

Review paper

Report on a second round robin measurement of the thermal conductivity of CVD diamond

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Abstract

The results of a round robin series of measurements of the thermal conductivity and thermal diffusivity of chemical-vapor-deposited (CVD) diamond are reported. The present round robin (RR2) is an outgrowth of an earlier series (RR1) aimed at understanding which measurement techniques are best suited to measuring the high conductivity of CVD diamond. RR2 includes diamond specimens of higher homogeneity, non-diamond specimens of lower conductivity as controls, and measurements by 14 laboratories using five techniques, with all techniques but one used by more than one laboratory. The data are converted to thermal conductivity at 25 °C to facilitate comparisons among specimens and laboratories. The statistical analysis excludes outliers using Chauvenet's criterion, resulting in data from typically two or three laboratories being excluded for each specimen. The analysis arrives at mean values in the range 1300–2000 W m⁻¹ K⁻¹ for the diamond samples, as expected because of the conditions of preparation, with uncertainties in the range 1.5–4%. For the non-diamond materials, SiC and AlN, the results are 268 W m⁻¹ K⁻¹ ± 2.2% and 178 W m⁻¹ K⁻¹ ± 2.5%, respectively. Comparing techniques, the d.c.-heated bar is found to be the most accurate, typically ± 5% or better. Under favorable conditions, Ångström's thermal wave method can apparently yield relative uncertainties of ± 5–10%, and the mirage effect ± 5–15%. Too few laboratories used the transient thermal grating and laser flash methods to make general comments on their accuracy, but one expects a comparable accuracy if used on specimens that are fine-grained and thermally isotropic. Deviations, sometimes large, from these optimal accuracies are examined, and it is suggested that certain experimental details are important for achieving accuracy. It is also found that the estimates of experimental uncertainty provided by most laboratories seriously underestimate the actual deviations of their data from the mean conductivity. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Measurement of the thermal conductivity of diamond is difficult for a number of reasons. Most measurement techniques are optimized for use on materials with thermal conductivity κ in the range of copper and below, i.e. $\kappa \leq 400 \text{ W m}^{-1} \text{ K}^{-1}$, whereas gem-quality natural diamond can exhibit values up to ~ 6 times higher, $\kappa = 2500 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature [1]. The quality of synthetic diamond prepared by chemical vapor deposition depends on the preparation conditions, ranging from visually opaque and black, with $\kappa \sim 100 \text{ W m}^{-1} \text{ K}^{-1}$, to clear and colorless with $\kappa > 2000 \text{ W m}^{-1} \text{ K}^{-1}$. Furthermore, the conductivity near the bottom, or substrate side, of a specimen of CVD diamond several hundred micrometers thick is usually considerably lower than the conductivity near the top of the same specimen, by as much as a factor of four [2]. To make the situation even more complicated, anisotropy as high as a factor of two has been observed for certain regions of thick films, i.e. heat is conducted more easily in the direction perpendicular to the plane of the film than parallel to it [3].

These unusual features have been correlated with the columnar microstructure of the polycrystalline CVD material. The columnar grains are oriented perpendicular to the substrate, and the lateral dimensions of the grains at the growth surface become larger as the film grows thicker. It has been shown that some thermal scattering centers tend to aggregate along the columnar grain boundaries [4–7]. Indeed, microscopic measurements [8] capable of measuring thermal diffusivity on a scale of a few tens of micrometers near the surface show large variations ($\sim 50\%$) between some large grains. The variations are attributed to defective grain boundaries and/or microcracks. It has also been shown that those thermal-phonon scattering centers that are elongated, such as multiple twin intersections, are usually oriented with their long axis parallel to the columnar axis [9] and may be located within grains rather than at grain boundaries [6].

The above results show that for most thick specimens of CVD diamond, the thermal conductivity cannot be fully defined by a single number. A complete description would require both κ_{\parallel} and κ_{\perp} to be specified as a function of the distance from the substrate face. Although this is possible for research measurements, it is completely impractical for commercial purposes. With the advent of commercial markets for which the high thermal conductivity of CVD diamond is an attractive feature, it is becoming increasingly important to have thermal measurement techniques that are reliable and that give suitable averages over any typical specimen.

To address this need, it was decided in 1994 to conduct round robin (round robin: “a written petition, memorial, or protest to which the signatures are affixed in a circle

so as not to indicate who signed first.” [10]) measurements [11,12] of the thermal conductivity κ and/or the thermal diffusivity D of a group of CVD diamond samples of wide-ranging quality. The thermal diffusivity is defined as $\kappa/\rho C$, where ρ is the mass density, and C is the heat capacity per unit mass. The round robin (RR1) emerged from a series of workshops on the properties of CVD diamond conducted at NIST under the leadership of A. Feldman. Ten specimens of three different geometries, with κ in the range $400\text{--}1700 \text{ W m}^{-1} \text{ K}^{-1}$, were contributed by four diamond suppliers, and measurements were made by 10 laboratories using seven different techniques. The results for each specimen showed unexpectedly large variations from laboratory to laboratory. The results [13] were inconclusive regarding either the most accurate values of conductivity for those particular specimens or a preference for a particular measurement technique. It was proposed that the large variations from laboratory to laboratory might be due to specimen inhomogeneity and to the way in which each technique samples the spatial distribution of the local thermal conductivity.

Building on the experiences with RR1, a second round robin, RR2, was initiated in 1995 by a working committee from RR1, included in the present list of co-authors and again organized under the auspices of NIST. This second round robin included a number of new features:

- the homogeneity of the diamond specimens was improved by requesting that the suppliers polish away at least $50 \mu\text{m}$ of material from the substrate side of $300\text{--}500\text{-}\mu\text{m}$ -thick specimens;
- the rough facets of the growth face were also to be removed by abrasive polishing;
- the specimens were to be identified with inscribed labels on the growth surface;
- all specimens were the same size, $7 \times 20 \text{ mm}$ (the diamond specimens were initially $7 \times 40 \text{ mm}$, as described below);
- more diamond specimens of the same shape were included (eight);
- thickness variations over each specimen were requested to be under 2%;
- 11 specimens of two non-diamond materials were included as controls; their identity was not revealed to the measuring labs;
- more labs were included (15) to improve the statistical significance of the results;
- each measurement technique, except for one, was used by more than one laboratory; and
- the laboratories were asked to estimate the temperature of the specimen at the location and time of the measurement so that the temperature dependence of the thermal properties could be taken into account.

The goals of RR2 were twofold: (1) to determine which techniques, if any, are capable of giving consistent results, and (2) to determine reliable values of κ for

these particular specimens. The present report shows that progress has been made toward both goals, so that meaningful comparisons can be made between different measuring methods. It has also become clear that the uncertainties estimated by most measuring laboratories for their own measurements are seriously underestimated.

2. Procedural details

2.1. Participants

The specimens were donated by three manufacturers of CVD diamond and one manufacturer of each of the two previously unidentified non-diamond materials, SiC and AlN. This information is listed in Table 1, along with a brief description of the manufacturing method.

Measurements of thermal conductivity or diffusivity were performed in 14 laboratories, one of which used two different techniques. The names of the laboratories and responsible persons, as well as abbreviated descriptions of the techniques used, are listed in Table 2. The heat capacity of several of the AlN specimens was also measured at Holometrix, Inc. (Bedford, MA).

2.2. Specimens

Specimens of CVD diamond were requested from the suppliers with the intention of covering the approximate range $\kappa = 1000\text{--}2000 \text{ W m}^{-1} \text{ K}^{-1}$. Most of the specimens were not of the very highest quality that the manufacturer was capable of producing, as they were specifically requested to fall within a fairly wide range of conductivity. Specimens C2 and C6 were clear, C4 and C8 were less transparent, and C1, C3, C5, and C7 were considerably darker but still translucent. Emphasis was placed on obtaining high lateral homogeneity over each specimen. The size of the specimens, ultimately $7 \times 20 \text{ mm}$, was chosen as a compromise among the needs of the various measuring techniques. However, the 20-mm length was estimated to be slightly too short for the low-frequency, modified Ångström method measuring high conductivity diamond. To accommodate these laboratories, the suppliers provided four $7 \times 40 \text{ mm}$ spec-

imens that were measured by five laboratories and then cut in half to make eight diamond specimens for the remaining laboratories. It is expected that the two halves of a long sample should be close, but not necessarily identical, in conductivity.

