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Thermal Conductivity of Natural and Synthetic Diamonds with Differing Isotope Contents

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ABSTRACT

The temperature-dependent thermal conductivity k(T) between 90 K and 550 K of CVD (chemical vapor deposition) diamond films, and the room-temperature thermal diffusivity $\alpha(300)$ of synthetic diamond gems with different isotopic compositions, have been measured. In addition previous k(T) data for natural Type IIa diamond between 10 K and 1200 K were reanalyzed. Analysis of k(T), using a comprehensive Klemens-Callaway model, was directed towards understanding factors affecting the dramatic enhancement of room-temperature thermal conductivity k(300) of diamond gems with increasing isotopic purity. We conclude that phonon-isotope scattering in diamond gems alone is ineffective in explaining the k(300) differences. Other factors such as isotope clustering or phonon-vacancy and other point defect scattering must also contribute to the reduction in thermal conductivity.

INTRODUCTION

Applications for diamond in a wide range of technologies has stimulated interest in its synthesis by a variety of routes including both films and gems. Synthesis has been extended to compositions in which the isotopic composition may be varied in a controlled manner. The synthetic diamond materials now available have generated a new wave of measurements of thermal conductivity of diamond after a quiescence of a quarter of a century.

Diamond has long been recognized as having the highest thermal conductivity of any dielectric material at room temperature. In his successive analyses of materials with potential for high thermal conductivity Slack (1987) identified the preferred adamantine crystal structure combined with a high Debye temperature and a small Grueneisen constant as key enhancement parameters. Recent interest in the thermal conductivity of diamond has been stimulated by the unexpected discovery by Anthony et al. (1990) of a 50% increase in k(300) when the isotopic impurity ^{13}C was decreased by a factor of 15 from the natural abundance of isotopes.

This enhancement could not be attributed to phonon-isotope scattering alone even if this scattering was at the level predicted theoretically. A new model, the "smeared phonon dispersion" (SPD) was introduced by Bray and Anthony (1990) to explain the enhancement. In this model the presence of the second isotope (^{13}C) at random sites in the ^{12}C lattice smears the phonon dispersion and increases the phonon-phonon Umklapp scattering. It was proposed that removal of the ^{13}C sharpens the phonon dispersion with a resulting dramatic increase in the thermal conductivity in the "isotopically pure" material compared with the "natural abundance" diamond. However, recent application of the CPA (coherent-potential approximation) model and Raman spectroscopy to diamond does not show enough effect on the phonon dispersion to explain the room-temperature thermal conductivity k(300) enhancement (K.C. Hass et al. 1992).

In order to investigate further the source of the enhanced thermal conductivity of isotopically pure diamond, we have analyzed our own data on k(T) for CVD (chemical vapor deposition) films of two distinct isotopic compositions and re-analyzed k(T) of natural Type IIa diamond. A comprehensive Klemens-Callaway model previously applied (Dinwiddie and Onn, 1990) to AlN was used in the analysis. Our analysis of type IIa diamond shows that the phonon-point defect scattering contribution in diamond is far smaller than that used in the analysis of k(T) by Morelli et al. (1985). It is still however about 5 times larger than the prediction of point defect scattering considering the mass difference for isotopes only (Klemens, 1958) indicating that scattering by other mechanisms must also be considered.

This model is also capable of explaining the strong dependence of k(300) on the isotopic concentration in the synthetic gems provided that other scattering mechanisms exist (e.g. isotopic clusters or lattice vacancies). Further data for k(300) of synthetic diamond gems is also presented here for the first time. Both new and previously published room temperature thermal conductivities k(300) of synthetic diamond gems are re-analyzed in light of this new evidence.

