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Spectral concentration of thermal conductivity in GaN—A first-principles study

Jivtesh Garg,1 Tengfei Luo,2 and Gang Chen3

1School of Aerospace and Mechanical Engineering, University of Oklahoma, Norman, Oklahoma 73019, USA
2Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA
3Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

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We find using first-principles analysis of thermal conductivity (k) in isotopically pure Gallium nitride (GaN) that almost 60% of the heat is conducted by phonons in a very narrow frequency range of 5–7 THz (spanning only 9% of the frequencies in GaN). This spectral focusing of thermal conductivity is found to be due to a combination of two effects—a large increase in lifetimes of phonons through suppression of anharmonic scattering in the 5–7 THz frequency range coupled with a large phonon density of states at the same frequencies. Understanding of the effect is provided by solving the phonon Boltzmann transport equation in the single mode relaxation time approximation along with the use of harmonic and anharmonic force constants derived from density functional theory. The results can have important implications for engineering the thermal performance of devices based on GaN. Published by AIP Publishing.

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Gallium nitride (GaN), a wide bandgap semiconductor, has important applications in electronic devices.1–4 Recently, using first-principles formalism, Lindsay et al.5 demonstrated that isotopically pure GaN can have a very high k of ~400 W/mK. This high k was explained in terms of diminished anharmonic scattering of lower frequency phonons induced by an energy gap in the phonon dispersion of GaN. In this work, we find using first-principles methods another unusual feature of thermal transport in isotopically pure GaN, namely, a spectral focusing of k. Almost 60% of the heat is found to be conducted by phonons in a very narrow frequency range of 5–7 THz, spanning 9% of the frequency range in GaN. This result is in contrast to materials such as silicon, where phonons with frequencies up to 6 THz (spanning ~40% of the overall frequency range) are found to make significant contribution to k.4,5

We analyze the frequency dependence of k of wurtzite-GaN using a first-principles approach6,7 based on the solution of the phonon Boltzmann transport equation (PBTE) in the single-mode relaxation time approximation (SMRT).8 Wu et al.9 demonstrated that in GaN, SMRT approximation leads to excellent agreement (within 4.5%) with the exact iterative solution of PBTE, justifying the use of SMRT approximation in this work. Necessary ingredients required to predict k, namely, the 2nd and 3rd order interatomic force constants, (IFCs) are derived from density functional theory (DFT).10,11 Finally, k is computed using the following expression:8

\[
k_\lambda = \frac{\hbar^2}{N\Omega k_B T^2} \sum_\lambda c_\lambda^2 \omega_\lambda^2 \tau_\lambda (\pi_\lambda + 1) \tau_\lambda,
\]

where c, \omega, \pi, and \tau are the phonon group velocities, frequencies, equilibrium populations, and relaxation times, \lambda represents the vibrational mode (q\lambda) (q is the wave vector and j is the phonon polarization), x is the Cartesian direction, and T, \Omega, and N are the absolute temperature, primitive unit cell volume, and size of q–point mesh used, respectively. In isotopically pure GaN, the scattering rate, 1/\tau_\lambda, of a phonon mode \lambda is determined by anharmonic scattering processes. These scattering rates are computed using the lowest-order three phonon processes through the following equation:10

\[
\frac{1}{\tau_\lambda} = \frac{\pi}{2N} \sum_{\lambda',\lambda''} |V_3(-\lambda, \lambda', \lambda'')|^2 \delta(\omega(\lambda) + \omega(\lambda') - \omega(\lambda''))
\times [2(n_{\lambda'} - n_{\lambda''})\delta(\omega(\lambda') - \omega(\lambda'')) + (1 + n_{\lambda'} + n_{\lambda''})\delta(\omega(\lambda) - \omega(\lambda') - \omega(\lambda''))],
\]

(2)

where V_3(\lambda, \lambda', \lambda'') are the three-phonon coupling matrix elements.