It was requested that the final thickness of the specimens be in the range $300\text{--}500 \mu\text{m}$. As it turned out, the thicknesses were mostly in the range $500\text{--}700 \mu\text{m}$, with the exception of four thinner AlN specimens. It was requested that the thickness should not vary by more than 2% over each specimen. The diamond specimens were polished to a mirror finish top and bottom after abrasive removal of some tens or hundreds of microns of the material of inferior quality from the bottom (the side originally against the substrate). The four 40-mm-long diamond specimens were identified by marks C1, C2,...C8 laser-scribed near a corner. Each long piece had two labels, one at each end (C1 and C5, C2 and C6, C3 and C7, and C4 and C8), to identify the $7 \times 20 \text{ mm}$ specimens after the long pieces were cut in half. The label for C2 was mistakenly inscribed as C1 but with a distinctive font that was the same as that for C6. The ID labels were inscribed on the growth surface of C2 and C6, as requested. The other six diamond specimens were found to be inscribed on the bottom (substrate) face, as determined by optical and scanning-electron microscopy at Bell Labs after the thermal measurements were completed. The supplier of C2 and C6 measured the distribution of grain sizes, after polishing, to be $8\text{--}80 \mu\text{m}$ on the substrate face and $17\text{--}180 \mu\text{m}$ on the growth face. Optical-microscopic examination of all eight diamond specimens at Raytheon Co. (Lexington, MA) after the measurements were completed revealed internal surfaces, such as microcracks. These defects were most prevalent in the darkest specimens, which also had the lowest thermal conductivity.

The non-diamond specimens were supplied as $7 \times 20 \text{ mm}$ and laser-scribed or hand-scribed U1–U25 for identification. The CVD SiC specimens were cut from much thicker material. After the measurements were completed, it was realized that the SiC had a columnar microstructure with the possibility of anisotropy in κ . Further details of all the specimens are provided in Table 3.

Table 1
Suppliers of the CVD diamond, SiC, and AlN specimens

Material	Supplier	Contact	Method
CVD diamond C1, C3, C5, C7	Diamonex, Allentown, PA	J.E. Yehoda	Hot-filament CVD
CVD diamond C4, C8	Norton Diamond Film, Northboro, MA	K.J. Gray	d.c. arc jet CVD
CVD diamond C2, C6	Raytheon Co., Lexington, MA	T.M. Hartnett	Microwave CVD
CVD SILICON CARBIDE®	Morton International, Woburn, MA	J.S. Goela	CVD
Aluminum nitride	Carborundum Microelectronics, Phoenix, AZ	R. Enck	Sintered

The use of a trade name is for descriptive purposes only.

Table 2
List of laboratories and measurement methods used

Measuring laboratory	Contact	Method
Daimler Benz AG, Ulm, Germany	H. Verhoeven	Transient thermal grating
Fraunhofer Institute, IAF, Freiburg, Germany	R. Zachai E. Wörner P. Koidl	d.c.-heated bar
Holometrix, Inc., Bedford, MA, USA	R. Campbell	Laser-flash specific heat
KRISS, Yusong, Taejon, South Korea	D.-J. Seong	Modified Ångström
LEMTA-ENSEM, Vandœuvre, France	B. Remy D. Maillat A. Degiovanni	Laser-flash diffusivity
Lucent Technologies, Murray Hill, NJ, USA	J.E. Graebner	d.c.-heated bar
Nagoya University, Nagoya, Japan	I. Hatta	Modified Ångström
NIST, Gaithersburg, MD, USA	A. Feldman N. Balzaretta	Modified Ångström
Ulvac Sinku-Riko, Inc., Yokohama, Japan	R. Kato	Modified Ångström
Soonchunhyang University, Choongnam, South Korea	H.-B. Chae T.-K. Lee	d.c.-heated bar
South Bank University, London, UK	R.E. Imhof B. Zhang	Modified Ångström and transient thermal grating
Tsinghua University, Beijing, People's Republic of China	Y.Q. Gu	Modified Ångström
Université Pierre et Marie Curie-Paris VI, Paris, France	D. Fournier J.P. Roger	Mirage
University of Würzburg, Würzburg, Germany	H. Altmann J. Fricke	Modified Ångström
Wayne State University, Detroit, MI, USA	P.K. Kuo	Mirage

Table 3
Characteristics of the 19 specimens used in Round Robin 2

Number	Sample	Material	t (μm)	Δt (μm)	S ($10^{-3} \text{ } ^\circ\text{C}^{-1}$)	κ_m ($\text{W m}^{-1} \text{ K}^{-1}$)	σ ($\text{W m}^{-1} \text{ K}^{-1}$)	$2\sigma/\kappa_m$ (%)	σ_m/κ_m (%)
1	C1	Diamond	526	100	-2.2	1370	168	24	3.0
2	C2	Diamond	558	40	-3.7	1962	256	26	4.1
3	C3	Diamond	496	100	-1.42	1410	63	9	1.5
4	C4	Diamond	728	250	-2.8	1428	103	14	2.3
5	C5	Diamond	536	100	-1.5	1292	104	16	2.5
6	C6	Diamond	532	40	-3.7	1925	212	22	3.8
7	C7	Diamond	503	100	-2.2	1393	54	8	1.7
8	C8	Diamond	708	250	-2.6	1471	102	14	2.3
9	U3	SiC	565	—	-2.9	272	8	6	1.0
10	U4	SiC	522	—	-2.9	271	34	25	4.4
11	U5	SiC	550	—	-2.9	259	18	14	2.5
12	U6	SiC	547	—	-2.9	267	13	10	1.5
13	U7	SiC	562	—	-2.9	270	11.5	8	1.6
14	U1	AlN	628	—	-2.94	182	20	21	3.4
15	U2	AlN	631	—	-2.94	174	22	25	4.5
16	U10	AlN	250	—	-2.12	175	8.7	10	1.6
17	U15	AlN	250	—	-2.12	178	10	11	2.0
18	U20	AlN	249	—	-2.44	180	12	13	1.8
19	U25	AlN	252	—	-2.44	177	11	12	1.9

The thickness, t , is an average of the measurements of five laboratories, whereas Δt is the amount removed from the substrate side of the diamond specimens. S is the fractional slope of κ vs. T near 25°C obtained from the data of laboratories L1 and L2 in Figs. 1 and 2. The mean conductivity, κ_m , and standard deviation, σ , are obtained from the conductivity and diffusivity measurements converted to conductivity at 25°C , after elimination of outliers as described in the text. The uncertainty σ_m in the determination of the mean is calculated as $\sigma/N^{1/2}$, where N is the final number of data points for a specimen after elimination of outliers.

2.3. Measurement techniques

Table 4 presents a brief description of the measurement technique used by each of the 14 laboratories,

with the laboratories designated arbitrarily by labels L1, L2, ..., L15 to preserve anonymity as much as possible. One laboratory is represented by two different Ln labels, as this laboratory used two different methods.

Table 4
List of methods used by laboratories L1–L15

Lab ID	Property	Details of technique used
L1	κ_{\parallel}	d.c.-heated bar, attached electrical heater, many TCs attached precisely to a metal film on the surface, vacuum, no radiation shielding, no surface loss correction, one-dimensional model
L2	κ_{\parallel}	d.c.-heated bar, attached electrical heater, two TCs, vacuum, triple radiation shielding, no surface loss correction
L3	κ_{\parallel}	d.c.-heated bar, two electrical heaters evaporated on to sample to provide sensitive test for surface losses, five TCs, moderate vacuum (~ 0.13 – 1.3 Pa, or 1 – 10 mTorr), radiation shielding, surface-loss correction (0–4% decrease, largest for AlN)
L4	D_{\parallel}	a.c. calorimetric thermal wave, modulated-laser heating on side opposite TC, $1 \mu\text{m}$ graphite film on unknowns, $0.1 \mu\text{m}$ Bi film on diamond, 1.25 – 2.5 Hz for unknowns, 2.5 – 10 Hz for diamond, phase and amp. data combined to eliminate surface loss, no correction for reflections, measured near center of 40-mm diamond specimens, one-dimensional model
L5	D_{\parallel}	a.c. calorimetric thermal wave, optical heating on side opposite TC, $1\text{-}\mu\text{m}$ Bi film, 0.5 – 2 Hz, used amplitude data, measured one end of 40-mm diamond specimens
L6	D_{\parallel}	a.c. calorimetric thermal wave, optical heating on side opposite $25\text{-}\mu\text{m}$ TC, vacuum, graphite spray coating, large correction for edge reflection (20-mm diamond specimens), amplitude data, 1 – 12 Hz, one-dimensional model
L7	D_{\parallel}	a.c. calorimetric thermal wave, optical heating on the same side as $75\text{-}\mu\text{m}$ TC, graphite spray coating, 1 – 15 Hz, phase and amplitude data combined to eliminate surface loss, one-dimensional model, tried to cancel edge reflection by choice of location (TC at 10 mm from each end of 40-mm diamond). Also used $3\text{-}\omega$ technique to measure κ_{avg} of C3
L8	D_{\parallel}	Thermal wave, optical heating, infra-red detection on same face, 9 – 25 Hz, used phase and amplitude data, one-dimensional model
L9	D_{\parallel}	Thermal wave, 0.2-mm Ag heater strip, movable TC, 72 – 386 Hz, used phase data, measured one part of 40-mm diamond specimens, vacuum, one-dimensional model
L10	D_{\parallel}	Thermal wave, focused optical heating, focused infra-red detection on the same side, 10 – 20 Hz, $0.3\text{-}\mu\text{m}$ Ti film, equipment difficulties
L11	D_{avg}	Mirage, optical heating, Au film, deflected probe beam, 100 Hz– 5 kHz, measured top and bottom, three-dimensional model
L12	D_{avg}	Mirage, optical heating on $0.1\text{-}\mu\text{m}$ Au film, reflected probe beam, 4 – 35 kHz, three-dimensional model, assume isotropic diffusivity
L13	D_{\parallel}	Transient thermal grating, grating period 60 – $180 \mu\text{m}$, reflected focused probe beam, averaged many local measurements top and bottom, $0.3\text{-}\mu\text{m}$ Ti film
L14	D_{\parallel}	Transient thermal grating, grating period $44 \mu\text{m}$, diffracted probe beam, $0.3\text{-}\mu\text{m}$ Ti film, equipment problems
L15	D_{\perp}	Laser flash, 13-mm laser beam, uniform profile, $<20\text{-ns}$ pulse, infra-red detection at opposite face, $0.3\text{-}\mu\text{m}$ Ti film

TC: thermocouple.

