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Phonon transport in amorphous carbon using Green–Kubo modal analysis

Wei Lv[1] and Asegun Henry[1,2,a]

[1]*George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*
[2]*School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, USA*

Amorphous carbon (a-C) is an important material often used in microelectronics. Using a recently developed approach, termed Green–Kubo modal analysis, we were able to calculate the thermal conductivity of a-C, which yielded excellent agreement with experiments, by employing a simple correction to the specific heat. The results show that the heat capacity substantially limits the thermal conductivity of a-C at room temperature and it is dominated by contributions from diffusons between 10 and 40 THz. Furthermore, the phonon relaxation times in a-C do not vary significantly with increasing temperature, which is quite unusual by comparison with the behavior observed for other materials. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4948605]

Amorphous carbon (a-C) layers, also known as diamond-like carbon (DLC) films, have been widely applied as solid lubricants, protective coatings, and wear-resistant coatings.[1–3] The tribology of a-C coatings has been the subject of intensive studies for the last 20 years, and a number of experiments have also examined the tribological properties of a-C films.[4–6] Also, more recently, heat-assisted magnetic recording (HAMR) shows a great potential of increasing data density for hard disk storage[7–9] and understanding heat conduction in HAMR devices becomes crucial, because of the introduction of a laser as a heat source in the system.[10] In order to facilitate high power density heat dissipation to the environment, the thermal conductivities of the lubricant layer, DLC films, and media layers become very important.

Prior work has measured the thermal conductivity of a-C layers,[11,12] but the phonons that are responsible for its thermal conductivity have yet to be determined, which would highlight any potential pathways toward increasing it. Molecular dynamics (MD) simulations are often used to study thermal transport, but equilibrium MD, via the Green–Kubo (GK) formula, predicts the thermal conductivity of a-C to be very high ($>15\,\mathrm{W\,m^{-1}\,K^{-1}}$) at room temperature, which is inconsistent with the experiments ($\sim 3\,\mathrm{W\,m^{-1}\,K^{-1}}$). This, however, is most likely due to the fact that MD is a classical method and therefore is unable to capture the quantum effects on the mode heat capacity at low temperatures. The notion of low temperature nonetheless is relative, as it generally refers to the temperature regime where the majority of the phonons reside in their ground state. For carbon materials, such as diamond, graphene,[13] and amorphous carbon, at room temperature the heat capacity is far below Dulong–Petit limit, which shows that most of the vibrational modes (60%) are not excited. As a result, for the temperature regime where the heat capacity is far below the Dulong–Petit limit, the GK method using classical MD is generally understood to be inapplicable. However, it may be possible that the discrepancy between classical MD-GK predictions and experiments could be resolved if one knew the contributions of different phonons made to the thermal conductivity as a function of phonon frequency, since the heat capacity of phonons only depends on their frequency and temperature. One could then presumably apply a quantum correction to the phonon/normal mode heat capacities to obtain reduced contributions for the many modes that are not fully excited, thereby resulting in a reduced thermal conductivity that might agree more properly with experiments. This approach has been employed previously by Lv and Henry, and excellent agreement with experiments was obtained for amorphous silicon (a-Si) and silica (a-SiO$_2$).[14,15]

Turney and McGaughey[16] have shown that applying such quantum specific corrections to crystalline materials is not in general rigorously correct, because it ignores a second quantum effect, namely, that reduced modal amplitudes affect not only the mode heat capacities but also the mode–mode interactions. This effect is intuitive, since the time it takes for a mode to couple to other modes is largely dependent on the amplitudes of the other modes, which is why wave packet studies require the amplitudes of all other modes to be zero.[17] However, one can envision instances where this second effect, which manifests itself in classical MD simulations as shorter relaxation times, can become negligible. For example, when the phonon–phonon interactions are more so dictated by the structure/composition as opposed to the intrinsic anharmonic coupling between low and high frequency phonons, it is possible that another mechanism will dominate the low frequency phonon–phonon interactions—which are the only interactions that remain important at low temperature, where most modes are not excited. Several examples of this situation could be a crystal at low temperatures, where the relaxation times are limited by the sample boundaries; a nanostructure (i.e., a nanowire) where the relaxation times are limited by its boundaries; a random alloy where the relaxation times are limited by point defect scattering; or presumably an amorphous material, where it is not clear if the relaxation times are an appropriate descriptor for the mode thermal conductivity.[18] In all of these cases, it is possible that a simple heat capacity correction will be

a)Author to whom correspondence should be addressed. Electronic mail: ase@gatech.edu

sufficient and will therefore yield good agreement with experiments as was found previously by Lv and Henry.[14,15] Nonetheless, it is important to acknowledge that applying a quantum correction only to the heat capacity is not formally correct, although it may yield accurate predictions if the second effect is negligible.