As part of the present study we have found it enlightening to re-analyze the k(T) data of Berman (1975) between 10 K and 300 K, in combination with k(T) of Vandersande (1991) above 600 K, for natural Type IIa diamond, since these combined data provide k(T) values over ranges of two orders of magnitude in temperature and three orders of magnitude in thermal conductivity. This new analysis identifies unambiguously the temperature dependence of the phonon-phonon scattering relaxation time for diamond establishing the power of T in the umklapp term to be three. As a result the enhancement in thermal conductivity for isotopically pure diamond gems can be explained either by the reduction of both isotopic impurities and other crystallgraphic point defects or by changes of the umklapp parameters due to the change in isotope concentration (but see *"Note added in proof"* below).

EXPERIMENTAL

The thermal conductivity of free-standing diamond film samples was measured between 90 K and 500 K using a guarded longitudinal-bar system designed to minimize errors attributable to thermal radiation up to at least 550 K. The film samples are surrounded by a thermal guard whose temperature gradient is controlled to match that of the sample. The entire assembly in turn is enclosed within a uniform furnace, the temperature of which is also controlled to provide an ambient temperature matched to the average temperature of the sample. The film samples measured were about 5 cm x 0.8 cm x 0.06 cm. Type K thermocouples about 2 cm. apart were used as temperature sensors, with heat input provided by a small wire-wound heater. The system has been described previously in detail (Dinwiddie, 1986).

The free-standing diamond films were synthesized at the General Electric Company using CVD techniques. The natural-abundance film contained 1.1% of ^{13}C while the "pure" film contained only 0.04% of ^{13}C as determined by mass-spectroscopic analysis of the combustion products of pieces of the films. Since the films were of uneven thickness a travelling microscope was used to measure thicknesses at three or more points along the samples. The thermal conductivity measurement results are presented in Figure 1.

Our in-plane room temperature values of k for the natural-abundance film were comparable to those obtained transverse to the same films using the mirage technique (Anthony et al., 1990) and perpendicular to the films using an ac diffusive heat wave technique (also known as 3ω technique) (Anthony, 1991). The differences may be attributed to the expected variations with position and to anisotropy due to the differing grain-boundary separation in-plane and transverse to the films. The k(T) we measured between 90 K and 300 K is comparable to that recently reported by Morelli et al. (1988) for similar films.

Thermal diffusivities $\alpha(300)$ of diamond gems at room temperature were measured using a flash-diffusivity technique. The values of k(300) were calculated using the expression:

$$k = \alpha \rho C_p \tag{1}$$

while density and specific heat of the gems at room-temperature is quoted from the

Handbook of Chemistry and Physics (Weast, 1987). Typical gem dimensions in the measurement direction exceeded 1 mm. Details of the technique will be published elsewhere (Witek and Onn, 1991)

EXPERIMENTAL RESULTS

The k(T) measurements for the two films are shown in Fig. (1). The data show a very similar temperature dependence up to 300 K but, surprisingly, the natural-abundance film has the higher thermal conductivity at all temperatures. Our subsequent quantitative Klemens-Callway analysis will show, as is apparent from the lowest-temperature data in Fig. (1), that much of this difference is attributable to a larger grain-size in the natural-abundance film. Above about 400 K k(T) is determined largely by phonon-phonon scattering though the grain size effect still contributes.

It is significant that the data for the "pure" and "natural abundance" films fall very close together despite their differing isotopic compositions. The impact of isotopic impurities on k(T) are obscured by the effects of grain sizes and other impurities even though the impurity contributions dominate near the peak in k(T)