We also study the k of natural GaN with isotopic disorder. Isotopic disorder leads to additional scattering, and these rates are computed using12

\[
\frac{1}{\tau_\lambda} = \frac{\pi}{2N} \omega_{\lambda}^2 \sum_{\sigma} \delta(\omega_\lambda - \omega_{\lambda'}) \sum_\pi g(\sigma) |\vec{v}(\sigma\lambda')\vec{v}(\sigma\lambda)|^2,
\]

(3)

where \sigma denotes the atomic sites in the unit cell and g takes into account the magnitude of mass disorder and is defined as g(\sigma) = \sum_i f_i(\sigma) |1 - m_i(\sigma)/\bar{m}(\sigma)|^2, where i, f, and m are the atomic species, concentration, and mass, respectively. \bar{m}(\sigma) is the average mass at site \sigma, and \vec{v} represents the vibration eigenvector. For gallium (60.11% ^{69}\text{Ga} and 39.89% ^{71}\text{Ga}), g_Ga = 1.97 \times 10^{-4}, while for N, the isotopic variation is negligible, g_N = 0. The total scattering rate, 1/\tau_\lambda, of a phonon mode \lambda in natural GaN is taken to be the sum of anharmonic and isotopic disorder scattering.
DFT calculations were done with the plane-wave pseudopotential code QUANTUM-ESPRESSO\textsuperscript{13} using a 75 Ry plane-wave cutoff and norm-conserving pseudopotentials in the local-density approximation (LDA). A $16 \times 6 \times 10$ Monkhorst mesh\textsuperscript{14} was used to describe the electronic properties. The 2nd order force constants were computed on a $6 \times 6 \times 6$ $q$-grid, while the 3rd order interactions were computed on a $2 \times 2 \times 2$ $q$-grid. Acoustic sum rules (ASR) were imposed on both 2nd and 3rd order IFCs.

The ground state atomic configuration of wurtzite GaN was determined by minimizing the energy with respect to in-plane, $a$, and out-of-plane, $c$, lattice constants; the internal parameter $u$ was chosen such that the residual forces on the atoms were zero. To achieve agreement between computed frequencies and measured values,\textsuperscript{15} it was found necessary\textsuperscript{3,9} to increase the computed lattice parameter by 1%. This is also in agreement with the use of LDA approximation in this work which is known to over-bind atoms by 1%–2%.\textsuperscript{16} Thus, while ground state parameters were derived by energy minimization to be $a = 3.129$ Å, $c = 5.096$ Å, and $u = 0.377$, the actual parameters used in this work were $a = 3.160$ Å, $c = 5.148$ Å, and $u = 0.377$. The phonon dispersion for this higher lattice parameter is shown in Fig. 1 along with measured values.\textsuperscript{15}

The computed lifetimes in isotopically pure and natural GaN are shown in Fig. 2. We next computed $k$ both along the in-plane direction ($k_{\text{in}}$) and along the $c$-axis of GaN ($k_{\text{out}}$). The predicted $k_{\text{in}}$ of isotopically pure GaN at 300 K is found to be 390 W/mK (Fig. 3) at 300 K, in excellent agreement with the result obtained earlier using an exact iterative solution\textsuperscript{3} (401 W/mK). The predicted $k$ of natural GaN is also in good agreement with measurements.\textsuperscript{17}

In Fig. 4(a), we show the spectral distribution of $k$ of GaN at 300 K and find that phonons in a very narrow frequency range of 5–7 THz have a dramatically enhanced contribution to overall $k$. Figure 4(b) shows that phonons in this frequency range contribute 60% to overall $k$. Figures 4(c) and 4(d) show the phonon mean free paths ($\lambda$) and the dependence of $k$ on them at 300 K. At a lower temperature of 100 K, the contribution of phonons between 5 and 7 THz to overall $k$ was found to diminish to about 36%, broadening the spectral distribution compared to 300 K. As the temperature is decreased to 100 K, phonons in the range of 5–7 THz become less populated, decreasing their contribution to $k$.