The primary reason the dominant phonons in a-C are unknown is because the traditional thermal conductivity analysis methods that have been proven and applied to crystals become highly questionable in an amorphous material.[15,18] The key difference is the fact that the structural disorder in an amorphous material changes the fundamental character of the vibrational modes. In amorphous materials, the normal modes of vibrations (e.g., phonons) are differentiated into three categories, namely, propagons, diffusons, and locons.[19,20] Propagons and diffusons are both delocalized modes,[20,21] but only propagons exhibit spatially periodic repeating vibrations that correspond to that of a propagating mode. These vibrations typically exhibit sinusoidal modulated displacement/velocity profiles similar to the phonons in crystalline materials. As a result, one can define their wavelength, wave-vector, and velocity, allowing them to be treated by expressions based on the phonon gas model (PGM).[22] Diffusons, however, do not propagate, since there is almost no spatial periodicity in their vibrations. This then prevents one from defining their wavelength, wave-vector, and velocity, which then prevents rigorous invocation of expressions for their contribution to thermal conductivity based on the PGM.

The problem is then that the majority of the modes in disordered materials are diffusons[14,21] and Allen and Feldman[19,21,23] developed the first scheme for assessing their thermal conductivity contributions without using PGM. However, although the A-F method explains the qualitative temperature dependence of thermal conductivity in a-Si,[19] it is quantitatively less accurate for other amorphous materials.[24] Recently, Lv and Henry, however, developed an alternative method, termed Green–Kubo modal analysis (GKMA) which is similar in spirit to the A-F method, but is more general in the sense that it can be uniformly applied to all phonons/normal modes without modifications based on the mode character, and it naturally includes temperature dependent anharmonicity, which was absent in the A-F model. In this sense, GKMA can treat both ordered crystals and disordered materials through one unified formalism. The GKMA method reproduces the results of other accepted methods for crystals and yields excellent agreement with experiments for a-Si and a-SiO$_2$ when a quantum correction is applied to the mode heat capacity.[14,15] In the following we show that GKMA also accurately reproduces the experimentally measured thermal conductivity of a-C, and also elucidates which phonons are responsible for it.[14]

Equilibrium MD simulations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).[25] The a-C structure is generated using a melt-quenching method as described by Li et al.[26] and we used the modified Tersoff potential[27] proposed by Sha et al.[28] that has been tested to accurately reproduce the mechanical properties of DLC and DLCH (hydrogenated diamond-like carbon). In order to offer the most fair comparison with the experimental results, we used a DLC structure with a density of 3.0 g/cm^3, which is identical to the DLC measured in the experiments.[11] This is important, because the thermal conductivity of a-C is known to depend strongly on the density, which ultimately determines the sp^2/sp^3 bonding ratio (e.g., graphite/diamond like bonding). After quenching the structure to the desired density (3.0 g/cm^3), we relaxed the structure first using a constant number of atoms, volume, and temperature (NVT), for 500 ps. After equilibration, all simulations are run with 0.25 fs time-step under NVE ensemble for 5 ns to collect sufficient statistics for the thermal conductivity computation. The total heat flux and mode heat flux are calculated every 5 fs to save computational time, and it was verified that the total thermal conductivity does not change with the frequency of the heat flux calculations (i.e., outputting the heat flux every 5 fs yields the same answer as every 0.25 fs). The lattice dynamics calculations were conducted in the General Utility Lattice Program (GULP),[29] which resulted in the eigenvectors and frequencies.