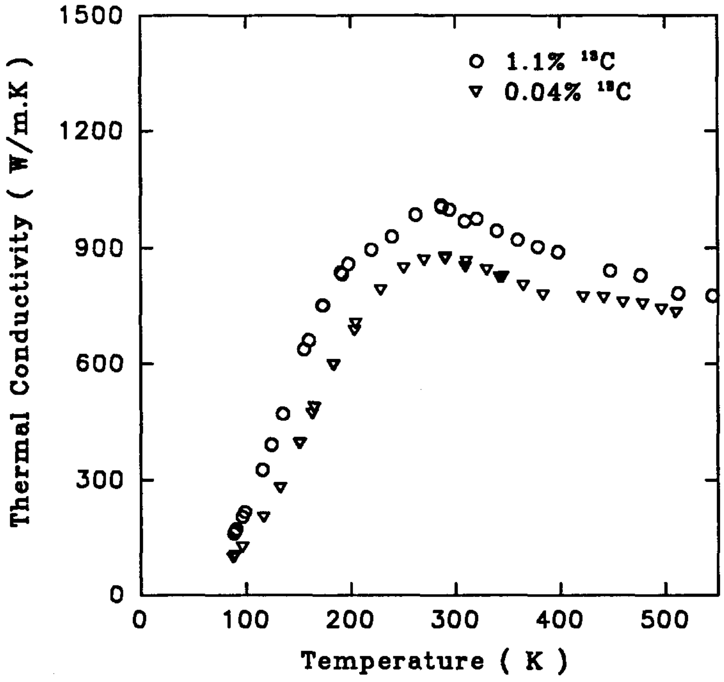

Figure 1. Temperature dependence of the thermal conductivity of two CVD diamond films with differing isotope content.

TABLE 1

Isotope dependence of the thermal conductivity of synthetic diamond gems at room temperature. Source: (a) this work; (b) Anthony et al. 1990.

Percent of ^{13}C	Thermal Conductivity k [W/(m.K)]	Source
0.04	3400 ± 100	a
0.07	3050 ± 60	a
0.07	3320	b
0.5	2580	b
1.04	2230	b
1.1	2180 ± 60	a
4.54	1400	b
~60	1140 ± 30	a

(~270 K). In other words, the isotopic concentrations of both films are too small to observe the isotope effect on k(T). A higher isotope ^{13}C content is needed to significantly reduce k(T) so that the effect can be observed.

In TABLE 1 we summarize the k(300) results for gems with a range of isotopic contents. These results show the strong dependence of k(300) on isotopic content which, at first sight, appears contradictory to the film results shown in Fig. (1). Quantitative analysis of the k(300) gem data is limited at present by uncertainties in the precise isotope ratios; these uncertainties will be removed by future non-destructive analysis.

ANALYSIS AND DISCUSSION

A. Klemens-Callaway Model for k(T)

The first suggestion that the isotope scattering contribution alone was ineffective in explaining the k(300) enhancement for isotopically pure diamond was made by Bray and Anthony (1990). Their analysis was limited to the "dominant phonon approximation" approach since only k(300) data was available at the time. This approach may be valid for large single-crystal gems at 300 K, where phonon-phonon scattering will dominate but with small contributions from impurity and isotope scattering, and from grain-boundary scattering.

It cannot be applied as readily to the film data of Fig. (1), where the peak thermal conductivity is at the center of the temperature range, and phonon scattering from isotopes, impurities, grain boundaries and other phonons will contribute more significantly over much of the temperature range for which data exists.

We have analyzed k(T) both for natural Type IIa diamond and for data of Fig. (1) for the pure and natural films, using a comprehensive Klemens-Callaway model (Dinwiddie and Onn, 1990). This model assumes an ideal Debye phonon spectrum and includes the phonon scattering through an overall phonon relaxation time $\tau(x)$. The thermal conductivity is then given by (Klemens, 1958 and Callaway, 1960):

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

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

$$x = \frac{\hbar\omega}{k_B T} \,, \tag{3}$$

where ω is the phonon frequency. In the case of diamond it is critical that analysis be carried out using the full Klemens-Callaway analysis since dominant phonon approximations typically make simplifying assumptions about the specific heat, such as that it is a constant. This is not the case for diamond, where Θ is 1860 K. The specific heat of diamond is, however, very well described, at least above about 50 K, by a simple Debye model, as reflected in Eq. (2). Only below about 50 K does the effective Debye temperature rise to 2250 K.

