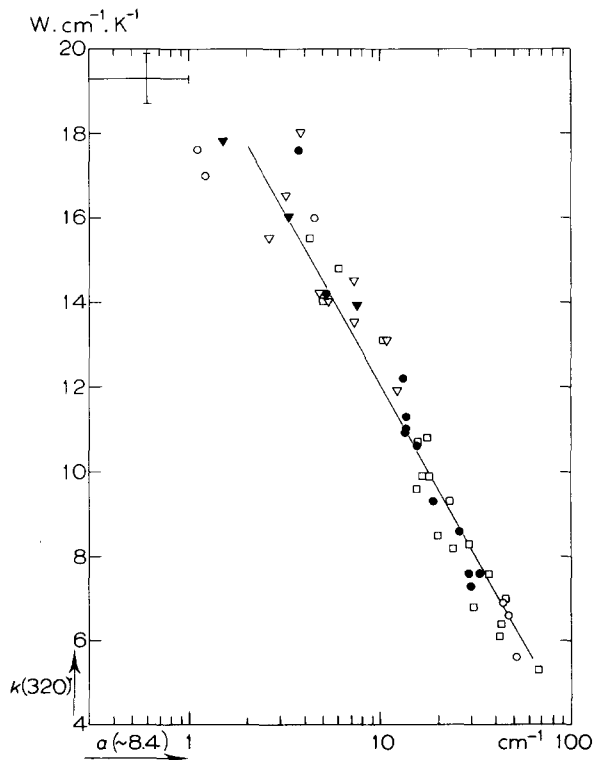

Fig. 5. Plot of conductivities at 320 K versus the maxima in the absorption at 8.30–8.55 μm for 49 type Ia diamonds. Table VI gives the significance of the symbols. The type II result is shown.

grals give slightly different weights to absorption at the two ends of the integration interval. The correlation coefficients are given in table V, and one of the resulting plots is shown (fig. 6). The integrals are not exactly a measure of the absorption system due to nitrogen, since they include a nearly constant absorption of 0.6 cm^{-1} and do not include B absorption peaks at 10 μm and higher wavelengths values. But corrections are small and would in all probability not lead to lower correlations.

The individual absorptions at the successive wavelengths of 7.3, 7.8 and ≈ 8.4 μm give increasing contributions to the integral values because the 7.3 μm absorption is a narrow peak and the ≈ 8.4 μm absorption is very broad. Their correlations with conductivity also increase and thus experimentally it is clear why the integrals correlate very well. However, the integrals involve calculations, whereas the maximum absorption
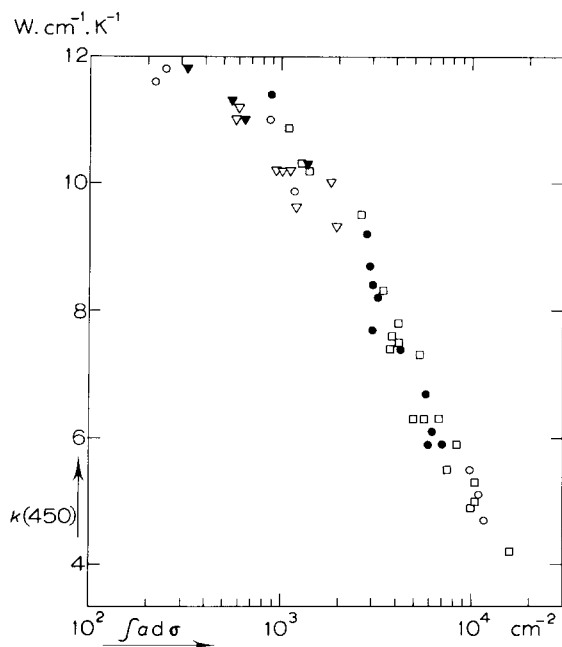
W. cm⁻¹.K⁻¹

Fig. 6. Plot of conductivities at 450 K versus the integrals of the absorption between 1000 and 1430 cm⁻¹ for 49 type Ia diamonds. Table VI gives the significance of the symbols.

at $8.30 < \lambda < 8.55$ μm is relatively easy to obtain and is also a good predictor of the conductivity. Moreover, the extrapolation of the line in fig. 5 is above the type II result.