The large increase in $k$-contribution of phonons in the 5–7 THz range at 300 K can be understood in terms of long phonon lifetimes (Fig. 2) coupled with a large phonon density of states (Fig. 1), both in the 5–7 THz frequency range. The increase in phonon lifetimes is in part due to a frequency gap in phonon dispersion of GaN (Fig. 1) which suppresses anharmonic scattering. To show this effect, we compare the computed phonon scattering rates for GaN with an artificial case where the phonon frequency gap is made zero. This comparison is performed (Fig. 5) for the longitudinal acoustic phonons (LA) along $\Gamma$-A (Fig. 1). The zero-frequency gap case is achieved by simply decreasing the frequencies of higher energy phonons by the magnitude of the frequency gap [Fig. 6(a)].

We split the phonon branches into low frequency (bottom six branches) denoted by $l$ and high frequency (upper six branches) denoted by $h$ (Fig. 1). Through anharmonic processes, $l$ phonons can scatter by decaying into lower

**FIG. 1.** Computed phonon dispersion and phonon density of states (DOS, arbitrary units) of GaN with 1% larger lattice constant than that derived from DFT. Symbols are the experimentally measured values (Ref. 15).

**FIG. 2.** Computed phonon lifetimes in isotopically pure and natural GaN and zero-frequency gap cases.

**FIG. 3.** Predicted thermal conductivity of isotopically pure and natural GaN. Solid lines are the values of $k_{\text{in}}$, while dashed lines correspond to $k_{\text{out}}$. The symbols are the experimentally measured data (Ref. 17).
energy phonons (decay processes) or by absorbing another phonon and converting into higher energy phonon (absorption processes). Figures 5(a) and 5(b) show that absorption scattering rates are dominant in the zero-frequency gap case and are particularly large in the 5–7 THz range. While the decay scattering rates are identical for both cases (zero-frequency gap case and GaN), absorption scattering rates in GaN are markedly lower compared to the zero-frequency gap case [Figs. 5(a) and 5(b)]. To achieve an understanding of this decrease in absorption scattering rates in GaN, we decompose the absorption process for an ‘l’ phonon mode into three processes (1) $l + l \rightarrow h$, (2) $l + h \rightarrow h$, and (3) $l + l \rightarrow h$ [shown in Figs. 5(c)–5(e)]. Scattering rates due to processes (1) and (2) are found to be identical in the two cases [Figs. 5(c) and 5(d)]. However, scattering through process 3 ($l + l \rightarrow h$) is significantly lower in GaN [Fig. 5(e)], leading to a decrease in the overall absorption scattering rate and therefore an increase in phonon lifetimes relative to the zero-frequency gap case (Fig. 2).

To understand the decrease in $l + l \rightarrow h$ scattering rates, it should be noted that, in the zero-frequency gap case, a phonon mode $(q, \omega)$ can scatter by absorbing another phonon mode $(q', \omega')$, yielding a higher energy phonon $(q'', \omega'')$ [Fig. 6(a)]. Such a channel satisfies both momentum and energy conservation $(q + q' = q''$ and $\omega + \omega' = \omega'')$, where $q$ is the wave-vector and $\omega$ is the frequency. In GaN, however, the third phonon mode $(q'', \omega'')$ required for the above scattering channel to be feasible lies in the frequency gap [Fig. 6(b)]. This forbids scattering of ‘l’ phonons through such channels, leading to a dramatic decrease in $l + l \rightarrow h$ scattering channels in GaN.