The phonon relaxation or scattering time $\tau(x)$ in Eq.(2) is obtained under the assumption that the relaxation times for all scattering processes are independent so that

$$\tau(x)^{-1} = \tau_g^{-1} + \tau_p^{-1} + \tau_u^{-1} \,, \tag{4}$$

where the relaxation time for each scattering process is given by

$$\tau_g^{-1} = v/1.12d \tag{5}$$

for grain boundary scattering, where v is the average phonon velocity and d the average grain boundary separation;

$$\tau_p^{-1} = I x^4 T^4 \tag{6}$$

for point defect scattering, which includes isotope scattering. I is related to the impurity or isotope concentration c_i by:

$$I = \frac{c_i a^3 k^4}{4\pi v^3 \hbar^4}\left(\frac{\Delta M}{M}\right)^2 , \tag{7}$$

where ΔM is the mass deficit associated with the point defect in a lattice with atoms of mass M, a is the atomic spacing and v is the velocity of sound. Equation (7) is valid only for small concentration of impurities with mass difference as the only effect of scattering.

The form of τ_u appropriate for describing Umklapp scattering has been the subject of much debate. The expression:

$$\tau_u^{-1} = Ax^2T^{\zeta}\exp(-B/T) \tag{8}$$

where A and B are constants, is generally accepted. The exponential constant B is also frequently expressed in terms of the Debye temperature and a fraction, b, where

$$b = \frac{\Theta}{B} , \tag{9}$$

with typical values of b ranging from 2 to 10.

Greatest uncertainty occurs for the power ζ of the temperature. Theoretical models give powers ranging from 1 to 8, while experimental studies indicate values between 3 and 5. The uncertainty arises from several sources, including the relative roles of normal and Umklapp scattering processes, the influence of radiative T^3 contributions at high temperatures, and, frequently, a lack of data for a wide enough temperature range to determine ζ unambiguously.

In fitting Eq.(2) to k(T) data we may use up to four unknown parameters, A, B, I and d from Eqs. (4, 5, 6,and 8). The nonlinear least square fitting is carried out on a SUN-4 mainframe computer. Eq. (2) is particularly suitable for this fitting approach because the various relaxation times influence k(T) at different points within the temperature range. We have previously used this approach to analyze k(T) of AlN substrates (Dinwiddie, 1991, Dinwiddie and Onn, 1990). In the case of AlN, the resulting impurity concentration and grain-size parameters compared very well with independent measurements, and the A and B parameters were consistent with the range expected for AlN.

B. Analysis of k(T) for Natural Type IIa Diamonds

Unfortunately the thermal conductivity data of Berman (1975) on natural Type IIa diamonds between 12 K and 300 K did not extend over a wide enough range of T to determine ζ unambiguously. This data has been supplemented very recently by

Vandersande et al. (1991) who extended measurements on Type IIa diamonds up to 1200 K. We have combined the two data sets and tried to fit Eq.(2) using different values of ζ.

The combined k(T) data for natural Type IIa diamond is shown in Fig. (2). Fits of Eq.(2) to values for ζ of 2, 3, 4, and 5 are shown. The curve for $\zeta = 3$ clearly provides an excellent fit when the data above 600 K is included, while all four umklapp powers provide comparably good fits for Berman's data below 300 K. The fit to $\zeta = 2$ is as divergent as the fit to $\zeta = 4$ above 600 K, but in different directions. The fit to $\zeta = 5$ is worst of all in the temperature range above 600 K. It is important to note that the fit with $\zeta = 3$ leads to an almost exact k ~ 1/T behavior at the highest temperatures, as observed in many materials other than diamond. On the low temperature end, the fit curve tends to T^3 as expected.

The parameters resulting from the fit with $\zeta = 3$ are given in TABLE 2. The B parameter gives a reasonable value of b = 3.7. Parameter A, which is related to the phonon-phonon scattering mean free path is also reasonable. The average "thermal" grainsize of 0.7mm is a large fraction of the sample dimensions (which is 1.0mm × 1.0mm) but typical of values in natural Type IIa diamonds, which are of

