

Thermal conductivity of diamond between 170 and 1200 K and the isotope effect

J. R. Olson and R. O. Pohl

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14853-2501

J. W. Vandersande and A. Zoltan

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

T. R. Anthony and W. F. Banholzer

General Electric Company, Research and Development Center, Schenectady, New York 12309

(Received 21 September 1992)

Measurements on the thermal conductivity of natural and synthetic single-crystal diamond are presented over a wide temperature range. The large isotope effect reported previously has been confirmed. The data have been analyzed using both the Debye model of thermal conductivity, which ignores the N processes, and the Callaway model in the limit that the N processes dominate the phonon scattering. It is found that the observed isotope effect can be accounted for by including the N processes alone, without having to postulate the existence of additional defects.

INTRODUCTION

The thermal conductivity of single-crystal diamond has recently received increased attention resulting from an announcement by General Electric and Wayne State University of a 50% enhancement at room temperature in thermal conductivity of synthetic diamond of high isotopic purity relative to that of natural type-IIa diamond or synthetic diamond of natural isotopic composition.¹ It has long been known that diamond has an extremely high thermal conductivity.² High-purity type-IIa diamond at room temperature has a thermal conductivity five times larger than that of copper and indeed is the highest value of any known material. Diamond is thus very useful for heat dissipation, and a 50% enhancement of the conductivity at room temperature would therefore be of considerable practical interest. It would also be of theoretical interest because the standard theories, which appear to work well in other solids,^{3,4} predicted only a few percent effect.^{5,6} Measurements reported recently by Onn *et al.*⁷ have confirmed the large isotope effect at room temperature and extended the temperature range up to 500 K.

The purpose of this paper is to report thermal conductivity measurements on two natural diamonds over a wide temperature range, between 170 and 1200 K, and on two synthetic diamonds, one with the naturally occurring 1.1% ¹³C, the other nearly isotopically pure (0.07% ¹³C), between 170 and 320 K. The high-temperature measurements on one of the natural diamond samples ($N1$) have previously been reported briefly.⁸ The high-temperature measurements on natural diamond will provide a baseline for theoretical comparison, while the lower-temperature measurements on natural diamond will allow a comparison with existing data to help establish the validity of the measurement technique. The measurements on synthetic diamond will allow a more quantitative evaluation of theories of isotope scattering in diamond. To anticipate the results, it is found that nearly isotopically pure ¹²C di-

amond has a thermal conductivity at room temperature ~40% larger than natural type-IIa diamond, in reasonable agreement with previous measurements.

EXPERIMENTAL DETAILS

The natural diamonds measured were determined to be type IIa (low nitrogen content) based on the UV absorption spectra. Both stones appeared colorless, but according to the supplier (DeBeers Corp.) they came from stones that had a slightly brownish hue. Sample $N1$ was $8.04 \times 8.84 \times 2.35$ mm³. Sample $N2$ was a cube 4.6 mm on each side.

The synthetic diamonds measured were grown at General Electric using a technique described elsewhere,¹ and are known to be high-quality single-crystal type-IIa diamonds.⁹ The synthetic diamonds were approximately $4 \times 4 \times 3$ mm in size.

Between 500 and 1200 K, the thermal conductivity of the natural diamonds was measured at the Jet Propulsion Laboratory using the flash diffusivity method described elsewhere.¹⁰⁻¹² Briefly, a xenon flash lamp applies a heat pulse through a sapphire light pipe to the front side of the sample (blackened, in this case with graphite and tantalum), while an InSb infrared detector measures the temperature rise on the rear side of the sample. The detector output is fed through an amplifier into a digital storage scope which displays the rear-face temperature as a function of time. This time dependence is analyzed to find the thermal diffusivity. The thermal conductivity is then calculated using the measured diffusivity, the measured mass density (3.51 g/cm³), and the published specific heat.¹³

Between 170 and 350 K, the thermal conductivity was measured at Cornell in an insertion-type cryostat using the 3ω thermal conductivity technique described elsewhere.¹⁴ Briefly, a narrow (50- μ m wide) Ag film several mm long, 1500- Å thick is deposited on a sample surface.

This line has a resistance of $\sim 12 \Omega$ at 300 K and serves as both a heater and thermometer. A sinusoidal current is passed through the line with angular frequency ω , which generates power varying as 2ω . This power creates thermal oscillations varying as 2ω , which cause the resistance of the Ag film to vary as 2ω . This resistance oscillation mixes with the input current and generates a component of the measured voltage which varies as 3ω . Its rms value $V_{3\omega}$ varies with frequency, and by measuring it as a function of frequency with a lock-in amplifier, the thermal conductivity Λ can be determined from¹⁴

$$\Lambda = \frac{I^3 R}{4\pi l} \frac{\ln(f_2) - \ln(f_1)}{V_{3\omega,1} - V_{3\omega,2}} \frac{dR}{dT} \quad (1)$$

I is the rms current through the metal line, R is the average resistance, and l is the length of the line; f_1 and f_2 are the two measuring frequencies ($f = \omega/2\pi$), $V_{3\omega,1}$ and $V_{3\omega,2}$ are the two measured $V_{3\omega}$ rms voltages, and dR/dT is the slope of the resistance calibration of the line. In practice one measures $V_{3\omega}$ at many frequencies, and in this case, $(V_{3\omega,1} - V_{3\omega,2})/[\ln(f_2) - \ln(f_1)]$ is replaced by the slope of the $V_{3\omega}$ versus $\ln(f)$ curve. A typical frequency scan is shown in Fig. 1.

