Some Aspects of the Thermal Conductivity of Isotopically Enriched Diamond Single Crystals

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New data on the thermal-conductivity temperature dependence $k(T)$ of both natural abundance and isotopically enriched synthetic diamond gems are presented. The existing data on the thermal-conductivity temperature dependence $k(T)$ of natural type-IIa diamond have been reanalyzed using a comprehensive Klemens-Callaway model. The high thermal conductivity of isotopically pure diamond is shown to be consistent with the model.

The role of isotopes as phonon scatterers with a resulting influence on the thermal conductivity k was first considered theoretically by Pomeranchuk [1] in 1942. Since then major advances in understanding the mechanism of phonon scattering by isotopes and other impurities have been made but several questions remain open. Interest in these questions has been stimulated by the recent discovery by Anthony et al. [2] of a 50% "enhancement" in the thermal conductivity of synthetic diamond when the isotopic impurity was decreased by a factor of 15.

Initial attempts to explain the high thermal conductivities concentrated on modified phonon models such as the "smeared phonon dispersion" introduced by Bray and Anthony [3]. The new data presented here on the temperature and isotope concentration dependences of the thermal conductivity of synthetic diamond gems, coupled with a reanalysis of existing data on $k(T)$ of natural type-IIa diamonds, lead us to the conclusion that the high thermal conductivity of isotopically pure diamond requires no special explanation but that extra phonon scattering mechanisms, additional to isotope scattering, are responsible for the "attenuated" thermal conductivity of diamonds that are not isotopically pure.

Diamond single-crystal gems are an ideal subject for studying isotopic effects on thermal conductivity because the isotope scattering is enhanced in low-atomic-weight elements and compounds where the difference in mass between isotopes becomes a significant fraction of the atomic weight. We note immediately, however, that a single atomic vacancy is approximately 150 times more effective as a phonon scatterer in ^{12}C than is a single ^{13}C atom.

Natural diamond, as found in nature, contains 1.07% ^{13}C and 98.93% ^{12}C. The simplicity of the crystal and chemical composition have encouraged many theoretical predictions of the effects of isotope content on the thermal conductivity. Calculations based on an approach by Ziman [4] indicated that an isotopically pure single crystal of diamond should have a room-temperature thermal conductivity only 2% greater than natural diamond. Another semiempirical calculation also predicts that the

thermal-conductivity enhancement should be less than 5% [5]. Only Berman and Martinez [6] have suggested a significant enhancement, about 50%, of the thermal conductivity of isotopically pure diamond, but their value for room temperature was based on a heuristic extrapolation from high-temperature values of diamond thermal conductivity.

Until the 1990s only theoretical discussion was possible. Production of both diamond films and high-quality gems of varied isotopic composition is now possible [7-9]. In this paper we present new data on both the temperature and isotopic concentration dependence of thermal conductivity of synthetic diamond gems.

Analysis of existing $k(T)$ data for natural type-IIa diamonds.— A key to the analysis presented here for the thermal conductivity of synthetic diamond gems is our reanalysis of existing $k(T)$ data on natural type-IIa diamonds. The combined data of Berman, Hudson, and Martinez [10] and of Vandersande, Vining, and Zoltan [11] provide $k(T)$ from 10 to 1250 K for type-IIa diamond with the natural (1.07%) ^{13}C abundance.

Our analysis uses a comprehensive Klemens-Callaway model previously successfully applied by Dinwiddie and Onn to $k(T)$ for aluminum nitride for which independent estimates of phonon scattering sources could be made [12]. This model is preferred for analysis of $k(T)$ of diamond since others, such as the "dominant phonon approximation," tend to contain unjustified assumptions, including the assumption of a constant specific heat: certainly not the case for diamond at room temperature when the Debye temperature Θ_D is 1850 K.

The Klemens-Callaway model [13,14] assumes an ideal Debye-type phonon spectrum, which in fact provides an excellent description of the specific heat above about 30 K, and includes the phonon scattering through an overall phonon relaxation time $\tau(x)$. The thermal conductivity is then given by

$$k(T) = \frac{k_B}{2\pi^2 v} \left[\frac{k_B T}{\hbar} \right]^3 \int_0^{\Theta_D/T} \tau(x) \frac{x^4 e^x}{(e^x - 1)^2} dx, \qquad (1)$$

where Θ_D is the Debye temperature, v is the average phonon velocity, and

$$x = \hbar\omega/k_B T , \qquad (2)$$

with ω the phonon frequency.