4.3. Interpretation of type Ia results

Since none of the bars gives a result significantly below the trend of results in figs. 4, 5 and 6 one may conclude that only one kind of impurity atoms simultaneously reduces the conductivity of type Ia diamond and gives characteristic absorptions. These absorptions have been correlated to nitrogen, which is thus the only effective phonon scatterer in type Ia diamond. The occurrence of A and B nitrogen, however, complicates the picture. Davies and Summersgill concluded that equal values of $a_A(7.8)$ and $a_B(7.8)$ correspond within a factor of 2 to equal percentages of A and B nitrogen. If the percentages were exactly equal the results in fig. 4 should not depend on the ratio of A to B nitrogen, whereas in fact a scatter was found which could be resolved by subclassification according to the ratio A to B.

Berman and Martinez [9,10] have measured the

conductivity of nine type Ia diamonds up to room temperature. Martinez [9] gives values at 300 K versus $\ln a(7.8)$, and the scatter of his results is about the same as in fig. 4. Two of Berman and Martinez' bars with many B features and $a(\approx 8.4) = 3.5$ cm⁻¹ gave a dip in conductivity around 10 K which they attributed to combination of B nitrogen and dislocation lines. Perhaps the effect of the dislocations is observable for bars with stronger B absorptions in the conductivity above room temperature. This would explain the scatter in fig. 4, but might on the other hand, also give systematic scatter in fig. 3.

A more plausible explanation of the scatter in fig. 4 is that the nitrogen percentages N_A and N_B obey the equations

$$a_A(7.8) = 300 \, N_A \text{ cm}^{-1} \tag{3}$$

and

$$a_B(7.8) = 600 \, N_B \text{ cm}^{-1} . \tag{4}$$

Eq. (3) is found by Kaiser and Bond [13] and is only based on type Ia diamonds with mainly A features. Eq. (4) is an assumption. It is Davies' upper limit [46], but does not agree with some results of Lightowlers and Dean [14]. With the assumption that possible differences in lattice distortion or in group size between A and B nitrogen are not observable in $k(320)$, the total nitrogen percentages were calculated from table III and eqs. (3) and (4). The results are given in fig. 7 and the regression line has been drawn. The coefficient of correlation between $k(320)$ and $\ln(N_A + N_B)$ is −0.96 and between $k(450)$ and $\ln(N_A + N_B)$ is also −0.96. The correlation is thus higher than in fig. 4. Combination of the regression lines in figs. 5 and 7 leads to a relation between $a(\approx 8.4)$ and $N_A + N_B$ (see section 5.2).

Impurities other than nitrogen have been found in diamond in the ppm or ppb ranges [37,16,28]. These may be present as micro-inclusions and would then not affect the conductivity above room temperature. If diffused through the diamond, a heavy (or very light) element would give extra reduction in conductivity due to point defect scattering. With the approximation of no lattice distortion this could be expected for

$$c \cdot \Delta M^2 \geq 200 , \tag{5}$$

where c is the impurity concentration in atomic ppm and ΔM the difference between the atomic-mass num-
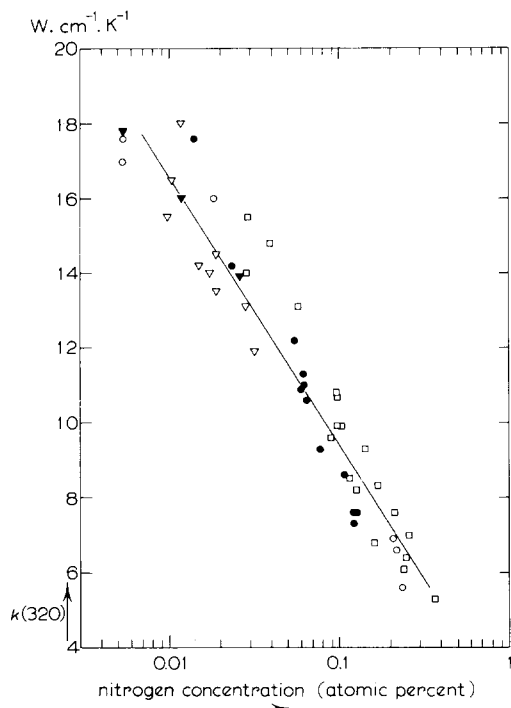
Fig. 7. Plot of conductivities at 320 K versus the values of $N_A + N_B$ calculated by means of eqs. (3) and (4) for 49 type Ia diamonds. Table VI gives the significance of the symbols.

5. Comparison with other experiments

5.1. Thermal conductivity work

Measurements of the diamond thermal conductivity up to 300 K have been reported recently by Berman and Martinez [9,10]. They used linear heat flow and thermocouples to measure temperature differences and gave results of experiments where two samples were exchanged between Martinez and me. These were type Ib and type IIa diamonds and the results agreed well, as subsequently was found for a type IIb sample. All these are of high thermal conductivity. However, a discrepancy was found for two type Ia diamonds as is shown in figs. 8 and 9. The results obtained by Martinez do not follow the trend in fig. 3.