The 3ω technique was originally developed to measure materials with relatively low thermal conductivities above 30 K, where other techniques suffer from problems with thermal radiation. Because this technique is essentially immune to radiation errors and easy to implement experimentally, and because of the ease of determining the sample geometry (which can be a problem for some other techniques, notably the standard four-probe dc technique, if the sample is unusually shaped or relatively small), it is ideal for thermal conductivity measurements on most materials.

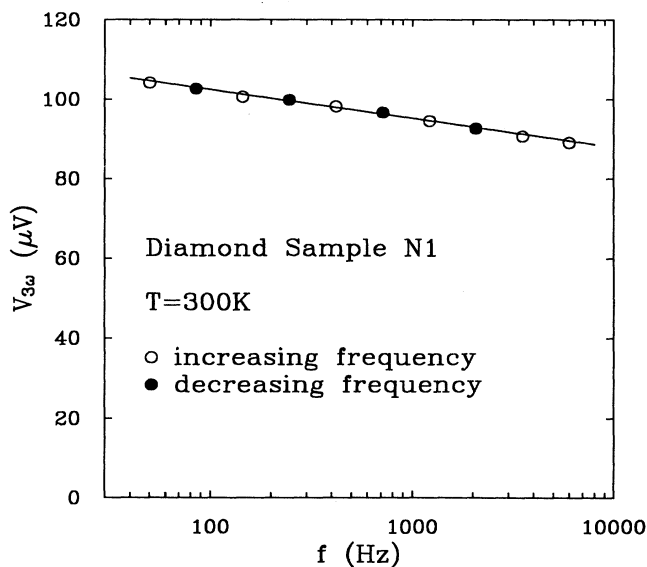


FIG. 1. A typical scan of $V_{3\omega}$ vs frequency. The frequency scan began at 50 Hz, increased to 6000 Hz (denoted by the open circles), then decreased (solid circles). For this scan, $I_{\text{rms}} = 0.050$ A, $R = 35.4 \Omega$.

The primary difficulty in measuring materials with very large thermal conductivities is that a large heat flow is required to generate an accurately measurable temperature drop. In the 3ω experiment, this manifests itself as a $V_{3\omega}$ that varies only slightly as a function of frequency, since it is inversely proportional to the thermal conductivity as seen in Eq. (1). (For typical experimental conditions, it was found that $V_{3\omega}$ varied by only about $15 \mu V$ over two orders of magnitude in measuring frequency at 300 K; see Fig. 1.) Consequently, any small extraneous voltage drift can lead to incorrect results. Several modifications were made to improve the accuracy of the technique. First, the temperature control of the refrigerator was improved to prevent temperature drifts which would lead to drifts in the resistance of the Ag line, and consequently to drifts in the measured voltage. In addition, the frequency was first scanned up, then back down to be certain there was no drift over the course of a scan (which would typically take 15 min). Also, a small inductive component in the leads and electronics was compensated for by adjusting the phase of the lock-in amplifier. This inductive component would cause a mixing of in-phase and out-of-phase $V_{3\omega}$ components, which would lead to erroneous frequency dependencies. Thirdly, the electrical contact between the Ag film and the current and voltage leads was improved. Conductive silver paint was used to make this connection, but it had to be cured overnight at roughly 70°C so that the resistance of the silver paint itself would not give an additional component to $V_{3\omega}$. The best contact was made by pressing gold pins down onto the pads of the Ag line and putting a small amount of silver paint on at the point of contact. This was only possible for sample N1, however, because of the small lateral dimension of sample N2 and the synthetic samples.

Another difficulty in measuring diamond arises from its high thermal diffusivity. The 3ω technique requires that the thermal diffusive wavelength $\lambda_{\text{th}} = \sqrt{D/2\omega}$, where D is the thermal diffusivity, be smaller than the sample dimensions and the length of the metal line. This restricted the frequency at room temperature to be greater than 50 Hz, while at 170 K the frequency had to be greater than 800 Hz. The lock-in amplifier limited the maximum frequency f to 16 kHz. The high thermal conductivity and limited frequency range prevented measurements below 170 K.

To test the 3ω technique, the thermal conductivity of high-purity silicon was measured from 300 K down to 50 K. These data agree very well with the accepted data,¹⁵ as shown in Fig. 2. In this case, the limitations mentioned above prevented measurements below 50 K. At 60 K, the thermal conductivity of silicon is as high as it is in diamond at 300 K. However, the thermal diffusivity of silicon at 60 K is approximately five times larger than that of diamond at 300 K, limiting the useful frequency range for the silicon measurement. In addition, the resistance of the metal film at 60 K is three times smaller than at 300 K, which causes the film to be three times less sensitive. Finally, the frequency synthesizer used is current limited for such a small resistance load, and consequently less power was generated in the metal film at low temper-