The phonon relaxation or scattering time $\tau(x)$ is obtained under the assumption that the relaxation times for all scattering processes are independent so that

$$\tau(x)^{-1} = \tau_g^{-1} + \tau_p^{-1} + \tau_u^{-1} . \qquad (3)$$

The relaxation time for each type of scattering is given by

$$\tau_g^{-1} = v/1.12d \qquad (4)$$

for grain-boundary scattering [15], where d is the average grain-boundary separation, and

$$\tau_p^{-1} = Ix^4 T^4 \qquad (5)$$

is determined by the impurity, vacancy, or isotope concentration scattering as suggested by Klemens [13]. The constant I is directly related to defect concentration by

$$I = \frac{c_i a^3 k_B^4}{4\pi v^3 \hbar^4} \left[\frac{\Delta M}{M} \right]^2 , \qquad (6)$$

where ΔM is the mass deficit associated with the point defect in a lattice with atoms of mass M and atomic spacing a. It is the ratio $(\Delta M/M)^2$ in this expression that makes a lattice vacancy over 100 times more effective a phonon scatterer than an isotopic impurity.

The appropriate form of τ_u, the umklapp scattering term, has been the subject of much debate since its introduction by Peierls [16]. The generally accepted form is

$$\tau_u^{-1} = Ax^2 T^\zeta \exp(-B/T) , \qquad (7)$$

where A and B are constants. The greatest uncertainty occurs for the power of the temperature ζ. Theoretical models have given powers ranging from 1 to 8 while experimental studies favor values between 3 and 5. The uncertainty arises from several sources including, theoretically, the relative roles of umklapp and normal scattering processes and, experimentally, the lack of data over a wide enough temperature range to determine ζ unambiguously.

Diamond, because of its high-temperature stability, offers the best opportunity for a clear experimental determination of ζ now that data on $k(T)$ between 10 and 1250 K are available [10,11]. Using these data we have applied a robust four-parameter nonlinear least-squares fitting program using Eq. (1) [17]. The four parameters returned by the program are d, I, A, and B from Eqs. (3)-(5) and (7). Since the form of $k(T)$ as expressed by Eq. (1) is such that each of the parameters dominates in a different temperature range, this fitting process successfully returns physically meaningful parameters as has been demonstrated previously with AlN [12].

The temperature power ζ from Eq. (7) was not used as a fitting parameter but the fit was repeated with integer
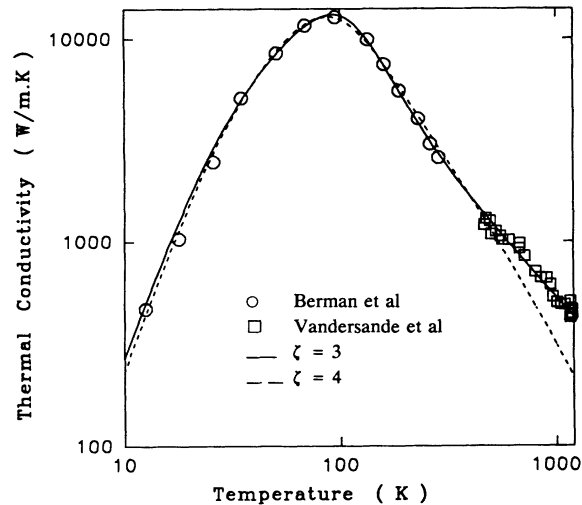

FIG. 1. Temperature dependence of the thermal conductivity of the natural type-IIa diamond gems [Ref. [10] (circles) and Ref. [11] (squares)] along with two multiparameter fits by the Klemens-Callaway model. The solid line denotes a fit of umklapp power of 3, and the dashed line denotes umklapp power of 4.

values of ζ between 1 and 5. In Fig. 1 we show the combined data of Berman [10] and Vandersande [11] between 10 and 1250 K compared with the curves resulting from fits by Eq. (1) with $\zeta = 3$ and 4. The former clearly provides the best fit to the highest temperatures. The fit for $\zeta = 2$ diverges upwards at the highest temperatures as much as the $\zeta = 4$ fit diverges downwards. It is important to note that using the data of Berman alone, which terminate at 300 K, it is impossible to distinguish between fits with ζ from 2 to 5 within the cited experimental uncertainties.

The additional high-temperature data of Vandersande (600 to 1250 K) is essential in establishing that the correct power of ζ in Eq. (7) is 3. Furthermore, the smoothed curve of the Klemens-Callaway fit with $\zeta = 3$ shown in Fig. 1 corresponds more closely than any other power of ζ to a $k(T) \sim 1/T$ dependence at high temperatures: a temperature dependence of k that is observed for a wide range of materials.