Unless noted otherwise, measurements were made on the 20-mm-long diamond specimens.

2.4. Schedule of measurements

To reduce the total time required for the RR2 measurements by a factor of ~ 2 , the specimens were circulated as two groups, diamond and non-diamond. Thus, at any given time, two laboratories were making measurements. Initially, the laboratories were requested to maintain a schedule of 10 days per laboratory per group of specimens, but after some experience with slow delivery of international express mail, the time period was increased to 2 weeks. As described above, the five laboratories that needed the longer diamond specimens made their measurements first. The specimens were then cut in half at Diamonex, Inc. (Allentown, PA), and the schedule of measurements was continued. Four laboratories requested an optically opaque coating, which was provided by $0.3 \mu\text{m}$ of Ti sputtered on to each face of the diamond specimens at Bell Labs. The measurements were begun in July 1996, the diamond samples were cut in August 1996, and most of the laboratories had measured both groups of specimens by May 1997. Several laboratories requested an opportunity for remeasurement because of improperly operating

equipment or insufficient time on the original schedule to perform a study as a function of temperature, and these remeasurements were performed in the summer of 1997. One of the laboratories (L6) that originally measured the four long diamond specimens remeasured the eight shorter specimens. One of the diamond specimens (C7) was accidentally broken in half after being measured by eight laboratories. Several additional laboratories asked to join the round robin but were not successful in measuring the diamond specimens. In this last effort, diamond specimen C6 was also broken. Finally, the specific heat of two of the AlN samples was measured to allow completion of the data analysis.

3. Data analysis

Most of the specimens were measured by 12–14 laboratories, providing enough data to justify the statistical analysis described below. As requested, each laboratory estimated the effective temperature T_{eff} of the specimen at the precise location and time of the measurement, which, for some measurement techniques, is not

a trivial estimate [14]. Two laboratories, L1 and L2, voluntarily measured the conductivity over a wide temperature range, both above and well below room temperature, with the d.c.-heated bar technique. This information was very useful in the conversion of all the data to a common temperature. The conductivity/diffusivity data and estimated values of T_{eff} are listed in Tables 5–7.

3.1. Diffusivity conversion

In order to allow a direct comparison of the diffusivity and conductivity data, the diffusivity values at the measuring temperature T_{eff} are first converted to conduc-

tivity values at the same temperature. Conductivity is chosen as the more useful quantity for heat flow applications, which are usually steady-state. For the conversion, one needs the heat capacity per unit volume, ρC . We assume that the mass density is a constant and use values of the temperature-dependent specific heat, C , from various sources.

The specific heat of CVD diamond has been shown to be within 1% of the bulk heat capacity of natural diamond, at least for CVD specimens greater than a few tens of micrometers thick [15]. Therefore we use the specific heat of the bulk [16], which is $1.790 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ at 25 °C and varies nearly as the square of the absolute temperature in this temperature

Table 5
Data for $\kappa(T_{\text{eff}})$ reported by laboratories L1–L3 and $D(T_{\text{eff}})$, laboratories L4–L15, for the diamond specimens

Number	1	2	3	4	5	6	7	8
ID	C1	C2	C3	C4	C5	C6	C7	C8
L1	1390 (25)	1910 (25)	1410 (25)	1430 (25)	1330 (25)	1900 (25)	1390 (25)	1540 (25)
L2	1402 (25)	2091 (25.5)	1453 (26)					1559 (24.5)
L3	1350 (23)	1920 (24)	1420 (23)	1450 (23)	1330 (23)	2040 (20)		1500 (20)
L4	7.3 (25)	12.4 (25)	7.5 (25)	8.6 (25)	7.3 (25)	12.4 (25)	7.5 (25)	8.6 (25)
L5	4.9 (20)	6.9 (20)	4.2 (20)	4.6 (20)	4.9 (20)	6.9 (20)	4.2 (20)	4.6 (20)
L6	8.8 (23.5)	13.0 (22)	8.6 (23)	8.6 (23)	8.7 (21.5)	9.1 (23.5)		7.4 (28)
L7	7.12 (26)	11.86 (26)	7.77 (26)	7.43 (26)	7.25 (26)	11.46 (26)	7.63 (26)	7.26 (26)
L8	6.64 (35)	7.70 (31)	6.61 (35)	6.54 (35)	5.99 (33)	8.29 (31)		6.73 (36)
L9	5.391 (33)	6.703 (34)	5.605 (36)	5.836 (34)	5.391 (33)	6.703 (34)	5.605 (36)	5.836 (34)
L10	4.15 (20)	6.20 (20)	1.35 (20)	7.39 (20)	7.64 (20)	6.35 (20)		
L11	6.6 (30)	10.5 (30)	7.7 (30)	8.2 (30)	6.3 (30)	10.5 (30)	8.0 (30)	8.2 (30)
L12	8.7 (25)	8.6 (25)	8.1 (25)	8.2 (25)	6.5 (25)	10.1 (25)	6.6 (25)	8.9 (25)
L13	6.9/9.5 (40)	11.1/9.3 (40)	8.1/8.3 (40)	7.2/8.2 (40)	5.4/8.2 (40)	11.1/9.9 (40)	5.3/8.1(40)	7.6/9.7 (40)
L14								
L15	9.23 (22)	12.19 (22)	9.83 (22)	10.45 (22)	9.26 (22)	11.84 (22)	8.83 (22)	10.57 (22)

The units of κ , D , and the effective temperature, T_{eff} , are $\text{W m}^{-1} \text{ K}^{-1}$, $10^{-4} \text{ m}^2 \text{ s}^{-1}$, and °C, respectively. The two values of diffusivity provided by laboratory L13 for each diamond specimen were taken from the ID-labeled/unlabeled surfaces, respectively.

Table 6
Data for $\kappa(T_{\text{eff}})$ reported by laboratories L1–L3 and $D(T_{\text{eff}})$, laboratories L4–L15, for the SiC specimens

Number	9	10	11	12	13
ID	U3	U4	U5	U6	U7
L1	279 (25)				269 (25)
L2					
L3			280 (25)	283 (24)	276 (24)
L4	1.23 (26.2)	1.20 (27)	1.31 (24.8)	1.27 (25.3)	1.30 (27.3)
L5	1.09 (26.5)	1.02 (26.5)	1.14 (26.5)	1.17 (26.5)	1.07 (26.5)
L6	1.59 (25)	1.17 (25)	1.53 (25)	1.19 (25)	1.67 (25)
L7	1.20 (26)	1.15 (26)	1.13 (26)	1.32 (26)	1.21 (26)
L8	1.26 (27)	1.45 (27)	1.13 (29)	1.11 (29)	1.14 (28)
L9				1.176 (32)	
L10	0.93 (20)	1.62 (20)	1.12 (20)	1.27 (20)	
L11	1.7 (23)	1.7 (23)	1.7 (23)	1.7 (23)	1.7 (23)
L12	1.30 (25)	1.25 (25)	1.25 (25)	1.30 (25)	1.25 (25)
L13	1.28 (27)	1.28 (27)	1.28 (27)	1.27 (27)	1.31 (27)
L14					
L15	1.52 (25)	1.51 (25)	1.52 (25)	1.53 (25)	1.56 (25)

The units are the same as those in Table 5.