Figure 1(a) shows the inverse participation ratio (IPR) of modes in a-C at different frequencies,[14,19] which highlights the third category of modes, which are termed locons. Locons are localized modes that typically occur at high frequencies, as one can see that the transition between diffusons and locons occurs around 65 THz, also indicated by the gray
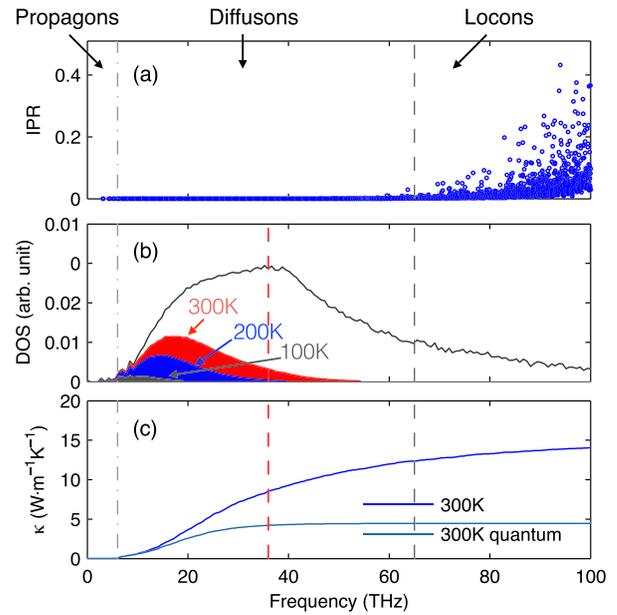
FIG. 1. (a) IPR of modes in a-C; the dashed-dotted line represents the cutoff (6 THz) between propagons and diffusons, which is estimated from checking vibrational shapes; the gray dashed line represents the cut-off (65 THz) between diffusons and locons, which is estimated from IPR of modes; (b) the black curve is the phonon density of states of a-C; the three color-shaded areas demonstrate how Bose–Einstein statistics suppress the heat capacity associated with certain modes, which was calculated by multiplying the quantum correction ($\frac{c_{quantum}}{c_{classic}}$) times density of states. The red, blue, and gray regions represent 300 K, 200 K, and 100 K, respectively, and the suppression is significant for all three temperatures. The red dashed line represents the cut-off frequency (36 THz) where the modes have non-negligible contribution to the thermal conductivity at 300 K. The modes with higher frequency have negligible contribution to the thermal conductivity at 300 K. (c) Thermal conductivity accumulation vs. mode frequency for a-C using GKMA at different temperatures with and without the quantum specific heat correction.
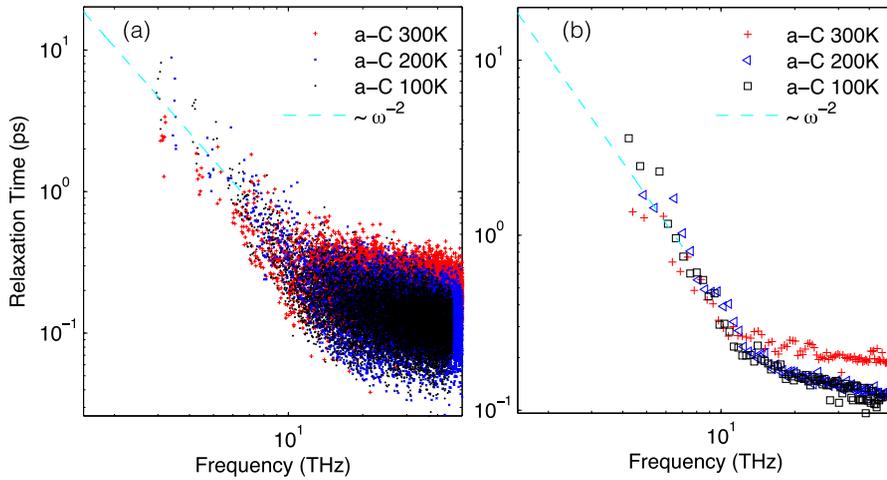
FIG. 2. (a) Relaxation times calculated from time-domain normal mode analysis at different temperatures (100 K, 200 K, and 300 K) for a-C. The low frequency modes' relaxation times decay proportional with ω^{-2}. The relaxation times change minimally between 100 and 300 K. (b) The averaged relaxation times vs. frequency. The mean relaxation times are calculated in equal frequency (0.45 THz) intervals, which then more clearly shows the minimal differences in relaxation times as temperature changes.