To understand the large scattering through $l + l \rightarrow h$ processes in the 5–7 THz frequency range in the zero-frequency gap case, we first show that $l + l \rightarrow h$ processes do not significantly scatter low frequency phonons for this case. To see this, notice that scattering of an ‘l’ phonon of frequency $\omega$ through the $l(\omega) + l(\omega') \rightarrow h(\omega'')$ process requires that sum of the frequencies $\omega$ and $\omega'$ be greater than $\sim 10$ THz ($\omega + \omega' > 10$ THz) since frequencies $(\omega'')$ of ‘h’ phonons in the zero-frequency gap case are greater than $\sim 10$ THz [Fig. 6(a)]. Now, when the ‘l’ phonon mode being scattered has a low frequency (small $\omega$), the second ‘l’ phonon mode should
have a high frequency \( \omega' \) to satisfy \( \omega + \omega' > 10 \text{THz} \); at the same time, \( \omega' < 10 \text{THz} \) since the maximum frequency for ‘\( l \)’ phonons is \( \sim 10 \text{THz} \) (Fig. 1). For the \( \omega = 1 \text{THz} \) phonon, this leads to the condition that \( 9 \text{THz} < \omega' < 10 \text{THz} \). This forces the second phonon mode to lie close to the edge of the frequency range. Since this region is only a small fraction of the entire frequency range, such scattering channels are few, and therefore, the \( l + l \rightarrow h \) processes do not play a significant role in the scattering of low frequency phonons in the zero-frequency gap case.

Increasing the frequency \( \omega \) of the phonon (\( q \)) being scattered, however, allows the frequency of the second phonon-mode to span a much larger region of the frequency range, resulting in an increase in such channels in the zero-frequency gap case. For example, for scattering of the phonon mode with \( \omega = 5 \text{THz} \), the frequency of the second phonon mode should satisfy \( 5 \text{THz} < \omega' < 10 \text{THz} \); this spans a much larger region of the frequency range, compared to the case of scattering of a low frequency phonon mode. This increase in scattering of higher frequency phonons (in the range of \( 5–7 \text{THz} \)) through \( l + l \rightarrow h \) processes leads to a large decrease in lifetimes of phonons (Fig. 2) for the zero-frequency gap case in the \( 5–7 \text{THz} \) range.

In GaN, however, for phonons in the frequency range of \( 5–7 \text{THz} \), these channels are almost completely absent due to the frequency gap [Fig. 6(b)] in the phonon spectrum. Even for scattering of the highest frequency in the above range, \( \omega = 7 \text{THz} \), feasibility of an \( l(\omega) + l(\omega') \rightarrow h(\omega'') \) channel requires that \( \omega' = \omega'' = 7 \text{THz} \), and since \( \omega'' > 16 \text{THz} \) in GaN for ‘\( h \)’ phonons, this implies that \( \omega' > 9 \text{THz} \); combined with the condition that \( \omega'' < 10 \text{THz} \), this leads to \( 9 \text{THz} < \omega' < 10 \text{THz} \), leading to very few scattering channels available to scatter \( \omega = 7 \text{THz} \) phonons through the above process. At lower frequencies (\( \omega \)), such scattering channels are completely eliminated (e.g., at \( \omega = 5 \text{THz} \)), the above conditions lead to \( \omega' > 11 \text{THz} \), which is not feasible since the maximum value of \( \omega' \) is \( \sim 10 \text{THz} \) as seen in Fig. 1). In GaN, therefore, for phonons in the \( 5–7 \text{THz} \) range, scattering through \( l + l \rightarrow h \) processes is almost zero [Fig. 5(c)].