Table 7
Data for $\kappa(T_{\text{eff}})$ reported by laboratories L1–L3 and $D(T_{\text{eff}})$, laboratories L4–L15, for the AlN specimens

Number	14	15	16	17	18	19
ID	U1	U2	U10	U15	U20	U25
L1						
L2	192.5 (27)		187.7 (27)		201.2 (27)	
L3	175 (25)	175 (25)	177 (24)	173 (24)	178 (24)	176 (25)
L4	0.74 (26.3)	0.77 (26.3)	0.73 (25.6)	0.72 (24.3)	0.69 (25.7)	0.74 (24.5)
L5	0.79 (26.5)	0.72 (26.5)	0.71 (26.5)	0.72 (26.5)	0.80 (26.5)	0.68 (26.5)
L6	1.54 (25)	1.01 (25)	0.87 (25)	0.94 (25)	0.76 (25)	0.84 (25)
L7	0.76 (26)		0.718 (26)		0.761 (26)	
L8	1.03 (29)	1.18 (29)	0.69 (28.5)	0.67 (29.5)	0.67 (29)	0.67 (26)
L9	0.573 (30)	0.559 (31)		0.779 (33)		0.704 (32)
L10	1.18 (20)	1.32 (20)	0.99 (20)	0.90 (20)	0.83 (20)	0.89 (20)
L11	0.9 (23)	0.9 (23)	0.8 (23)	0.8 (23)	0.8 (23)	0.8 (23)
L12	0.72 (25)	0.65 (25)	0.73 (25)	0.80 (25)	0.77 (25)	0.77 (25)
L13	0.71 (27)	0.67 (27)	0.66 (27)	0.69 (27)	0.68 (27)	0.71 (27)
L14	1.05 (20)	0.98 (20)	1.01 (20)	1.24 (20)	0.73 (20)	
L15	0.87 (25)	0.81 (25)	0.76 (25)	0.76 (25)	0.73 (25)	0.74 (25)

The units are the same as those in Table 5.

range. A fifth-order polynomial is fitted to the specific heat data to interpolate to the required temperature, T_{eff} , for each data point. The resulting $C(T_{\text{eff}})$, the density $\rho = 3515 \text{ kg m}^{-3}$, and the measured diffusivity, $D(T_{\text{eff}})$, are multiplied to obtain $\kappa(T_{\text{eff}})$.

The specific heat of SiC is taken from data obtained from J. Goela of Morton, Inc. (Woburn, MA). The data are represented by a linear fit near room temperature:

$$\rho C(T_{\text{eff}}) = 2.138 \times 10^6 + 9120(T_{\text{eff}} - 25 \text{ }^\circ\text{C}),$$

where ρC is in units of $\text{J m}^{-3} \text{ K}^{-1}$, and the density is assumed to be 3210 kg m^{-3} .

The specific heat of AlN specimens U1 and U2 was measured at Holometrix, Inc., using a calibrated laser flash technique. The results, very similar to data for other AlN material, are also represented by a linear equation:

$$\rho C(T_{\text{eff}}) = 2.387 \times 10^6 + 5880(T_{\text{eff}} - 25 \text{ }^\circ\text{C}).$$

The density is taken to be 3280 kg m^{-3} . These expressions for the heat capacity of SiC and AlN are estimated to be accurate to within approximately 5–10% over the temperature range of interest. The good agreement (see below) between the d.c.-heated-bar results and the mean conductivities (determined mostly by diffusivity results) suggests an even better accuracy for the heat capacity.

3.2. Temperature adjustment

The values of T_{eff} for all 19 specimens span the range 20–40 °C. To correct for the non-negligible temperature dependence of the thermal conductivity, all values of $\kappa(T_{\text{eff}})$ are adjusted to a temperature of 25 °C by using the measured temperature dependence as a guide. The data in Figs. 1 and 2 are used to calculate a fractional

slope $S \equiv [1/\kappa(T)]d\kappa(T)/dT$, which is found to be roughly constant over the range of T_{eff} for the measured specimens. Independent data for C1, C2, C3, and C8 from lab L2 are in substantial agreement with the data in Fig. 1. The value of S for each specimen is given in Table 3.

Each value of conductivity $\kappa(T)$ is converted to $\kappa(25 \text{ }^\circ\text{C})$ by the following expression:

$$\kappa(25 \text{ }^\circ\text{C}) = \kappa(T_{\text{eff}}) / [1 + (T_{\text{eff}} - 25 \text{ }^\circ\text{C})S].$$

For typical data in Table 8, the fractional correction $\Delta\kappa/\kappa = (T_{\text{eff}} - 25 \text{ }^\circ\text{C})S$ is $\leq 1\%$. In the most extreme case ($T_{\text{eff}} = 40 \text{ }^\circ\text{C}$), the correction is 5.5% for specimen C2 or C6, for example. The resulting values of $\kappa(25 \text{ }^\circ\text{C})$ are listed in Table 8. They are also plotted by specimen in

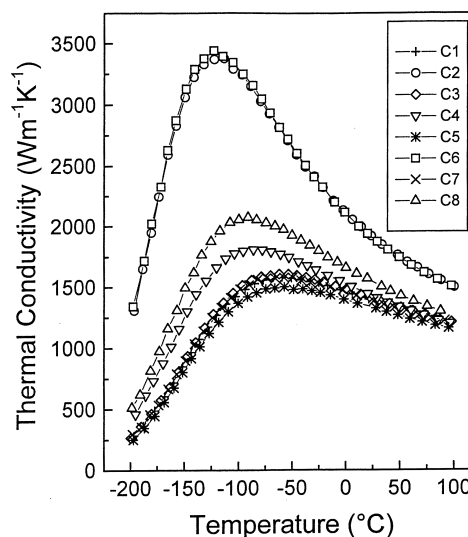


Fig. 1. Thermal conductivity vs. temperature for the diamond specimens, reported by laboratory L1.

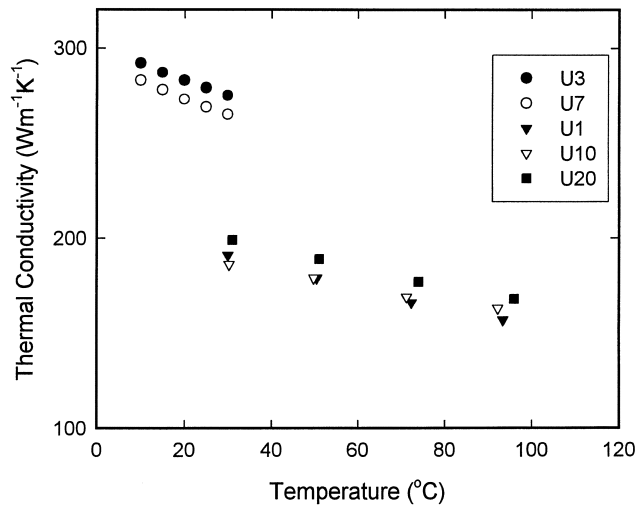


Fig. 2. Thermal conductivity vs. temperature for the SiC specimens U3 and U7, reported by laboratory L1, and the AlN samples U1, U10, and U20, reported by L2.

Figs. 3–5. The experimental uncertainties estimated by the individual laboratories have been converted to conductivities, where necessary, and are included as the error bars in Figs. 3–5; they are shown in the positive direction only, above each bar, for convenience in plotting.

3.3. Statistical analysis

It is difficult to perform a proper statistical analysis on the present data because of the uncertain weights that should in principle be given to the various methods due to their inherent, but undetermined, differences in bias and precision. While realizing also the problem of

a limited data set, we have nevertheless chosen the following statistical procedure, bearing in mind that the final averages are not necessarily the most accurate values.

We proceed with the analysis by rejecting data lying very far from the mean, and by assuming equal weights and a normal distribution for the remaining data. Examination of the data in Figs. 3–5 reveals a number of points lying well away from the general spread of values for any given specimen. Such values, known as outliers, can reasonably be excluded from the calculation of a final average value if they satisfy certain statistical criteria. We have used Chauvenet's criterion [17], according to which a value can be excluded if less than half a data point is expected (assuming a normal distribution) to lie further from the mean than the point in question. For example, if the total number of data points for any particular specimen is $N=14$, the normal distribution would lead one to expect a probability of $1/(2 \times 14)$ at a distance of $\pm 2.1\sigma$ from the mean, where σ is the standard deviation. We have used the population standard deviation $\sigma = (\sum (\kappa - \kappa_m)^2 / N)^{1/2}$ rather than the sample standard deviation calculated with $N-1$ instead of N . The slightly smaller values of σ tend to compensate for our simplified use of 2.0σ in Chauvenet's criterion. For $N=12$, 10, or 8, the corresponding distances are 2.03σ , 1.96σ , or 1.86σ , respectively. If a point is excluded using this criterion, the recalculated mean and standard deviation will be slightly changed, and the process can be repeated with the remaining points. Successive iterations should finally leave a data set with no outliers.