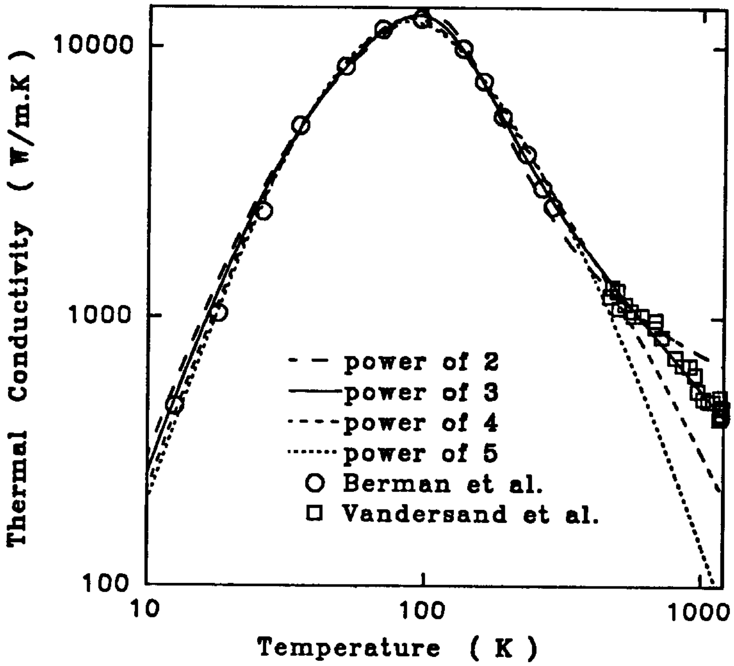

Figure 2. Combined data for k(T) for natural Type IIa diamond gems from Berman (1975) and Vandersande (1991). Smoothed lines represent fits of Eq. (2) with $\zeta = 2, 3, 4$, and 5. See text for further details.

TABLE 2

Parameters resulting from fitting the Klemens-Callaway model (Eq. 2) to the k(T) data for three diamond materials.

Sample	A	B [K]	b	I	g [m]
Natural Type IIa	690 ± 70	508 ± 10	3.7	$4.0 \pm 0.4 \times 10^{-2}$	$7.1 \pm 0.7 \times 10^{-4}$
High Purity Film	780 ± 100	390 ± 20	4.8	*	$3.8 \pm 0.8 \times 10^{-7}$
Natural-Abundant Film	680 ± 80	326 ± 8	5.7	*	$6.6 \pm 1.4 \times 10^{-7}$

the highest grades of the natural single crystals. The accuracies in the fit parameters were obtained by adding ± 10% to the actual data of thermal conductivity and fitting the result sets.

The point defect parameter I = 0.040 is an order of magnitude different from the value I = 0.346 reported by Morelli et al.(1988) but is comparable to the value I = 0.034 reported by Berman and Martinez (1976) for the 1.1% ^{13}C isotope concentration of natural type IIa diamond. Using Eq.(7) we obtain $I_7 = 0.0075$. There are two possible reasons for the discrepancy of the fit value from I_7, (1) impurity clustering, and (2) other point impurities also contribute to the point defect scattering. When the clustering alone is considered, an average clustering of 5 ^{13}C atom will cause the impurity parameter to increase by a factor of 5 under the Rayleigh scattering of the point defects, while 1 ppm vacancies in the crystal will cover the same effect. This result suggests that Eq.(7) provides an upper limit of the role of isotope scattering in diamonds, a conclusion which we will corroborate below in analysis of our diamond film k(T) data. If this conclusion is correct then isolated isotopic purification alone cannot explain the variations of k(300) given in TABLE 1.

C. Analysis of k(T) for the CVD Diamond Films

Our present data on the isotopically pure and natural-abundance diamond films shown in Fig. (1) extend over a wide enough temperature range to permit fitting to Eq. (2), with four resulting parameters A, B, I and d. We used $\zeta = 3$ in Eq.(2) for the Umklapp scattering expression.

The parameters obtained from these fits are listed above in TABLE 2. The A parameters are both comparable to the value obtained for Type IIa, while the B parameters are both smaller. The different trends in k(T) above 400 K in Fig. (1) are directly attributable to the difference in B values: for samples of the same grainsize the pure film would be a better conductor above 400 K because of the lower value of B. We note also that, for the same grain size, at relatively high temperatures (say higher than 100 K),the natural film would not be a better thermal conductor than the Type IIa diamond, because of the smaller value of B.