dashed line. Since the locons are not excited at room temperature, they are unable to contribute to the thermal conductivity. The cut-off between propagons and diffusons happens at around 6 THz as shown by the gray dashed-dotted line in Fig. 1. The cut-off frequency is estimated by inspecting the normal mode shapes. Figure 1(b) shows the calculated density of states (DoS) for a-C and the color-shaded regions represent the specific heat suppression function times DoS, $DoS(\omega) \cdot \frac{C(\omega)_{quantum}}{C(\omega)_{classic}}$ at three temperatures (100 K, 200 K, and 300 K). At Dulong–Petit limit, the classic volumetric mode specific heat is $\frac{k_B}{V}$, which is a constant. Hence, the area under the black DoS curve is proportional to the Dulong–Petit specific heat. And the areas of the color-shaded zones represent the quantum corrected specific heat at the three temperatures. Fig. 1(c) shows the thermal conductivity accumulation with and without the heat capacity quantum correction at room temperature (300 K). The red dashed line represents the cut-off frequency where the mode thermal conductivity contribution becomes negligible (36 THz) at 300 K. Due to the stiff bonds and light mass of carbon atoms, the frequencies in a-C are high. Consequently, Figs. 1(b) and 1(c) show that only a small fraction of the modes (<40%) can contribute to the thermal conductivity at room temperature.

Figure 2 shows the relaxation times for low frequency modes (<40 THz) at multiple temperatures (100 K, 200 K, and 300 K), calculated using time domain normal mode analysis.[15,30] The mode relaxation times decay rapidly following a ω^{-2} trend for the modes below 8 THz, as indicated by the cyan dashed line in Fig. 2. Another interesting observation is that the relaxation times are not strongly temperature dependent, which is different from a-Si and a-SiO$_2$.[14,15] Figure 2(b) shows the mean relaxation times averaged in a 0.45 THz interval. It is obvious that the relaxation times do not change significantly when increasing temperature, and the relaxation times of the modes with frequency between 10 and 40 THz even increase at 300 K. In order to quantify the change in relaxation times with temperature, we compared the ratio of the relaxation times at 300 K to 100 K for a-C and a-Si. As shown in Figure 3(b), the relaxation times reduce from 100 K to 300 K in a-Si, where on average the values at 300 K are ~58.8% of their values at 100 K. This is due to the increased anharmonicity and interactions with other modes, which reduce the time a mode can remain

correlated with itself. However, in Fig. 3(a), the same ratio between relaxation times at 100 K and 300 K for a-C is, on average, slightly larger than unity ~125%. Given the large spread in the relaxation time ratio, the average serves as only a rough indication of the behavior, yet it is quite remarkable that on average the relaxation times are roughly equivalent at the two temperatures. Furthermore, even though there is a wide spread in the relaxation time ratios, the average still provides some meaningful perspective since the non-quantum corrected GK thermal conductivity ratios ($\kappa_{100K}/\kappa_{300K}$) for a-Si and a-C are 1.25 and 2.25, respectively. This result is interesting, because it supports the arguments put forth by Lv and Henry, which have been presented elsewhere,[18] that the relaxation time is not an appropriate descriptor for describing transport via non-propagating modes. In this sense, non-propagating modes will likely require the creation of a new descript that differs from the PGM to properly describe their transport.
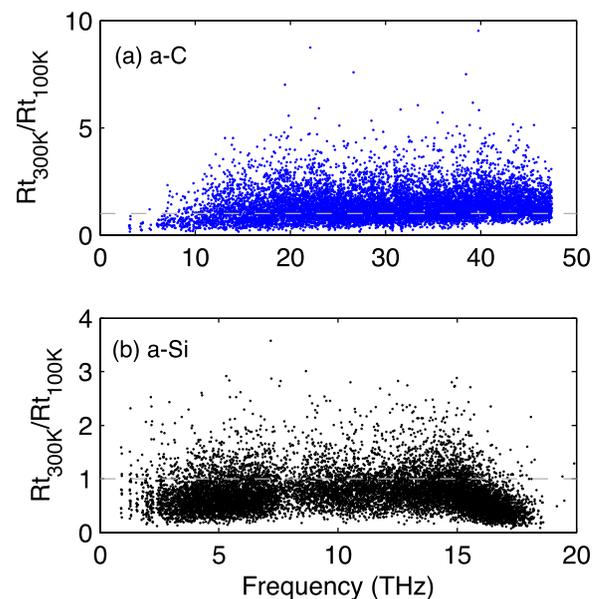
FIG. 3. The ratio of the relaxation times at 300 K to the relaxation times at 100 K for (a) a-C and (b) a-Si. For a-C, the ratios oscillate about unity, which indicates that the relaxation times are insensitive to the temperature change. However for a-Si, ratio falls below unity, indicating the usual behavior, whereby relaxation times decrease with increasing temperature.