The data in Table 8 for each specimen are analyzed for outliers in this manner using a criterion of approxi-

Table 8

Thermal conductivity for all specimens and laboratories, after conversion of the data of Tables 5–7 to conductivity at 25 °C

Number	ID	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12	L13	L14	L15
1	C1	1390	1402	1344	1304	834	1550	1284	1296	1035	706	1233	1554	1674		1601
2	C2	1910	2095	1913	2215	1165	2246	2142	1465	1314	1047	1977	1536	2122		2107
3	C3	1410	1455	1416	1340	717	1510	1400	1280	1094	230	1434	1447	1650		1710
4	C4	1430		1442	1536	780	1506	1341	1284	1136	1253	1537	1464	1934		1811
5	C5	1330		1326	1304	834	1506	1306	1144	1035	1304	1174	1161	1370		1611
6	C6	1900		2003	2215	1165	1599	2070	1577	1314	1072	1977	1804	2184		2045
7	C7	1390			1340	717		1376		1094		1495	1179	1364		1532
8	C8	1540	1557	1481	1536	780	1361	1309	1331	1136		1536	1590	1772		1832
9	U3	279			265	235	340	259	273		192	358	278	278		325
10	U4				260	220	250	248	314		334	358	267	278		323
11	U5			280	280	246	327	244	249		231	358	267	278		325
12	U6			282	272	253	254	284	244	264	262	358	278	276		327
13	U7	269		275	283	231	357	261	249			358	267	284		334
14	U1		193.6	175	178	191	368	182	251	141	274	213	172	171	244	208
15	U2			175	185	174	241		288	138	307	213	155	162	228	193
16	U10		188.5	177	175	171	208	172	167		204	189	174	159	236	181
17	U15			173	171	174	224		163	193	210	189	191	166	289	181
18	U20		202	178	165	193	181	182	163		194	189	184	164	170	174
19	U25			176	176	164	200		161	174	207	189	184	171		177

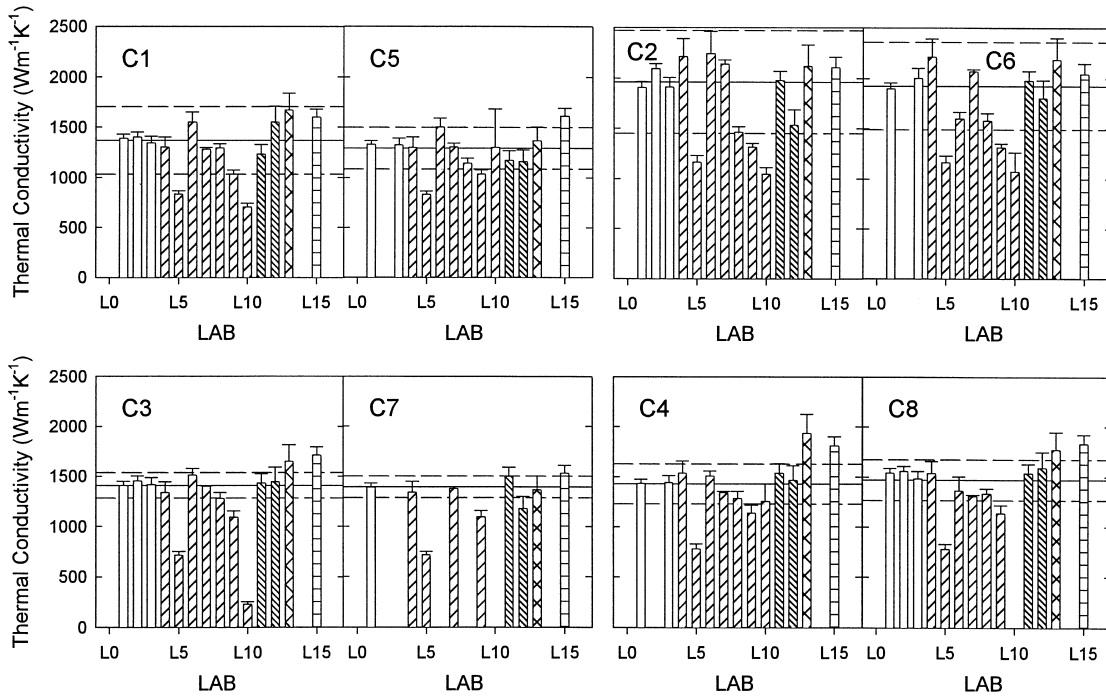


Fig. 3. Data of Table 8 for diamond plotted by laboratory for each specimen. The solid and dashed lines show the mean ± 2 standard deviations, respectively, as listed in Table 3. As distinguished by shading, laboratories L1–L3 used the d.c.-heated bar method, L4–L10 used modifications of Ångström’s thermal wave method, L11 and L12 used the mirage technique, L13 and L14 used a transient thermal grating technique, and L15 used the laser flash method. The error bars are the uncertainties estimated by each laboratory for their own data.

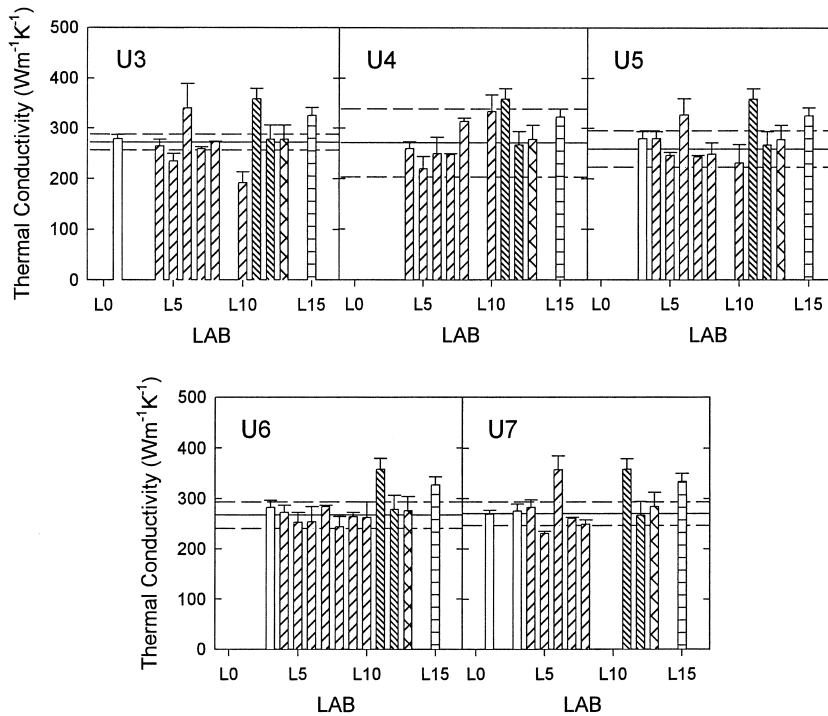


Fig. 4. Data of Table 8 for SiC plotted by laboratory for each specimen. The lines and shading have the same meanings as in Fig. 3.

mately 2.0σ , typically requiring two or three iterations before a stable data set (no outliers) is obtained. Typical behavior of the mean κ_m and the standard deviation are shown graphically in Fig. 6 for specimen C6, for which

N is reduced from 13 to 10 as three data points are discarded. The mean increases by 10%, and the standard deviation becomes half of its initial value upon exclusion of the three data points. The same analysis is applied to

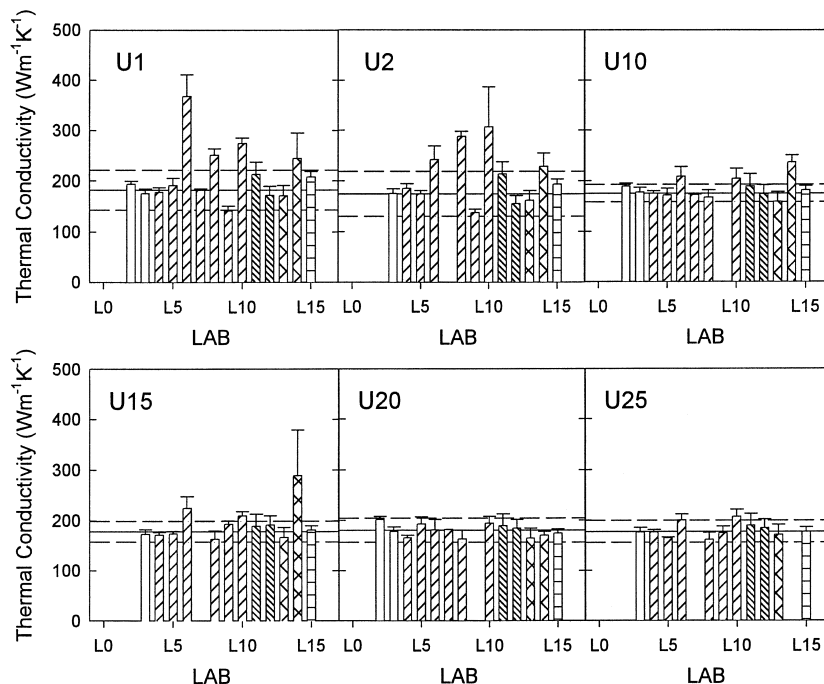


Fig. 5. Data of Table 8 for AlN plotted by laboratory for each specimen. The lines and shadings have the same meanings as in Fig. 3.