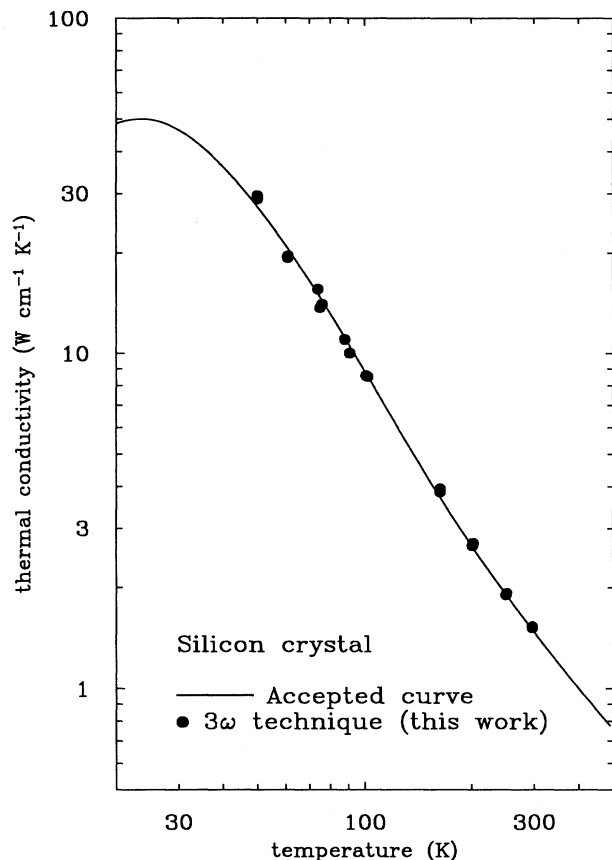


FIG. 2. Thermal conductivity of single crystal silicon measured with the 3ω technique. Shown for comparison (solid line) are published data from Ref. 15.

ature. The conclusion, then, is that the measurements at room temperature on diamond are at least ten times as accurate at those on silicon at 60 K. The measurements on diamond at 200 K have about the same accuracy as those on silicon at 60 K.

RESULTS

The thermal conductivity of the two natural diamond samples is shown in Fig. 3. Included for comparison are previously published data from Berman, Hudson, and Martinez¹⁶ and Burgemeister.¹⁷ Burgemeister measured 30 different type-IIa samples at 320 and 450 K, and all his data lie in the range shown. The measurements reported here at and below room temperature agree very well with these previously reported values. There is a $\sim 10\%$ difference between the two samples. This difference is believed to be due to differences in the number density of impurities or defects in the two samples. This has been qualitatively confirmed by measuring the UV absorption spectra. The height of the UV tail up to the absorption edge at $0.23 \mu\text{m}$ is an indication of the impurity content of type-IIa diamonds.¹⁸ Those of high purity have a very flat tail. Sample N2 has a higher UV absorption tail than sample N1, indicating it is less pure. As stated before, the natural diamonds measured had a slightly brownish hue due to impurities or defects.

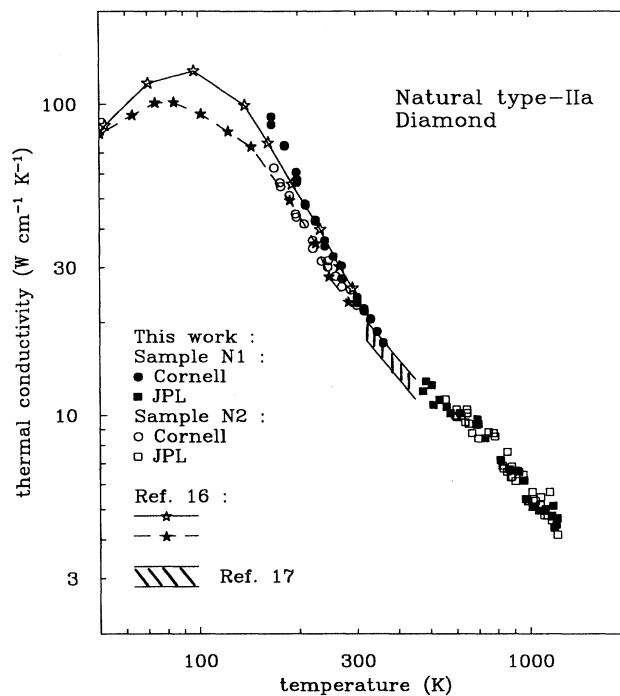


FIG. 3. Thermal conductivity of two type-IIa diamonds. Also shown are data measured by Berman, Hudson, and Martinez on two different type-IIa diamonds (Ref. 16), as well as data measured by Burgemeister on type-IIa diamond (Ref. 17). Burgemeister measured 30 different samples, all of which lie within the range shown. The lines shown through the data of Berman, Hudson, and Martinez are guides for the eye.

DeBeers Corp., which supplied the natural diamond samples for this work, indicated¹⁹ that it is likely that the samples supplied previously to Berman and Burgemeister were also from somewhat brownish samples (clearer samples being too valuable). It would be very desirable to measure less impure ("pure white") samples, to find the true intrinsic baseline for natural diamond.

The data at high temperatures agree with Burgemeister's values at 450 K, and extend up to 1200 K, higher than any previous measurements. This high-temperature extension will allow for better theoretical comparisons, a point which will be addressed shortly.