The I parameters for the natural-abundance film, 1.1% ^{13}C, and for the isotopically enriched film, 0.04% ^{13}C, are much smaller than that for the Type IIa diamond. These indicate the possibility that the temperature range higher than the temperature at which thermal conductivity peaks may not be large enough to accurately determine the umklapp parameters. Although these films are of high purity chemically, other than their isotope content, there are many other crystallographic defects in the films.

The thermal grainsize values,d, for the two films obtained from analysis are different, but both fall within a reasonable range for CVD films. It must be emphasized that this thermal grainsize will not necessarily correspond exactly with gross grainsizes as determined by SEM. Phonon scattering may occur at relict grain boundaries within gross grains, as has been shown to be the case for AlN, through TEM analysis of individual gross grains (Youngman et al., 1990). For this reason we call parameter d the "thermal grainsize".

D. Discussion of Diamond Gem k(300) Data

The isotope dependence of k(300) for synthetic diamond gems is summarized in TABLE 1. Analysis by Bray and Anthony (1990) using the "dominant phonon approximation" first suggested that $B_{pure} > B_{nat}$ (using the parameters from this work, $b_{nat}/b_{pure} = 1.45$). The B values they obtained were smaller than those listed for the films in TABLE 2 from the full Klemens-Callaway analysis, although we find $b_{nat}/b_{pure} = 1.2$ for the films.

Preliminary analysis of a limited range of k(T) data for two of these gem compositions gave values of A and B are comparable to those for the films, but the B values are without a similar ratio of b_{nat}/b_{pure}. Combining this preliminary result with our analysis above suggests that the Umklapp parameter B may depend upon the isotope content, while parameter A may not. It is now known, for instance, that synthetic gems have much narrower Bragg X-ray peaks, typically 12 to 17 arcsec, than are found for naturally occurring diamonds (Holloway et al., 1991). Further analysis of k(T) for the gems will be published elsewhere.

SUMMARY AND CONCLUSIONS

We have analyzed k(T) for natural Type IIa diamond and for two CVD diamond films, one nominally isotopically enriched with ^{12}C (99.96%) pure and the other having the natural isotopic content (98.9%). We also report new measurements of room-temperature thermal conductivity k(300) for synthetic diamond gems of varying isotopic content. We conclude that:

(i) in part because of the high Debye temperature, a full Klemens-Callaway analysis of k(T) is necessary in order to clearly separate the different contributions to phonon scattering in diamond;

(ii) the correct power of T in the phonon-phonon Umklapp-scattering relaxation time in natural type IIa diamond is 3, and this value appears to be appropriate for other forms of diamond;

(iii) for natural Type IIa and for synthetic diamond films the Klemens-Callaway model fit provides physically reasonable values of the thermal grain-size;

(iv) the phonon-point defect scattering is almost an order of magnitude weaker than previously reported, and is five times stronger than the prediction based on Rayleigh scattering of individual isotope impurity;

(v) the Umklapp exponent parameter B may be sensitive to isotope content, as well as crystal perfection, decreasing with increased isotopic purity, and this sensitivity is the basis of the phonon-smearing theory of isotope alloys.

From these conclusions it appears that at least two possible factors may contribute to the enhancement of k(300) for the isotopically pure synthetic gems. One is the possible change in the phonon-phonon Umklapp scattering contribution due to an isotope-dependent contribution to the B parameter accompanied by a crystal-perfection influence in A. The second possibility is that the removal of ^{13}C impurities is accompanied by a reduction of other phonon-scattering defects, thus enhancing k.

The isotope scattering contributions are too small to be determined in the case of natural CVD diamond film and isotopically enriched CVD diamond film in the presence of small grain size and many other crystallographic defects. A diamond film of 20% to 50% ^{13}C is needed to clearly observe the isotope scattering effect in films.