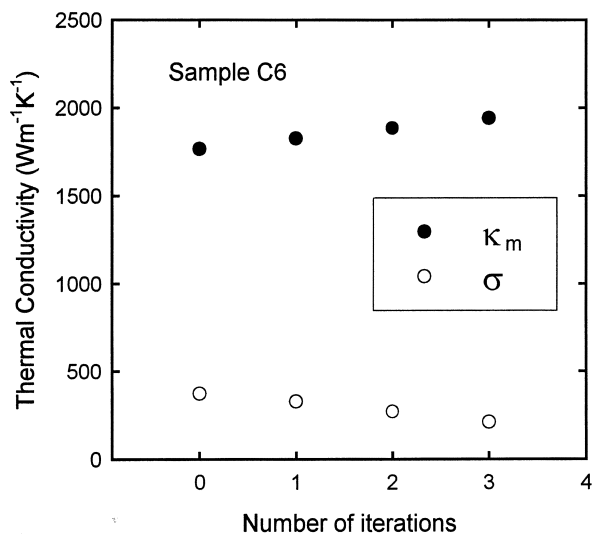


Fig. 6. Mean thermal conductivity κ_m and standard deviation, σ , calculated from the data of Table 8. All data points are included in the zeroth iteration. At each subsequent iteration, any data point(s) lying further from the mean than $\pm 2\sigma$ is deleted, and κ_m and σ are recalculated from the remaining points. As shown for diamond sample C6, σ is decreased significantly in three iterations during which, three outlying points are discarded. The remaining points all satisfy the $\pm 2\sigma$ criterion.

all the specimens with qualitatively similar results, and the final values for κ_m and σ are listed in Table 3. They are also included in Figs. 3–5 as the solid horizontal line at κ_m and the dashed horizontal lines at $\kappa_m \pm 2\sigma$ for each specimen. The outliers are those values of κ lying outside the range defined by the dashed lines.

Discarding data points should, of course, be done

only with great caution. We offer two additional comments in support of this application of Chauvenet's criterion. The elimination of outliers in all cases produces mean values that approach closely the values obtained with the d.c.-heated bar technique, which might be argued to be a very reliable technique (see below). The procedure also eliminates those points that appear intuitively to be mistaken, after a careful study of the data in Figs. 3–5. In any case, the original full set of data is available in Tables 5–7 for any alternative analysis.

There seems to be a trend for the diamond outliers to be generally below the final mean, whereas the non-diamond outliers generally lie above the final mean values.

The mean conductivity, κ_m , is used with the data of Table 8 to form the fractional deviation from the mean $(\kappa - \kappa_m) / \kappa_m$ for each data point. The results are plotted (Fig. 7 Fig. 8) as the percentage by laboratory to compare all the results of one laboratory with all the results of another. As in Figs. 3–5, the uncertainty given by each laboratory for each data point is plotted as an error bar, calculated here as a percentage of κ_m .

4. Discussion

4.1. Mean values

The mean values, obtained after discarding outliers, are listed in Table 3 and presented as horizontal solid lines in Figs. 3–5. (The laser flash diffusivity data are

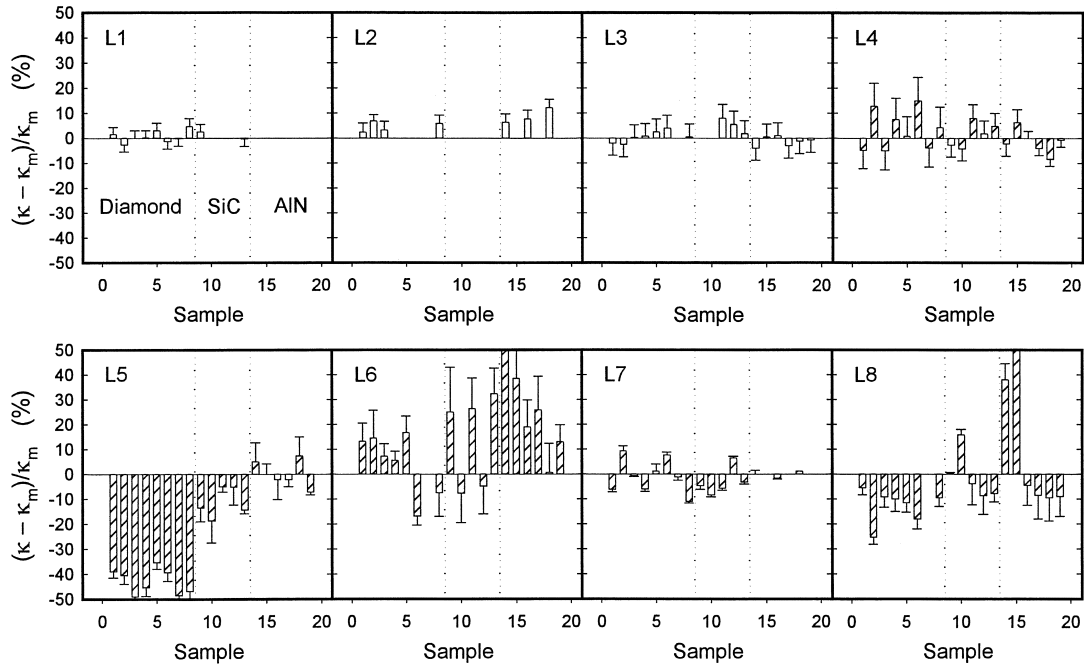


Fig. 7. Data of Table 8 expressed as a percentage deviation from the mean for each specimen, plotted by specimen for each laboratory, L1–L8. The error bars show the uncertainties estimated by each laboratory for their own measurements.

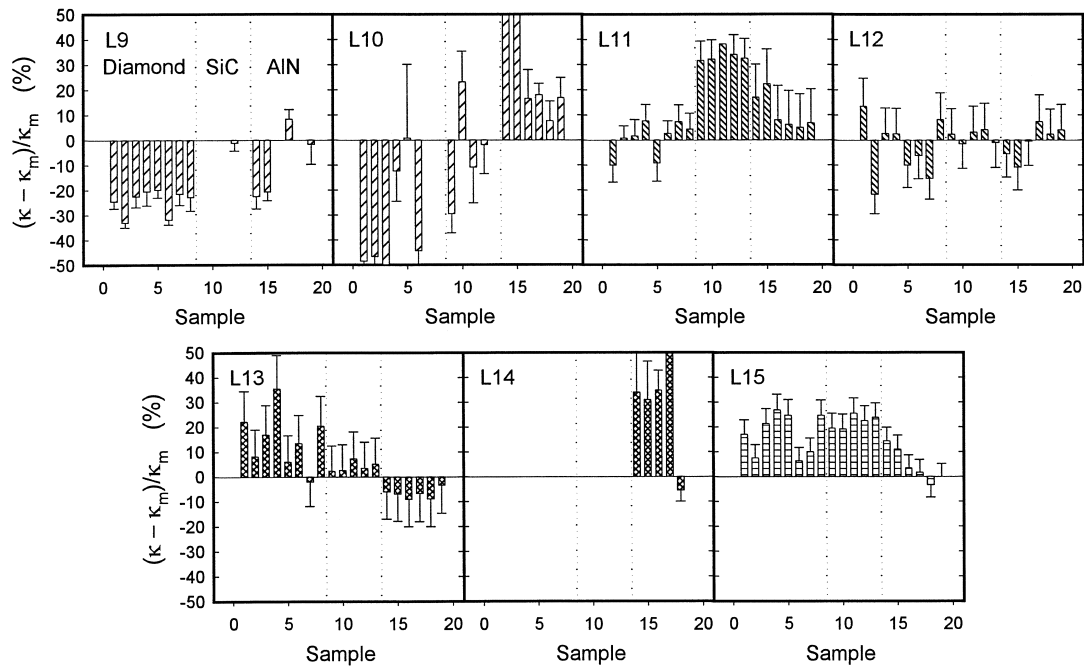


Fig. 8. Data of Table 8 expressed as a percentage deviation from the mean for each specimen, plotted by specimen for each laboratory, L9–L15. The error bars show the uncertainties estimated by each laboratory for their own measurements.

excluded from the calculation of the mean conductivities of the CVD diamond and the CVD SiC because of possible anisotropy.) There is fairly good agreement between the two halves of each of the original 40-mm-long diamond specimens: the values of κ_m for C1 and C5 are separated from each other by 5%, those for C2 and C6 by 1%, those for C3 and C7 by 0.5%, and those

for C4 and C8 by 2.5%. This good agreement could in principle be due partially to the fact that the data from the three labs L4, L5, and L9, taken only before the specimens were cut in half, were assumed to be representative of the whole specimen, and therefore each point was entered twice in Tables 5–7. For example, the result for C3 from laboratory L4 was also used for C7 from

laboratory L4. However, as it turned out, most of the points from two of these three laboratories were excluded as outliers, so this duplication of values cannot be a strong influence on the final values of κ_m . The differences in mean values between C1 and C5 and also between C4 and C8 are probably evidence of real differences, as these differences are observed to become even larger in the data of laboratory L1 for these specimens at low temperatures, Fig. 1. A value of $\kappa = 1453 \text{ W m}^{-1} \text{ K}^{-1}$, obtained by laboratory L7 for specimen C3 using the 3- ω method (which measures κ_{avg}), is within 3% of the value of κ_m obtained from all the other techniques (Table 3), providing further support for the accuracy of the κ_m values in diamond.