The thermal conductivity of synthetic diamond with 1.1% and 0.07% ^{13}C isotopic content is shown in Fig. 4, along with measurements by Onn *et al.*⁷ Shown for comparison is the highest-conductivity curve of Berman, Hudson, and Martinez and one set of high-temperature data (sample N1) on natural type-IIa diamond, both from Fig. 3. The measurements reported here agree very well with those of Onn *et al.*, where they overlap, and seem to show the same temperature dependence. The values for the nearly isotopically pure samples lie $\sim 40\%$ above those of natural type-IIa diamond, and $\sim 60\%$ above those of synthetic type-IIa diamond, in agreement with the originally reported isotope effect. It is interesting to note that synthetic type-IIa diamond thermal conductivity data are $\sim 15\%$ lower than the highest values for natural type-IIa diamond. There is conflicting evidence re-

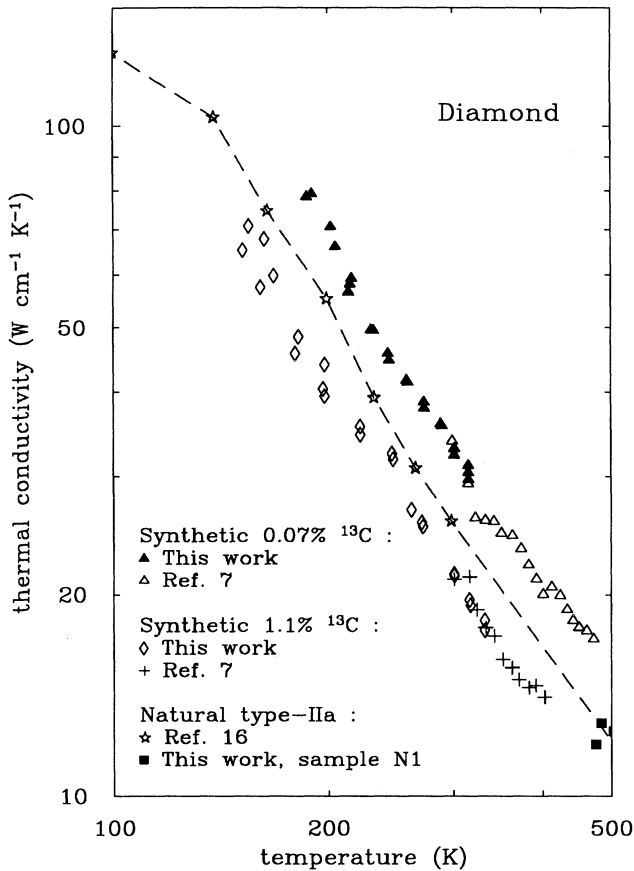


FIG. 4. Thermal conductivity of synthetic diamond with 0.07% and 1.1% ^{13}C isotope concentration. Shown for comparison are data on natural diamond measured by Berman, Hudson, and Martinez (Ref. 16) and high-temperature data on sample *N1*. The dashed line is a guide for the eye.

garding the quality of these synthetic diamonds relative to natural diamond. X-ray linewidths²⁰ for synthetic diamond are independent of isotopic composition and are fifteen times narrower than those of natural type-IIa diamonds. On the other hand, x-ray topography⁹ indicates that isotopically pure synthetic diamonds contain significantly fewer defects than natural diamond or synthetic diamond of natural isotopic abundance.

DISCUSSION

One is confronted with a situation where small concentrations of isotopic impurities lead to an unexpectedly large reduction in the thermal conductivity. In an attempt to quantify the phonon scattering resulting from isotopic impurities in diamond, the data have been analyzed using the Debye model of thermal conductivity,

$$\Lambda(T) = Nk_B \sum_{i=1}^3 v_i \left[\frac{T}{\Theta_{D_i}} \right]^3 \int_0^{\Theta_{D_i}/T} l(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (2)$$

where N is the number density of atoms (for diamond, $N = 1.762 \times 10^{23} \text{ cm}^{-3}$) and the sum over i denotes a sum over the one longitudinal and the two transverse phonon

modes, v_i is the sound velocity for that mode (for diamond,²¹ $v_l = 1.75 \times 10^6 \text{ cm/s}$, and $v_t = 1.28 \times 10^6 \text{ cm/s}$). Θ_{D_i} is the effective Debye temperature for mode i , given by

$$\Theta_{D_i} = 2.997 \times 10^{-11} v_i N^{1/3} sK. \quad (3)$$

$l(x)$ is the phonon mean-free path, and

$$x = \frac{hv_i}{k_B T \lambda}, \quad (4)$$

where λ is the phonon wavelength.

The assumption is made that the resistive scattering rates add, so that

$$l(x) = (l_{\text{bdry}}^{-1} + l_{\text{rayl}}^{-1} + l_{\text{umkl}}^{-1})^{-1} + \frac{\lambda}{2}. \quad (5)$$

The terms l_{bdry} , l_{Rayl} , and l_{umkl} are the phonon mean-free paths associated with the sample boundaries, points defects, and umklapp processes, respectively. The term $\lambda/2$, half the phonon wavelength, is included to avoid the nonphysical case where the mean-free path becomes short compared to the phonon wavelength.

The Debye model is sometimes referred to as the Klemens-Callaway model, but the authors feel that "Debye model" is more appropriate. Klemens made the assumption that the scattering rates add and ignored the N processes,²² while Callaway took N processes into account.²³ As an aside we note that when Callaway applied his theory to germanium, he ignored N processes and simply used the Debye model.