Most published conductivity results are given only in relation to $a(7.8)$ or to the nitrogen content via eq. (3). Results for type Ia diamond without such an indication have little significance nowadays [26,36]. Fig.

bers of the impurity and carbon. The right-hand figure follows from the effect of nitrogen on the conductivity (also neglecting lattice distortion). Eq. (5) agrees with Slack's estimate fairly closely [7].

4.4. Type Ib results

This type of diamond gives electron paramagnetic resonance signals due to single substitutional nitrogen atoms [49] and shows absorptions at 8.85 μm [50]. Since bars 98, 99 and 100 also show absorptions at 7.8 μm, there is a minimum of 1.3 cm^{-1} at $\approx$8.4 μm, rather than a maximum (see section 2.3). The conductivity results in table IV fit the line in fig. 5 satisfactorily. However, the type Ib characteristic of these natural diamonds is not very pronounced. In synthetic diamond the 8.85 μm absorption can be much stronger [51,52], (see section 5.3). The values of a at 8.85 and 7.8 μm give, by means of the correlation found by Chrenko et al. [52] and eq. (3), 0.009 percent nitrogen. This result fits well in fig. 7.

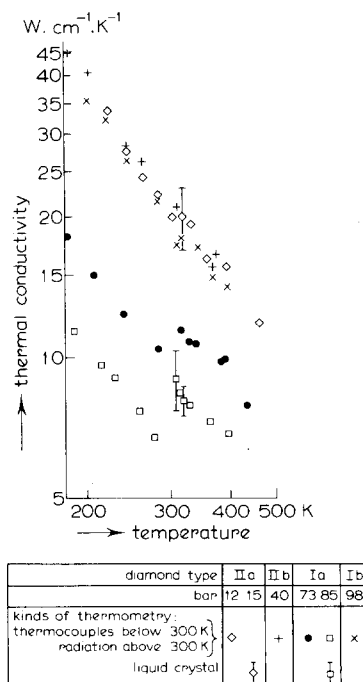| diamond type	IIa	IIb	Ia	Ib
bar	12 15	40	73 85	98
kinds of thermometry: thermocouples below 300 K radiation above 300 K	◇	+	● □	×
liquid crystal	⊹		⊺	

Fig. 8. Results for diamond bars exchanged between Martinez and the author. The conductivity values below 300 K were obtained by Martinez with thermocouples. This figure is an extension of fig. 1 of ref. 10.
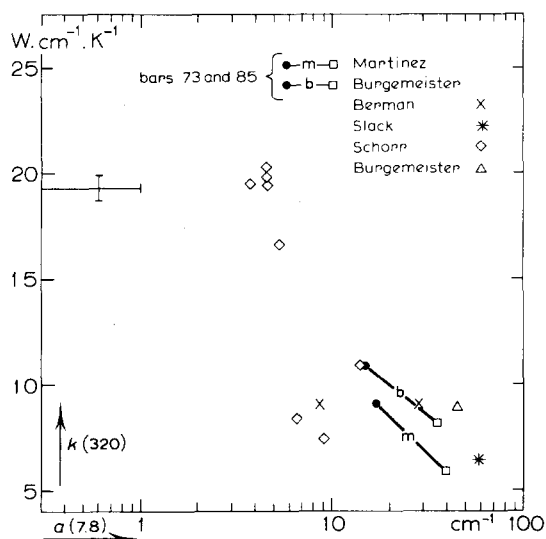
Fig. 9. Conductivities at 320 K of bars 73 and 85. Data ob-
tained by extrapolation of Martinez' values have been con-
nected by a line. The same was done with my results. Values
derived from published type Ia diamond conductivity data in
refs. 5, 7, 23 and 25, respectively, are given for comparison.
The type II result is shown again.

9 gives the type Ia results of Berman [5] and of Slack
[7]. Fig. 9 gives also data derived from Schorr's results
[23]. A result for a type Ia diamond cube of 3/4 mm
edge is also given for completeness [25]. Martinez'
data for bars 73 and 85 are representative of his results
for nine type Ia diamonds [9]. My results for these
bars also fit well in fig. 4. Therefore, two lines were
drawn through these symbols, and their divergence
shows the systematic character of the differences in
conductivity. The differences in $a(7.8)$ are not signifi-
cant. Fig. 9 shows that the results in the literature do
not help to resolve the discrepancy because too few
diamonds with large absorption values were measured.
Also the correlation between conductivity and $\ln a(7.8)$
is not optimum (see section 4). The results for type IIa
diamond given by Berman, Slack, Schorr and Martinez
are not plotted, they all agree with those reported in
section 3.1.