Measurements of sample C4–C8 before being cut in half were performed at Norton Diamond Film (Northboro, MA), using a d.c.-heated bar technique, resulting in a value of $1480 \text{ W m}^{-1} \text{ K}^{-1}$. The same value was obtained with the converging wave method [18] on the 45-mm-square piece from which C4–C8 was cut. This value is within 2% of the average of the κ_m values for C4 and C8 in Table 3.

The non-diamond materials, SiC and AlN, are expected to be very consistent from specimen to specimen as these materials were manufactured as standard products in batch mode. Indeed, again after eliminating outliers, the values of κ_m for SiC are all within 3.5% of the average, $268 \text{ W m}^{-1} \text{ K}^{-1}$, and the values of κ_m for AlN are all within 2% of the average, $178 \text{ W m}^{-1} \text{ K}^{-1}$. Furthermore, both of these average values are within the general ranges expected by the manufacturers of these materials.

4.2. Estimated uncertainties

The uncertainties estimated by each laboratory for their own measurements are shown in Figs. 3–5, 7 and 8. These estimates are, in most cases, significantly smaller than the deviation of any particular data point from the mean for that specimen. More realistic estimates are obtained from laboratories L1, L3, L4, L12, and L13. By technique, the most realistic estimates occur for the d.c.-heated bar technique.

4.3. Standard deviation by material

The standard deviation, σ , gives a measure of the 95% confidence level, $2\sigma/\kappa_m$, which is listed for each specimen in Table 3 and which is used in Chauvenet's criterion and plotted as dashed lines in Figs. 3–5. (Again, the values of κ_m and σ are those obtained after discarding outliers.) The 95% confidence limits are seen to fall in the range 6–26% for the 19 specimens. The average value for the eight diamond specimens is 17%, for the five SiC specimens, 13%, and for the six AlN, 15%. Thus, there appears to be good consistency in the

reliability of the measurements from one material to another. Several exceptions are worth noting. The 95% confidence limits for C2 and C6, 26% and 22%, respectively, are both quite high, which may be associated with the particularly high conductivity of these specimens. The values for U1 and U2 are also quite high at 21 and 25%, respectively. These specimens are almost three times as thick as the other AlN specimens, but they also differ in that the numbering system arbitrarily placed them more directly in sequence with the higher-conductivity SiC series, U3–U7, which may have led to some confusion.

Whereas the standard deviation, σ , measures the spread in values about the mean, the center of the distribution (the mean) is determined with better precision. The uncertainty σ_m in the determination of the mean κ_m for each specimen is calculated [17] as $\sigma_m = \sigma/N^{1/2}$, where N is the final number of data points, typically 9 to 11, used to calculate κ_m after exclusion of outliers. The uncertainty is in the range 1.5–4% for the eight diamond specimens. The average uncertainty for the SiC is 2.2% and for the AlN, 2.5%.

4.4. Comparison of techniques

We discuss the techniques here only briefly, as there have been several reviews of thermal conductivity/diffusivity measurements in diamond [19–21] as well as discussions of thermal measurements in general [22,23].

The d.c.-heated bar technique, one of the oldest techniques, has several advantages: it measures κ directly, it is easy to arrange for one-dimensional heat flow to simplify the analysis, and the steady thermal gradient can be measured with good precision, leading to high accuracy if the dimensions of the sample are uniform and known with high accuracy. The chief disadvantage is that the method is labor-intensive and slow. Another disadvantage is that thin specimens of poorly conducting material are susceptible to significant radiative or convective losses that tend to yield too large a value of κ if not accounted for. The correction can be accomplished [21] by measuring the deviations from a linear thermal gradient and/or by using a second heater. The maximum radiative loss can be calculated [24] by assuming the maximum emissivity ($\epsilon = 1$). The formula of Ref. [24] can be used, but a more accurate expression, used here, is $\tanh(\mu l)/\mu l$, which can be derived from the analysis of Ref. [23] (pp. 139–140). The sample length is l , and μ is the surface loss parameter defined in Ref. [23]. If radiation is not taken into account, the maximum error at 25 °C would be $\sim +0.2\%$ for diamond, $\sim +1\%$ for the SiC, and $\sim +3.5\%$ for the thin AlN specimens. Any conduction through residual gas would cause an additional error.

All three laboratories using this technique obtained results close to the mean values in Fig. 7: L1 and L3

within 5% and L2 with a similar spread of values but consistently $\sim 5\%$ higher. We note that laboratory L2 used only two thermocouples to measure the thermal gradient, and the laboratory also expressed some concern about the thermal resistance between the specimen and the glued-on heater. We also note that the L2 deviations from the mean values for AlN in Fig. 7 are $\sim 3\text{--}4\%$ above the deviations for diamond, which suggests that this difference is due at least partially to the lack of corrections for surface loss. Furthermore, the similarity of the data for diamond from laboratory L1 (without surface loss correction) and from L3 (with correction, Table 4) suggests that the latter corrections were due mainly to residual gas conduction.

Ångström's thermal wave technique [25] uses a periodic source of heat at frequency, f , applied to some region of a thin bar in order to generate one-dimensional thermal waves that are guided by the edges of the bar. By measuring the phase or amplitude of the temperature variations along the bar, one can determine the diffusion length $\delta = (D/\pi f)^{1/2}$ and, therefore, D . The wavelength of the thermal wave is $\lambda = 2\pi\delta$. In principle [26], one can choose f high enough to make δ small enough to reduce the effect of surface losses. One can also use an appropriate combination (the geometric mean) of phase and amplitude data to eliminate surface loss effects in the analysis [25,27–32]. Typical modern techniques use optical heating for its convenience. Because of the difficulty in determining how much absolute power is absorbed from the optical beam, the use of optical heating restricts one to measuring D rather than both D and κ . Thermometry is usually accomplished with thermocouples, infra-red sensing, or the temperature-dependent optical reflectivity of a metal film. The relatively slow response of thermocouples limits one to low frequencies, causing long diffusion lengths with possible complications from thermal wave reflections at the ends of the specimen [33,34].

The modified calorimetric method [35,36], a thermal wave technique so named because of its development as a modification of a calorimeter, uses a movable mask to control which part of the specimen is heated and a single thermocouple to measure temperature at a fixed point. Laboratories L4–L7 used this technique with mixed results. The deviations of κ from κ_m are much smaller for L4 and L7 than for L5 and L6 (see Fig. 7). We note that both phase and amplitude data were used by L4 and L7, but not by L5 or L6. Laboratory L4 used scanned laser heating, which provided a stronger signal. Furthermore, L4, L5, and L7 measured the long (40 mm) specimens of diamond with no corrections for thermal reflections, whereas the data of L6 for diamond were obtained with the cut specimens, and large corrections were applied for thermal reflections. Laboratory L4 used laser heating, which provided a stronger signal

and was considered especially important for the short and/or high-conductivity specimens.

Laboratory L8 used faster (infra-red) detection and paid special attention to using both phase and amplitude. The results are generally 5–15% below the mean values, except for specimens 14 and 15 (U1 and U2), which are anomalously high.

Laboratory L9 used a fixed electrical heater at a rather high frequency and a movable thermocouple, resulting in deviations of 20–30% below the mean. Because of thermal contact noise, only phase data were used. Also, the laboratory expressed concern about the possibility that the temperature of the specimen was higher than that of the thermal ground because of inadequate contact.

Laboratory L10 generated low-frequency thermal waves optically at a small spot and detected the temperature at a small spot using infra-red detection. Experimental breakdowns kept the deviations large but, curiously, negative for diamond and positive for AlN.

It is interesting that certain thermal-wave laboratories, L4 and L7, are clustered closely about the mean values. The important issues for the modified Ångström techniques apparently include (1) minimizing the effects of thermal wave reflections by using sufficiently long specimens, (2) using both phase and amplitude to account for surface loss, (3) choosing an appropriate frequency so that the diffusion length is larger than the thickness of the specimen but much smaller than the specimen length, and perhaps most important for relatively small specimens of high diffusivity, (4) using laser heating to create a strong enough signal.