The four free parameters obtained from the fit by Eq. (1) with $\zeta = 3$ are given in Table I. The umklapp associated parameters, A and B, are comparable to those obtained from $k(T)$ for diamond films [17]. B is approximately $\Theta_D/3$ as is found in many other materials. The grain-boundary parameter d is 0.75 mm which, given the ~ 1-mm dimensions of the single-crystal diamond gem used by Berman, the data for which are dominant below 100 K, is a very reasonable value. Values of d of the order of a few microns are typically obtained when this same fitting routine is applied to polycrystalline diamond films [17].

The impurity parameter I is over 5 times higher than would be expected if the sole impurities present were the 1.07% ^{13}C isotope atoms; $I(^{13}C) = 0.0075$ from Eq. (6).

TABLE I. Fitting parameters for temperature dependence of the thermal conductivity for type-IIa natural diamond.

Data source	A (K^3/sec)	B (K)	I (K^4/sec)	d (mm)
[10,11]	690 ± 50	510 ± 30	0.040 ± 0.004	0.73 ± 0.16
[10,11] and this work	820 ± 60	540 ± 30	0.042 ± 0.004	0.75 ± 0.16

While there may be some residual uncertainty in the assumed sound velocity in Eq. (1) this is not enough to explain the discrepancy in I values and, as Berman has discussed at some length, there must be other phonon scattering centers, such as interstitial nitrogen, present in the natural type-IIa diamond.

While more detailed study of the composition and microstructure of the diamonds used by Berman and Vandersande would be needed to identify unambiguously the source of the additional phonon scattering, it is significant to note that the presence of only 70-ppm vacancies [$\Delta M/M = 1$ in Eq. (6)] is sufficient to explain the enhancement of I to 0.042 K^4/sec from the value of 0.0075 K^4/sec expected for 1.07% ^{13}C. An even lower concentration is sufficient if the additional scattering effects of the strain fields surrounding the vacancies are included.

Thermal conductivity of synthetic diamond gems. —We have measured the thermal diffusivity of several synthetic diamond gems with various isotopic compositions using a photoflash method described elsewhere [18]. This method gives a direct measurement of the thermal diffusivity α, without the additional corrections used by Vandersande, even for thin single crystals of diamond. The thermal conductivity $k(T)$ was obtained from $\alpha(T)$ using the well-known specific heat $C_p(T)$ of diamond [19] and the measured density ρ, which was assumed constant over our limited temperature range:

$$k(T) = \alpha(T)\rho C_p(T) . \tag{8}$$

The results obtained for nominally isotopically pure diamond (^{13}C < 0.05%) and for a synthetic gem with the natural abundance (1.07%) of ^{13}C are shown in Fig. 2. Also shown, for comparison, are the data points of Berman and Vandersande, used in our fitting procedure described above, which fall within the limited range of this graph. The data for the natural abundance synthetic gem fall very close to bridging the gap between the Berman and Vandersande data while the isotopically purer gem has $k(T)$ consistently higher: as much as 50% higher near 300 K.

To provide a valid comparison of the data for the two isotope compositions near room temperature we refitted the Klemens-Callaway model including our own data points between 300 and 550 K combined with those of Berman and Vandersande ranging from 10 to 1250 K. We again used the power $\zeta = 3$ for the umklapp scattering as described previously. The resulting A, B, d, and I parameters are shown in the second line of Table I. They agree within calculational uncertainty except for A. The
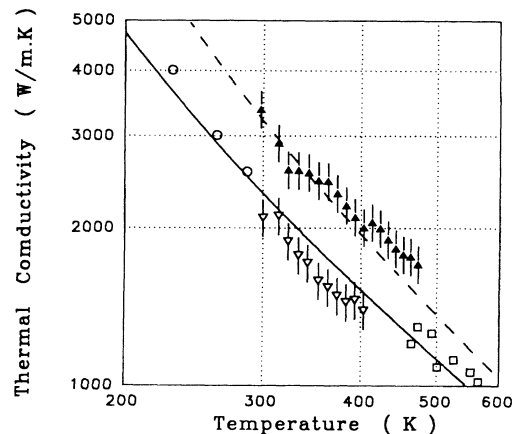

FIG. 2. Comparison of the temperature dependences of the thermal conductivities for the natural abundance and isotopically pure single crystals of the diamonds. The dashed line shows the Klemens-Callaway prediction for isotopically pure diamond. The solid line shows the temperature dependence of the thermal conductivity for natural abundance diamond as a result of the fit to Ref. [10] (circles), Ref. [11] (squares), and our data (open triangles for natural abundance diamond and solid triangles for isotopically pure diamond).

resulting smoothed fit is shown as the solid line in Fig. 2.