The data on natural diamond of Berman, Hudson, and Martinez (using highest values from Fig. 3) and one set of high-temperature data (sample *N1*) have been fitted by trial and error, using phonon mean-free paths of the form

$$l_{\text{bdry}}^{-1} = \frac{1}{A} \quad (\text{Ref. 24}),$$

$$l_{\text{Rayl}}^{-1} = \frac{B}{\lambda^4} \quad (\text{Ref. 25}), \quad (6)$$

$$l_{\text{umkl}}^{-1} = C \frac{T}{\lambda^2} e^{-D/T} \quad (\text{Ref. 26}).$$

A good fit is found for the following parameters: $A = 0.1 \text{ cm}$, $B = 4.0 \times 10^{-25} \text{ cm}^3$, $C = 2.0 \times 10^{-12} \text{ cm/K}$, $D = 550 \text{ K}$. These parameters are listed in Table I, and are close to those previously published,⁷ with minor differences arising because a slightly different form of the Debye model has been used here. This fit is shown as the dashed curve in Fig. 5. The data for the nearly isotopically pure samples were then fitted by changing only the point scattering term. A reasonable fit was found for $B = 0.6 \times 10^{-25} \text{ cm}^3$, see Table I. Thus it was necessary to reduce B by $3.4 \times 10^{-25} \text{ cm}^3$; this is the Rayleigh term caused by the isotope scattering. Turk and Klemens²⁷ have calculated the Rayleigh term, taking into account not only the mass difference of the impurity but also the difference in volume occupied. They found that

$$l_{\text{Rayl}}^{-1} = \frac{\Omega_0}{4\pi} \delta \left[\frac{\Delta M}{M} + 2\gamma\alpha \right]^2 \left[\frac{2\pi}{\lambda} \right]^4, \quad (7)$$

TABLE I. Parameters for Debye model fits for diamond.

Sample	A (cm)	B (cm ³)	C (cm/K)	D (K)
Natural type-IIa	0.1	4.0×10^{-25}	2.0×10^{-12}	550
Synthetic enriched ¹² C	0.1	0.6×10^{-25}	2.0×10^{-12}	550
Natural type Ia (C7)	0.1	1.89×10^{-24}	2.0×10^{-12}	550
Natural type Ia (C5)	0.1	1.6×10^{-23}	2.0×10^{-12}	550

where Ω_0 is the volume per atom equal to $1/N = 5.68 \times 10^{-24}$ cm³, δ is the atomic fraction of the impurity (assumed to be $\ll 1$), $\Delta M/M$ is the fractional mass difference for the impurity, γ is the Grüneisen parameter equal to 1.1 for diamond,¹⁶ and α is the fractional volume difference of the impurity. For 1.1% ¹³C in ¹²C, where $\Delta M/M = \frac{1}{12}$ and $\alpha = 0.0005$ (Ref. 20), l_{Rayl}^{-1} calculated from Eq. (7) is 5.38×10^{-26} cm³. This is 6.3 times smaller than the scattering rate determined here. Onn *et al.*⁷ found the calculated scattering rate to be 5.4 times smaller than the measured scattering rate.

It has been shown¹⁶ that atomic impurities can also lead to an unexpectedly large reduction in the thermal conductivity of diamond. There is a variation of $\sim 10\%$ between different type-IIa samples below 450 K, although the atomic impurity concentrations differ by only a few parts per million (ppm).²⁸ Measurements have been reported on type-Ia diamond samples with known nitrogen impurity concentrations.¹⁶ (Type-Ia diamonds contain higher concentrations of nitrogen than type-IIa, and are

divided on the basis of UV and IR absorption features.¹⁶) Two of these, the ones labeled C7 and C5 in Ref. 12, have been analyzed with the Debye model, and the data and fits are shown in Fig. 6. The additional Rayleigh scattering necessary to fit these two sets of data was found to be $1.49 \times 10^{-24} \lambda^{-4}$ cm³ and $1.56 \times 10^{-23} \lambda^{-4}$ cm³, respectively, see Table I. For N in ¹²C, where $\Delta M/M = \frac{2}{12}$ and $\alpha = 0.15$,²⁷ these values correspond to 15 and 88 times the values predicted using Eq. (7).

The source of the enhancement of the point defect scattering is uncertain. There are other systems where impurities lead to unexpectedly large reductions in the thermal conductivity. In β -B for example, which, like diamond, has a very rigid lattice ($\Theta_D = 1520$ K), the addition of 3% carbon impurities reduces the thermal conductivity by almost a factor of 10 at 220 K (Ref. 29) (which corresponds to the same reduced temperature T/Θ_D as room temperature in diamond).