The mirage technique [37,38] uses periodic optical heating of a small spot on the surface, generally at a high frequency, and detection of the thermal waves by the deflection of a probe beam by the (temperature-dependent) index of refraction of the air above the specimen. The method requires very little specimen preparation, but a complicated model is required to relate the beam deflection to the three-dimensional flow of heat away from the spot. The method differs from Ångström's method in that the edges of the specimen are not used to guide the thermal waves. The technique measures primarily D_{\parallel} with some admixture of D_{\perp} , depending on the relative locations of pump and probe beams and on the magnitude of the diffusion length, δ , in relation to the specimen thickness. Neither measuring lab provided an estimate of the D_{\perp} admixture.

Laboratory L11 used a skimming probe beam, obtaining good results ($\sim 2\text{--}10\%$) for the diamond but somewhat worse agreement for the SiC. The latter may be due to poor adhesion of the gold film to the SiC. The value of δ was comparable to the thickness of the specimen for all three materials. Also, for the lowest frequency used, the thermal diffusion length was smaller than the width of the sample for each material. No

differences were found in the diffusivity measured on the top or bottom of the diamond specimens, which is perhaps not surprising in view of the relatively large value of δ for these specimens. Using a value of δ greater than or comparable to the thickness is, of course, an advantage if one is seeking a value of diffusivity that is averaged over the specimen thickness in a single measurement.

Laboratory L12 used the mirage effect with generally higher heating frequencies, and with a probe beam that was reflected from the specimen surface at a low angle before being detected. The thermal diffusion length was less than the specimen thickness in all cases. The diamond values were reported only as averages of data from the top and bottom of each specimen. The results are evenly distributed about the mean values (Fig. 8) with a spread of approximately ± 10 –15%.

The decay in time of a thermal grating on the surface with grating spacing, Λ , probes the material to a depth $\sim \Lambda/\pi$ [39], so that laboratories L13 and L14 probed only ~ 15 –50 μm below the surface. Two quite different detection techniques were used. Laboratory L13 used a very local probe, focused to ~ 5 μm , which is a powerful technique for measuring the dynamics within a single grain of diamond. Significant differences (up to 40%) were observed between the ID-labeled and unlabeled faces of each diamond specimen (Table 5), even after averaging 30–40 measurements on each face. In each case, the lower diffusivity value was found on the face that turned out to be originally the bottom (substrate side), demonstrating that at least the bottom 15–50 μm of material are of inferior quality. One is inclined to accept the gradient observed by L13 because of the preponderance of data and because the gradient is always in the same sense (lower conductivity on the finer-grained substrate side). Regarding the absolute values, however, the top-and-bottom-averaged results of laboratory L13 (Table 8 and Fig. 8) are consistently 5–30% above the mean values for diamond. This phenomenon might be explained if there was preferential probing of large grains because of their smoother, more reflective top surfaces, rather than probing of grain boundaries or microcracks, which have a lower reflectivity and also lower diffusivity. The consistently high values for the absolute value of κ_m would presumably yield similarly high values for the gradient as well, suggesting that the true gradient is closer to 25–35% rather than 40%. This is still well below the factor of four sometimes observed between bottom and top of as-grown specimens. In the case of the finer-grained non-diamond material, the results are in much better agreement with the mean values (~ 5 –10% at worst).

Laboratory L14 used the diffraction of an unfocused probe beam to give an average over ~ 1 mm^2 . Rather high values were obtained for AlN, the only material measured before the equipment failed.

In the laser flash technique, a laser pulse is used to heat the front surface of a specimen while a detector monitors the temperature rise at the rear surface as the heat diffuses through. As long as the beam intensity is uniform across the specimen, the laser pulse is short compared to the diffusive transit time, and the local value of D_{\perp} does not vary too rapidly within the specimen [20], the temperature rise as fitted by the solution of the one-dimensional diffusion equation should yield a good average value of D_{\perp} . All of these conditions were satisfied in the measurements of L15. Laboratory 15 obtained results that were very close to the average for the thin AlN samples but ~ 10 –30% higher than the mean values for the diamond, the SiC, and the two thick AlN specimens. This suggests a certain amount of thermal anisotropy in both the diamond and the SiC, as one might expect because of the columnar growth. There may also be a significant correlation of the measured diffusivity with the specimen thickness, considering the higher values obtained for C4, C8, U1, and U2.

5. Conclusion

The secondary goal of RR2 was to obtain accurate values for the thermal conductivity of the specimens. The results in Table 3 show uncertainties, σ_m , which are in the range of 1–5% of κ_m for all specimens. Certain specimens such as the high-conductivity C2 and C6 exhibit greater deviations from the mean, which are undoubtedly associated with difficulties encountered in measuring such high conductivity with some methods. The process of excluding statistical outliers makes the average conductivity in all cases approach closely the results from the d.c.-heated bar technique, which is expected to have a high accuracy. This behavior promotes confidence in the internal consistency of the data. Thus, the values for the conductivity of these diamond specimens are thought to be reasonably well determined, and lie in the range 1300–2000 $\text{W m}^{-1} \text{K}^{-1}$.

The SiC specimens are all expected to have nearly the same conductivity, and this is clearly seen in the analysis after exclusion of outliers. The results for κ_m are 268 $\text{W m}^{-1} \text{K}^{-1} \pm 2.2\%$. Similarly, for the AlN, $\kappa_m = 178 \text{ W m}^{-1} \text{K}^{-1} \pm 2.5\%$.

With a fairly high degree of confidence in the κ_m values for each specimen, it is possible to assess the suitability of the various techniques used here for thermal conductivity measurements in CVD diamond, which is the primary goal of RR2.

As noted above, the d.c.-heated bar method offers high accuracy and measures κ directly, but at the cost of slow and laborious specimen preparation and measurement. Also, it requires specimens with very uniform dimensions.

The various modifications of Ångström's thermal wave technique are generally less demanding in specimen preparation but require a careful choice of heater placement and frequency to ensure one-dimensional heat flow and minimal interference from wave reflections. For the high conductivity of diamond, the limitation of thermocouple response to relatively low frequencies may be a significant problem if one is to avoid the impractical requirement of 40-mm-long specimens. Also, the use of both amplitude and phase data is apparently important for accuracy. As with all the techniques, an absorbing film must be applied to the specimen if optical heating is to be used, and the use of an intense (laser) heating source is important to obtain a strong signal.

The mirage technique, usually used with higher frequencies than with Ångström's method, is more localized and therefore less dependent on the specimen dimensions. Specimen preparation is minimal, and one-sided measurements make it possible to measure specimens on substrates. However, the experimental set-up and the modeling are both more elaborate. The results from two laboratories indicate that differences in technique are important for accuracy.

The transient thermal grating technique involves perhaps even more complicated experimental apparatus and requires specimens polished to a mirror finish, but the interpretation of the data is simple and straightforward. As with the mirage technique, it is ideally suited to specimens on substrates. Because of the small depth of measurement, however, it seems better suited to thin specimens (<100 μm) and/or research than to the routine measurement of thick specimens. For general measurements on large-grained materials such as CVD diamond, the diffracted probe beam technique should give a better average value than the tightly focused and deflected probe beam with its very high lateral resolution.

The laser flash technique, conceptually simple and requiring little specimen preparation other than an absorbing surface layer, is in principle as well suited to diamond as it is to materials of a lower diffusivity. However, the short duration required of the heating pulse and the fast response required of the photodetector [14] make most set-ups too slow for measuring CVD diamond. Perhaps the most serious drawback is that it measures D_{\perp} rather than the parallel component requested by most CVD diamond suppliers [40]. We point out that, although not used by any of the measuring laboratories L1–L15 for the present specimens, the laser flash technique can be modified to provide patterned rather than uniform heating, thereby measuring D_{\parallel} rather than D_{\perp} and requiring less stringent constraints on the laser and detector system. The converging wave technique [18] used at Norton Diamond Film on samples C4 and C8 is one example of this approach.

The question of thermal anisotropy in the diamond

or SiC specimens has not been resolved. This problem would benefit from (1) laser-flash measurements from a number of laboratories to allow a more meaningful statistical analysis, and (2) quantitative estimates of the relative proportions of D_{\parallel} and D_{\perp} measured by the mirage techniques.

The choice of a method to be used usually depends on many considerations [19,21] such as the required accuracy, the available operator skill, the size and shape of the specimens to be measured, and the cost of the equipment. The present work is intended as a guide on the question of accuracy.

The use of more homogeneous specimens has undoubtedly contributed to the higher degree of internal consistency of RR2, compared with that of RR1. The well-characterized specimens will be made available as standards to improve the accuracy of experimental apparatus for the measurement of high-conductivity materials. The results should also help suppliers or users of diamond to select a measuring method or measuring laboratory to obtain thermal data for their material. In order to preserve anonymity for those measuring laboratories desiring it, the first author can serve as an initial liaison between measuring laboratories and those seeking to have measurements performed on samples other than those discussed here.

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