(a)

(b)
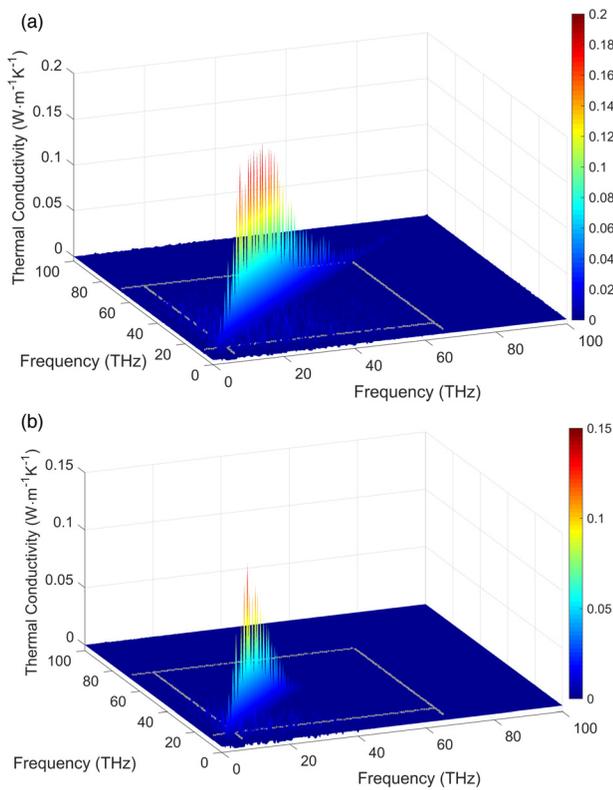
FIG. 4. Thermal conductivity contributions from mode–mode correlations with (a) and without (b) quantum correction (300 K) of a-C. The gray lines represent where the mode character changes from that of propagons to diffusons and diffusons to locons. The rectangular region that is framed by the gray lines represents the diffuson contributions, and from (b), it is clear that the majority of the thermal conductivity contributed by diffusons and is primarily due to the autocorrelations.

Figure 4 shows a 3D view of the mode–mode correlations, where the two axes in horizontal plane represent the frequencies of the two modes interacting, while the vertical axis is the magnitude of the correlation between the two modes and represents the thermal conductivity contributions in Fig. 4. The gray lines represent the cut-off lines as shown in Fig. 1(a). The diagonal elements represent the auto-correlations, which is the dominant contribution for a-C. Interestingly, it is also clear from Fig. 1 that the diffusons between 10 and 40 THz comprise 70% of the room temperature thermal conductivity. The four gray cut-off lines frame the diffuson region. By inspection of the normal mode shapes, the frequency range where the mode character switches from that of propagons to diffusons occurs around 6 THz. This then suggests that propagons only comprise 13% of the thermal conductivity at room temperature. The result is somewhat counter-intuitive given the fact that at room temperature the specific heat is less than 20% of the Dulong–Petit limit for a-C, which is close to the regime where many crystals such as silicon experience their peak thermal conductivity where anharmonicity begins to dominate over other scattering mechanisms. The intuition inferred from studying crystalline materials would then suggest that at such a low temperature, the dominant phonons should have low frequencies and long mean free paths given the suppression of most other modes. However, the results indicate that unlike a crystalline material, in a-C the lowest

frequency modes do not have the highest thermal conductivity contributions on a per mode basis and they do not dominate the thermal conductivity at low temperature.