The nitrogen present in type-Ia diamond is known to be clustered,^{30,31} and N impurities in clusters of n will

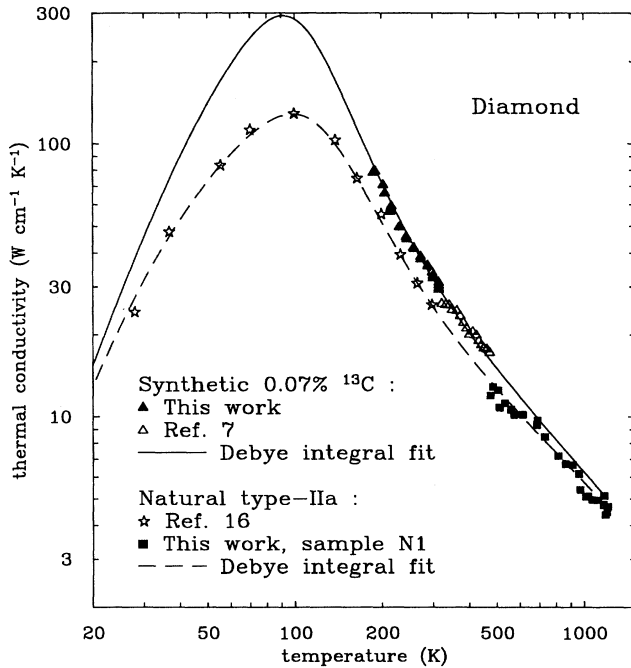


FIG. 5. Thermal conductivity of natural type-IIa diamond and synthetic diamond with 0.07% ¹³C isotope concentration. The dashed line is the fit calculated from the Debye model as described in the text. The solid line is the fit for the nearly isotopically pure diamond, where the point defect scattering (Rayleigh term) was the only parameter changed.

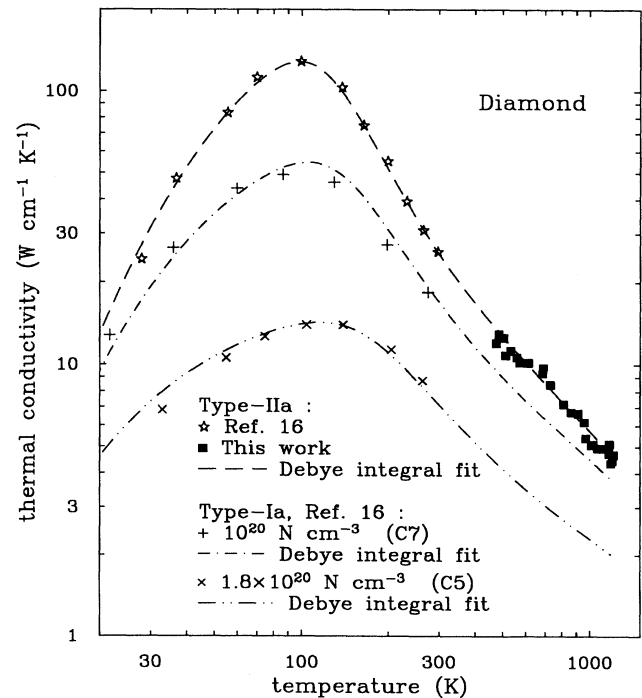


FIG. 6. Thermal conductivity of natural type-IIa and type-Ia diamond. The lines are the fits calculated from the Debye model as described in the text. The point defect scattering was the only parameter different in the calculations.

scatter n times more effectively than N individual impurities. However, the clusters are generally thought to be small,³² not the 15 or 88 needed to explain the discrepancy between the fit and the calculated scattering rate.

Onn *et al.*⁷ have proposed that low concentrations of lattice vacancies are adequate to explain the observed "isotope" effect. However, the relatively small variation ($\sim 10\%$) of the thermal conductivity of different natural type-IIa diamonds (see Fig. 3) would indicate that they all have roughly the same vacancy concentration, which seems unlikely. Furthermore, there is little reason to expect synthetic, isotopically enriched ^{12}C diamond to have fewer vacancies than synthetic diamond with 1.1% ^{13}C .

A likely explanation has been considered by Berman³³ and Hass *et al.*,³⁶ who have examined the role of N processes. In the Debye model, the nonresistive three-phonon N processes are ignored. These scattering processes do not themselves lead to a degradation of the heat flow, but instead restore the phonon distribution to a displaced Planck distribution compatible with the heat flowing. Suppose there were a defect that strongly scattered phonons at a particular frequency f_0 . In the Debye model, phonons with frequency f_0 would not contribute to the thermal conductivity, but phonons of other frequencies would be unaffected. N processes would act to channel other phonon modes into that frequency, effectively reducing the thermal conductivity contribution from the other modes as well. The N -process scattering rates in diamond are largely unknown, so a quantitative computation is not possible. However, if one assumes that the N -process scattering rate is much larger than the resistive scattering rate, then both the Callaway model²³ and the Ziman variational method³⁴ lead to the same result:³³

$$\Lambda(T) = Nk_B \sum_{i=1}^3 v_i \left[\frac{T}{\Theta_{D_i}} \right]^3 \times \frac{[\int_0^{\Theta_{D_i}/T} x^4 e^x / (e^x - 1)^2 dx]^2}{\int_0^{\Theta_{D_i}/T} l^{-1}(x) x^4 e^x / (e^x - 1)^2 dx}, \quad (8)$$

where $l^{-1}(x)$ is given by the inverse of Eq. (5). The data on natural type-IIa diamond have been fitted using phonon mean-free paths as given in Eq. (6). A good fit has been found for the following parameters: $A = 0.055$ cm, $B = 1.5 \times 10^{-26}$ cm³, $C = 1.4 \times 10^{-12}$ cm/K, $D = 730$ K. These values are listed in Table II. Not surprisingly, these parameters are somewhat different than those found using the Debye model. The Rayleigh scattering term was then adjusted to achieve a best fit to the data on the nearly isotopically pure diamond. It was found that $l_{\text{Rayl}}^{-1} = 0$ in this case. See Table II. Thus $1.5 \times 10^{-26} \lambda^{-4}$