We then used the same parameters to calculate $k(T)$ with $I = 0$. The resulting curve, the dashed curve in Fig. 2, is an excellent fit to the data for the isotopically pure gem. We note that the difference between the two smoothed lines (solid and dashed) in Fig. 2 corresponds to a difference in the impurity parameter I more than 5 times greater than that appropriate for ^{13}C of 1.07% [i.e., $I_{\text{fit}}/I(^{13}\text{C}) = 5.4$].

We confirm from this analysis that the inherent thermal conductivity of isotopically pure diamond at room temperature is ~ 3500 W/mK, as reported here and by other investigators [2]. This is the value to be expected once the correct umklapp scattering parameters are identified. Natural type-IIa diamond and synthetic diamond with ^{13}C impurities must contain other phonon scattering centers which reduce their thermal conductivity below the "ideal" value expected with ^{13}C impurities alone.

As further evidence of this concept we present in Fig. 3 the room-temperature values of thermal conductivity for synthetic gems with a wide range of ^{13}C isotope concentrations including the data of ourselves and others [8,17]. The solid line is the Klemens-Callaway model prediction based on the parameters of Table I and the known concentration of ^{13}C atoms, assumed to be Rayleigh scattering centers which interact with phonons at a rate described by Eq. (5).

The measured conductivities agree with the curve at only two concentrations, both very low. At the second-highest concentration, measurements on two different gems give different thermal conductivities, one in agree-
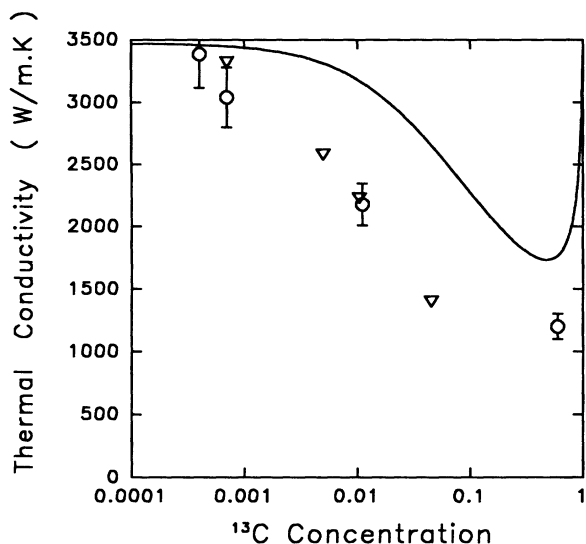
FIG. 3. The thermal conductivity of the synthetic diamond single crystals vs isotope content. The solid line represents the Klemens-Callaway prediction. The circles represent our experimental data and triangles represent the work of Anthony and Banholzer [7-9].

ment with the model, the other of lower conductivity. At all higher concentrations of ^{13}C the experimental points fall below the curve. The ratios $[I_{data}/I(^{13}C)]$ of the I values corresponding to the data points (I_{data}) to those corresponding to the isotope ^{13}C $[I(^{13}C)]$ range from 2.8 to 23.

It is not possible to form firm conclusions at present on the nature of the additional impurities incorporated into the synthetic diamond gems as the concentration of "impurity isotope" increases. We note, however, that a small change in lattice parameter with ^{13}C concentration has been reported recently [11] and that the isotopically pure synthetic gems are known to have a high degree of crystalline perfection [20]. While we can identify a low, virtually undetectable, concentration (~70 ppm) of lattice vacancies as adequate to explain the phonon scattering when the mass difference alone is considered we cannot claim that this scattering mechanism is unique. When the maximum amount of strain field [17] is considered the vacancy concentration may be as small as 1 ppm.

Analysis of $k(T)$ using a Klemens-Callaway model for natural type-IIa diamond between 10 and 1250 K has established the appropriate phonon scattering model and parameters for diamond, most importantly the correct power ($\zeta=3$) of the umklapp scattering term. Comparison of our newly reported data for the isotopic dependence of k at room temperature and of $k(T)$ near room temperature with this model leads to the conclusion that isotopically pure diamond should have a thermal conductivity of 3500 W/mK at room temperature and that phonon scattering processes additional to isotope scattering explain the attenuated value of ~2300 W/mK obtained for natural type-IIa diamonds and natural abundance synthetic diamond gems at room temperature. Measurements of $k(T)$ over a wider temperature range and for a wider variety of isotopic compositions than reported here would provide very valuable further insight into this intriguing question.

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