Figure 5(c) shows that scattering through \( l(\omega) + l(\omega') \rightarrow l(\omega'') \) processes also decreases, as the frequency is increased from \( 5 \) to \( 7 \text{THz} \). To see this, notice that \( \omega'' < 10 \text{THz} \) for ‘\( l \)’ phonons in GaN (Fig. 1), and therefore, for the above processes to be feasible, \( \omega' < 10 \text{THz} \). An ‘\( l \)’ phonon of frequency \( \omega \) (\( \omega \) between \( 5 \) and \( 7 \text{THz} \)) can scatter through the above channel by absorbing a low frequency (\( \omega' \)) phonon, and however, the density of states at lower frequencies is small (Fig. 1), weakening this scattering path. The phonon (\( \omega \)) can also scatter by absorbing a phonon of similar frequency (\( \omega \sim \omega' \)), yielding a high frequency phonon (\( \omega'' \)). However, momentum conservation prohibits such channels. Phonons with frequencies \( \omega \sim 5 \text{THz} \) typically have wavevectors in between the Brillouin zone center and the edge. The absorption of another similar phonon and enforcing the addition of wavevectors (as is the case for absorption processes) will lead to the final phonon lying close to the zone edge. The highest frequency ‘\( l \)’ phonons, however, are close to the Brillouin zone center, making such channels infeasible. Together, the above effects lead to diminished scattering of phonons in the frequency range of \( 5–7 \text{THz} \) through the \( l + l \rightarrow l \) channel. As \( \omega \) increases, the range available for \( \omega' \) decreases even further (\( \omega' < 10 \text{THz} \) - \( \omega \)), causing a further decrease in the above scattering channels.

Finally, it is also observed that scattering of ‘\( l \)’ phonons through \( l(\omega) + h(\omega') \rightarrow h(\omega'') \) also decreases sharply for \( \omega > 5.5 \text{THz} \) [Fig. 5(d)]. This can be understood since the lowest value of \( \omega' \) for ‘\( h \)’ phonons in GaN is \( \sim 16 \text{THz} \) (Fig. 1), leading to \( \omega'' = 21.5 \text{THz} \) for scattering of the \( \omega = 5.5 \text{THz} \) phonon through the lowest energy ‘\( h \)’ phonon. Phonons with \( \omega'' = 21.5 \text{THz} \) lie very close to the top of the frequency spectrum and have a low density of states, leading to weak scattering through such processes. An increase in \( \omega \) leads to complete elimination of these channels since \( \omega'' \) no longer lies within the frequency range of phonons in GaN. A decrease in all three processes \( l + l \rightarrow l, l + h \rightarrow h, \) and \( l + l \rightarrow h \) coupled with a large phonon density of states in the \( 5–7 \text{THz} \) range leads to the observed spectral focusing of \( k \).

Analysis presented in this work is based on three-phonon scattering processes alone. Feng et al.,18 by studying boron arsenide (BAs), demonstrated that four-phonon processes become important, even at \( 300 \text{K} \), when three-phonon scattering becomes diminished. The overall effect of four phonon processes in GaN, however, is likely to be smaller. In BAs, three-phonon scattering was shown to diminish due to two effects—frequency gap and bunching of acoustic phonons.4 In GaN, however, the second effect does not play a role since frequencies of \( l \) phonons are widely spread (Fig. 1), causing overall three-phonon processes to be stronger in GaN, thus mitigating the role of four-phonon scattering events in GaN compared to BAs. Spectral focusing presented in this work can be expected for materials with a frequency gap in the phonon spectrum since it enhances the lifetimes of higher frequency acoustic phonons, enhancing their contribution to \( k \). For complete elimination of \( l + l \rightarrow h \) channels, frequency gap \( \Delta \omega \) should be greater than the largest frequency (\( \omega_{\text{max}} \)) of \( l \) phonons, \( \Delta \omega \geq \omega_{\text{max}} \).

In summary, we have used first-principles methods to study the frequency dependence of \( k \) of GaN. Spectral decomposition revealed that nearly 60% of the heat was conducted by phonons in a narrow frequency range of \( 5–7 \text{THz} \) (spanning 9% of the frequency range in GaN). The effect is found to be due to a large increase in phonon lifetimes in the \( 5–7 \text{THz} \) range, mediated by a frequency gap in the phonon spectrum of GaN that suppresses anharmonic scattering and due to a large phonon density of states in the \( 5–7 \text{THz} \) range. These results can have important implications for thermal management in GaN based devices.

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