Figure 5(a) shows the comparison of GKMA and GK predictions at five different temperatures (100 K, 150 K, 200 K, 250 K, and 300 K) along with experimental data from Shamsa et al.[11] The GK predicted thermal conductivity is much higher than the experimental values and the trend is incorrect. However, the results show that even though the GK prediction is far too high, the underlying mode–mode interactions contained in the classical MD simulations are still meaningful, because the quantum correction on the heat capacity, enabled by GKMA, brings the predictions into excellent agreement with experiments. Figure 1S in supplementary material[31] shows the prediction of GKMA for the temperature range from 0 K to 500 K. The continuous curve is calculated from the interpolation of the mode thermal conductivity at the five temperatures, and the interpolation scheme is described in the supplementary material.[31] The thermal conductivity continues to increase, not saturated even at 500 K, since there are more modes starting to activate and contribute to the thermal conductivity. The data in Fig. 4 show minimal interactions between low and high frequency modes, and thus, the hypothesis that the second quantum effect on phonon–phonon interactions is negligible appears confirmed by the good agreement obtained by only including the first quantum effect on the heat capacity. At room temperature, more than 60% of the modes in a-C are not excited and therefore cannot contribute to the thermal conductivity and it is quite remarkable that when these contributions are suppressed by the quantum heat capacity correction, the remaining contributions reproduce the experimental values and trend correctly.
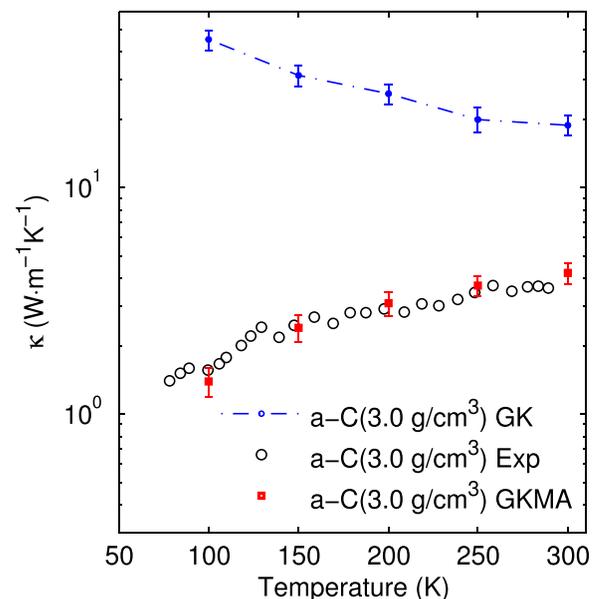
FIG. 5. Thermal conductivity vs. temperature for a-C comparing with experiments.[11] Reproduced with permission from Appl. Phys. Lett. **89**, 161921 (2006). Copyright 2006 American Institute of Physics. GK calculated results (blue) and GKMA calculated results (red) at 5 temperatures (100 K, 150 K, 200 K, 250 K, and 300 K). The continuous thermal conductivity vs. temperature (0 K to 500 K) result interpolated from the five temperature spectral thermal conductivity is shown in the supplementary material.[31]

In this letter, we used the GKMA method to study the mode level contributions to the thermal conductivity of a-C, using the Tersoff potential. The phonons in a-C range from 0 to 100 THz and at room temperature (300 K) or lower, less than 40% of the modes are excited. As a result, the native GK method over predicts the thermal conductivity by a factor of $\sim 3\times$, but by obtaining the individual mode contributions through GKMA, application of a quantum heat capacity correction suppresses the contributions of high frequency modes, bringing the corrected results into excellent agreement with experiments. The modal analysis also revealed that even though the thermal conductivity of a-C is strongly temperature-dependent the relaxation times are not, and thus it further brings into question whether or not relaxation times are useful descriptors for non-propagating mode contributions. Finally, it was found that, at room temperature, propagons only comprise 13% of the thermal conductivity and thus the majority of the thermal conductivity of a-C comes from diffusons, even though at 300 K, more than 60% of the modes ($\omega > 36$ THz) are suppressed by their specific heat.

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[31]See supplementary material at http://dx.doi.org/10.1063/1.4948605 for a detailed description of the GKMA procedure, and a continuous curve of the GKMA predicted thermal conductivity for temperature range from 0 K to 500 K from interpolation between 5 temperature results and extrapolation to 500 K, using the accumulation at 300 K.