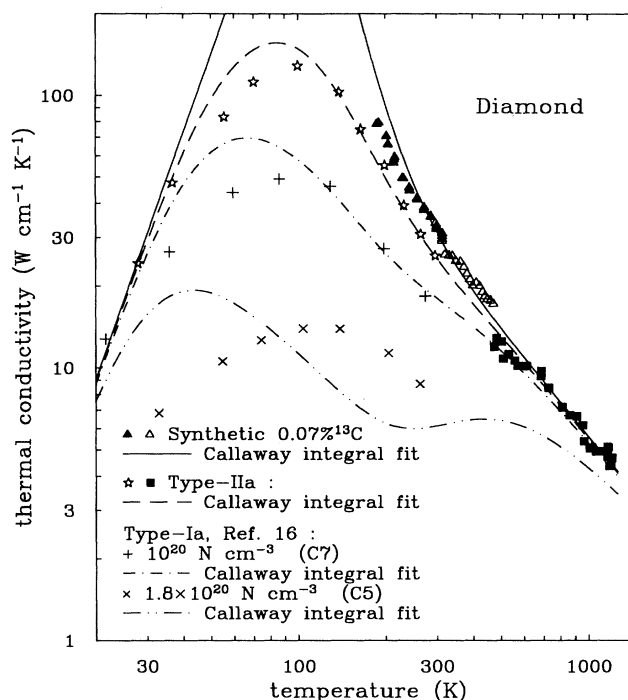


FIG. 7. Thermal conductivity of synthetic nearly isotopically pure diamond, and natural type-IIa and type-Ia diamond. The lines are the fits calculated from the Callaway model as described in the text. The point defect scattering was the only parameter different in the calculations.

cm³ had to be removed. This corresponds to 3.6 times less scattering than predicted by Eq. (7). In this case, making the assumption that the N processes dominate enhances the isotope scattering by a factor of 23 over the case when the N processes are ignored.

Hass *et al.*³⁶ have performed a similar fit. Rather than assuming that the N -process scattering dominates at all temperatures, they used a particular form for the N -process scattering rate, $\tau_N^{-1} = 0.011xT^5$, where $\tau^{-1} = vl^{-1}$, and x is given by Eq. (4). Because of this assumption, the parameters they found were somewhat different than those reported in this work. They also used a smaller temperature range ($T \leq 300$ K) and a different form of the umklapp scattering rate now known to fail at higher temperatures.⁷ The conclusion reached by Hass *et al.* is the same as the one reached here: The observed isotope effect can be explained by existing theory by taking into account the effect of N processes.

The two type-Ia samples analyzed previously have also been fitted using Eq. (8), and these fits are also shown in Fig. 7. In this case, a best fit was achieved by adding

TABLE II. Parameters for Callaway model fits for diamond (in the limit that N processes dominate the phonon scattering).

Sample	A (cm)	B (cm ³)	C (cm/K)	D (K)
Natural type IIa	0.055	1.5×10^{-26}	1.4×10^{-12}	730
Synthetic enriched ^{12}C	0.055	0	1.4×10^{-12}	730
Natural type Ia (C7)	0.055	4.5×10^{-26}	1.4×10^{-12}	730
Natural type Ia (C5)	0.055	2.5×10^{-25}	1.4×10^{-12}	730

$3.0 \times 10^{-26} \lambda^{-4} \text{ cm}^3$ and $2.35 \times 10^{-25} \lambda^{-4} \text{ cm}^3$, respectively, see Table II. These values correspond to 3.0 times less and 1.3 times more scattering, respectively, than calculated using Eq. (7). In this case, making the assumption that the N processes dominate enhances the Rayleigh scattering by factors of 45 and 66 over the case when the N processes are ignored. It is clear that the temperature dependence is wrong in this limit, but it does demonstrate that the N processes can enhance the effect of the isotope scattering enough to account for the observed isotope effect in diamond. One could conceivably use the full Callaway model to determine a form of the N process scattering rate as Nepsha has done,³⁵ but the authors feel this requires measurements on a wider range of isotope abundances and over a broader temperature range [as was performed on LiF (Ref. 3)] to provide meaningful conclusions.

CONCLUSIONS

The thermal conductivity of synthetic isotopically pure diamond and natural type-IIa and type-Ia diamond has been analyzed using the Debye and Callaway models of thermal conductivity. It has been found that the impurities (either the ^{13}C or N) scatter phonons much more strongly than predicted by the Debye model, which ignores the N processes, whereas they scatter less strongly than predicted by the limiting case of the Callaway model where N processes dominate the scattering. However,

the assumption that the N processes dominate leads to an incorrect temperature dependence.

If the Debye model accurately describes the temperature dependence of the thermal conductivity even as the temperature becomes a significant fraction of the Debye temperature, then an enhancement in the thermal conductivity of nearly isotopically pure diamond should be measurable out to 1200 K. If the N processes dominate, then isotopically pure type-IIa and type-Ia diamond should all have roughly the same thermal conductivity at high temperatures. Experiments are planned to measure nearly isotopically pure ^{12}C synthetic diamond and type-Ia diamond using the laser flash diffusivity method.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Dr. Robert Berman, The Clarendon Laboratory, University of Oxford, for stimulating and enlightening discussion. We would also like to acknowledge Dr. Robert Caveney, Diamond Research Laboratory, DeBeers for supplying the two natural diamond samples measured, and Dr. Frank DiSalvo for the use of his thermal evaporator. The research at Cornell was supported by the National Science Foundation, Grant No. DMR9115981. The research at the Jet Propulsion Laboratory was performed under contract with the National Aeronautics and Space Administration, and was partially funded by the Wright Research and Development Center.