My results for type Ia bars 73 and 85 were checked
in additional measurements using probes of type IIa
diamond. The system was also checked with sapphire
samples. Further check experiments were done using
an independent means of temperature measure-

ment — liquid crystal thermometry. A heat flow caused
a colour pattern in a cholesteric liquid crystal mixture
(Merck chemicals) on the diamond surface. Such a
pattern was obtained similarly on copper or silver
reference probes. The illumination was with glass fiber
optics. The ratio of the lengths of these patterns led
to the conductivity of the diamond. Since the accuracy
of an individual result is relatively low (standard devia-
tion of 10–25%) and the measurements are simple,
the experiment was repeated many times. Mean values
with standard deviations are given in fig. 8 for bars 85
and 15, and tend to confirm the measurements with
radiation thermometry. The squares thus all refer to
the same type Ia diamond but are obtained with three
kinds of thermometry. As a check of the technique
the type IIa bar was measured.

Callaway analyses of diamond thermal conductivity
have led to interesting conclusions about the platelets
[53–55]. Berman, Hudson and Martinez [8] have
calculated also the number of nitrogen atoms per group
from their conductivity and $a(7.8)$ data. This gave
5–16 atoms per group which seems rather high [56].
In view of the discrepancy mentioned above the
results of similar calculations using the present higher
values of type Ia diamond conductivity would be
interesting.

5.2. Nitrogen measurements of some bars

The nitrogen contents of bars 58, 59, 63, 75, 82,
88 and 97 were measured by Sellschop, Annegarn,
Keddy, Madiba and Renan [57]. They used the nuclear
reaction

$$^{14}N(\alpha, n)\ ^{17}F \rightarrow\ ^{17}O + \beta^+ ,$$
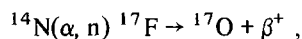
with a half life of 66 seconds and measured γ radiation
from the annihilation of β^+ [17]. The method yielded
the nitrogen content from the surface down to about
0.03 mm below it. Two sides of each of the seven bars
were investigated and it was found that the absolute
differences were less than 0.03 percent nitrogen. The
mean results are given in fig. 10, together with Kaiser
and Bond's result (eq. 3).

Assuming homogeneous nitrogen distributions one
may compare their surface measurements with the
results of section 4 which refer to bulk properties.
Qualitatively the results in fig. 10 are very similar to
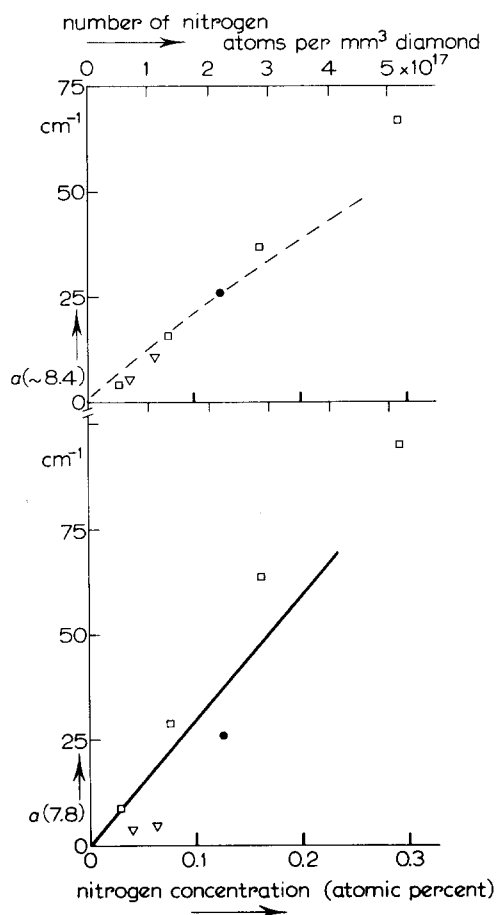those in figs. 4 and 5. The triangles and circle below

Fig. 10. Results obtained by Sellschop et al. from nitrogen measurements of seven bars. Table VI gives the significance of the symbols. The full line represents eq. (3) found by Kaiser and Bond. The broken line follows from the correlation between conductivity and ln $a(\approx 8.4)$ and that between conductivity and ln($N_A + N_B$).