Further measurements of k(T) for a wider range of isotopic compositions of diamond with samples synthesized by several techniques which give differing degrees of crystalline perfection will be needed to verify these provisional conclusions.

Note added in proof: Our further analysis of k(T) for diamond gems supports the concept that the enhancement of k in isotopically pure gems is due to the elimination of other phonon-scattering defects in addition to the ^{13}C impurity atoms (Onn et al, 1992)

REFERENCES

Anthony, T.R., Banholzer, W.F., Fleischer, J.F., Wei, L.H., Kou, P.K., Thomas, R.L., and Pryor, R.W., 1990. "Thermal Diffusivity of Isotopically Enriched ^{12}C Diamond", Physical Review B, pp. 1104-1111.

Anthony, T.R., Fleischer, J.L., Olson, J.R., and Cahill, D.G., 1991. "Thermal Conductivity of Isotopically Enriched Polycrystalline Diamond Films," J. Appl. Phys., **69**, 12, pp. 8122-8125.

Berman, R., Hudson P.R.W., and Martinez, M.J., 1975. Phys. C: Solid State Phys. **8**, L430-434.

Berman, R., and Martinez, M.J., 1976. Diamond Res. 7, 7-13.

Bray, J.W., and Anthony, T.R., 1990. "Comparison of Models for Predicting the Thermal Conductivity of Diamond with Different Isotope Compositions", Proceedings 2nd International Conference on the New Diamond and Science Technology, Materials Research Society, Washington, DC.

Callaway, J., 1960. "Effect of Point Imperfections on Lattice Thermal Conductivity", Phys. Rev. **120**, 4, 1149.

Dinwiddie, R.B., 1986. "An Apparatus for the Measurement of Thermal Conductivity in the Temperature Range 80 K to 550 K", M.S. Thesis, University of Delaware.

Dinwiddie, R.B., and Onn, D.G., 1990. "Temperature Dependence of the Thermal Conductivity of Materials for Microelectronic Packaging: Measuring and Modelling Effects of Microstructure and Impurities", Materials Research Society Symposium Proceedings Vol.167 "Advanced Electronic Packaging Materials" (MRS, Pittsburgh, PA)

Hass, K.C., Tamor, M.A., Anthony, T.R., and Banholzer, W.F., 1992. Phys. Rev. B, **45**, 13, 7171-7182.

Klemens, P.G., 1958. "Thermal Conductivity and Lattice Vibrational Modes", Solid State Physics: Advances in Research and Applications, Volume 7 Edited by Seitz and Turnbull, Academic Press, pp. 1-98.

Morelli, D.T., Beetz, C.P., and Perry, T.A., 1988. "Thermal Conductivity of Synthetic Diamond Films", J. Appl. Phys. **64**, 3063-3066.

Onn D.G., Witek A., Qiu Y.Z., Anthony T.R. and Banholzer W.F., 1992. "Some Aspects of the Thermal Conductivity of Isotopically Enriched Diamond Single Crystals", Phys. Rev. Letts. **68**, 2806-2809.

Slack, G.A., Tanzilli, R.A., Polh, R.O., and Vandersande, J.W., 1987. "The Intrinsic Thermal Conductivity of AlN", J. Phys. Chem Solids **8**, 7, pp 641-647.
Weast, R.C.(Editor-in-Chief), 1987. Handbook of Chemistry and Physics, 1987. 67th edition, CRC press, Boca Raton, Florida.

Vandersande, J.W., Vining, C.B., and Zoltan, A., 1991. "Thermal Conductivity of Natural Type IIA Diamond Between 500 K and 1250 K", Electrochemical Society Spring Meeting.

Youngman, R.A., Harris, J.H., Labun, P.A., Graham, R.J., and Weiss, J.K., 1990. "Inversion Domain Boundaries and Oxygen Accommodation in Aluminum Nitride", Materials Research Society Symposium Proceedings Vol.167 "Advanced Electronic Packaging Materials" (MRS, Pittsburgh, PA).