- ¹T. R. Anthony, W. F. Banholzer, J. F. Fleischer, L. H. Wei, P. K. Kuo, R. L. Thomas, and R. W. Pryor, *Phys. Rev.* **42**, 1104 (1990).
- ²R. Berman, F. E. Simon, and J. M. Ziman, *Proc. R. Soc. A* **220**, 171 (1953).
- ³R. Berman and J. C. F. Brock, *Proc. R. Soc. A* **289**, 46 (1965).
- ⁴T. H. Geballe and G. W. Hull, *Phys. Rev.* **110**, 773 (1958).
- ⁵J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 1960).
- ⁶G. A. Slack, *Phys. Rev.* **105**, 829 (1957).
- ⁷D. G. Onn, A. Witek, Y. Z. Qiu, T. R. Anthony, and W. F. Banholzer, *Phys. Rev. Lett.* **68**, 2806 (1992).
- ⁸J. W. Vandersande, C. B. Vining, and A. Zoltan (unpublished).
- ⁹T. R. Anthony and W. F. Banholzer, *Diamond Relat. Mater.* **1**, 717 (1992).
- ¹⁰J. W. Vandersande, C. B. Vining, and A. Zoltan, *Proceedings of the Second International Symposium on Diamond Materials* (Electrochemical Society, Pennington, NJ, 1991), Vol. 91-8, pp. 443-450.
- ¹¹J. W. Vandersande, C. Wood, A. Zoltan, and D. Whittenberger, in *Thermal Conductivity*, edited by D. W. Yarborough (Plenum, New York, 1988), Vol. 19, pp. 445-452.
- ¹²J. W. Vandersande, A. Zoltan, and C. Wood, *Int. J. Thermophys.* **10**, 251 (1989).
- ¹³A. C. Victor, *J. Am. Chem. Soc.* **36**, 1903 (1962).
- ¹⁴David G. Cahill, *Rev. Sci. Instrum.* **61**, 802 (1990). For earlier references, see David G. Cahill and R. O. Pohl, *Phys. Rev. B* **35**, 4067 (1987).
- ¹⁵Y. S. Touloukian, R. W. Powell, C. Y. Ho, and P. G. Klemens, *Thermal Conductivity of Metallic Elements and Alloys* (IFI/Plenum, New York, 1971), p. 326.
- ¹⁶R. Berman, P. R. W. Hudson, and M. Martinez, *J. Phys. C* **8**, L430 (1975).
- ¹⁷E. A. Burgemeister, *Physica* **93B**, 165 (1978).
- ¹⁸C. D. Clark, E. W. J. Mitchell, and B. J. Parsons, in *Properties of Diamond*, edited by J. E. Field (Academic, New York, 1979), p. 31.
- ¹⁹Dr. R. Caveney (private communication).
- ²⁰H. Holloway, K. C. Hass, M. A. Tamor, T. R. Anthony, and W. F. Banholzer, *Phys. Rev. B* **44**, 7123 (1991).
- ²¹G. Simmons and H. Wang, *Single Crystal Elastic Constants and Aggregate Constants* (MIT Press, Cambridge, MA, 1971).
- ²²P. G. Klemens, *Proc. R. Soc. A* **208**, 108 (1951).
- ²³Joseph Callaway, *Phys. Rev.* **113**, 1046 (1959).
- ²⁴H. B. G. Casimir, *Physica* **5**, 495 (1938).
- ²⁵P. G. Klemens, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz and D. Turnbull (Academic, New York, 1958), Vol. 7.
- ²⁶R. Peierls, *Ann. Phys. (Leipzig)* **3**, 1055 (1929).
- ²⁷Lawrence A. Turk and P. G. Klemens, *Phys. Rev. B* **9**, 4422 (1974).
- ²⁸J. W. Vandersande, *J. Phys. C* **13**, 757 (1980).
- ²⁹David G. Cahill, Henry E. Fischer, S. K. Watson, R. O. Pohl, and G. A. Slack, *Phys. Rev. B* **40**, 3254 (1989).
- ³⁰B. Zsigeti, *J. Phys. Chem. Solids* **24**, 225 (1963).
- ³¹M. Takagi and A. R. Lang, *Proc. R. Soc. A* **281**, 310 (1964).
- ³²G. Davies and I. Summersgill, *Diamond Research 1973* (Industrial Diamond Information Bureau, London, 1973), pp. 6-15.
- ³³R. Berman, *Phys. Rev. B* **45**, 5726 (1992).
- ³⁴J. M. Ziman, *Can. J. Phys.* **34**, 1256 (1956).
- ³⁵V. I. Nepsha, V. R. Grinberg, Yu. A. Klyuev, and A. M. Naletov, *Diamond and Related Materials* (to be published).
- ³⁶K. C. Hass, M. A. Tamor, T. R. Anthony, and W. F. Banholzer, *Phys. Rev. B* **45**, 7171 (1992).