Kaiser and Bond's line (bars with relatively large percentages of B nitrogen) are also relatively low in fig. 4, whereas the results in the upper part of fig. 10 are nearly on one line just as those in fig. 5. The results of the interpretation in section 4.3 (with the unusual assumption in eq. 4) are given by the broken curve in fig. 10. This curve is the combination of the lines in figs. 5 and 7. Quantitatively this interpretation does not lead to complete agreement of the nitrogen percentages in figs. 7 and 10. The largest difference is for bar 63 and is a factor of 2. This difference could be resolved by another unusual assumption, namely that

there is an additive constant in the relation between $a_B(7.8)$ and N_B [57].

5.3. Results for synthetic diamond

These results are incomplete since the synthesis parameters are unknown. Moreover, I investigated only a few samples of two different kinds, namely small single crystals and polycrystalline diamonds made by sintering fine diamond powder and a binder [58].

The single crystals were blocky shaped and showed rather strong absorptions near 8.9 μm. Four of them were polished to cubes of 0.6 mm edges and the thermal conductivities were measured with an accuracy of 20–25 percent. The mean results are given in table VII, and the standard deviations for these small samples were 15 percent. This result fits the trend of data in fig. 3. Via Chrenko et al. [52] the absorption correlates to ≈ 0.035 percent single substitutional nitrogen atoms. Although this value is below the line in fig. 7, the difference is within the limits of the accuracies of this experiment and Chrenko's work. Moreover, the samples were dark yellow to brown and not free from small cracks. These conductivity values are much lower than Slack's results for much purer synthetic diamond [7]. On the other hand, they are higher than values $k(320)$ = 5.4 and $k(450)$ = 4.4 Wcm^{-1}K^{-1} reported by Ositinkskaya et al. [26].

Three polycrystalline bars were investigated. Their weights would correspond to 2.5–2.8 atomic percent of metals such as iron, nickel, cobalt or copper which might have been used as the binder. For these diamonds eq. (5) has no meaning because the binder will be clustered. The thermal conductivities of these bars (lengths 4 mm) were measured with an accuracy of about 4 percent. The mean results are given in table VII and imply that above ≈ 400 K these polycrystalline diamonds conduct heat better than high-purity copper.

Table VII
Mean results for synthetic diamond

Samples	$k(320)$ (Wcm^{-1}K^{-1})	$k(450)$ (Wcm^{-1}K^{-1})	$a(\approx 8.9)$ (cm^{-1})
Single crystals	9.3	6.6	15
Polycrystalline	3.85	4.05	–

The conductivity values for these polycrystalline samples would not at all fit in fig. 3 because the dominant phonon scattering is on crystallite boundaries rather than on point defects. They are rather similar to those obtained by Pope et al. [59].

6. Conclusions

The thermal conductivity of type IIa diamond is high. No significant variation in the conductivities of thirty type IIa samples has been found, though brown ones could have slightly lower values. Between 320 and 450 K type IIb diamonds are as good thermal conductors as type IIa's. The conductivity values of type IIa diamond are in agreement with published results, but those for type IIb diamond are not. For type Ia diamonds conductivities down to about 1/3 of that for type II diamond have been found. The values correlate with the strengths of the 7.8 μm absorption, but the correlation with the maximum absorption at 8.30–8.55 μm is better. The absorption value at $\approx$8.4 μm is the most useful one for prediction of the conductivity. Fig. 11 shows typical results.

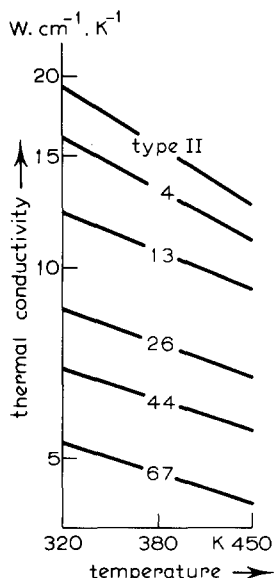Fig. 11. This is a resumé of the work. The conductivities of five type Ia diamond samples with their values of $a(\approx 8.4)$ shown, are given in a double-logarithmic plot. Also the result of type II diamond is given.

It is well established that the infrared absorptions at 7–10 μm are caused by nitrogen which can be present in two forms in the carbon lattice. The conductivity results could be interpreted in terms of the two forms of nitrogen alone. Thus impurities other than nitrogen apparently did not reduce the thermal conductivities above room temperature of the hundred gem quality type II or type I diamonds investigated. Hydrogen might give an effect in other diamonds with specific absorptions.

Acknowledgements

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