

Anisotropic thermal transport in bulk hexagonal boron nitride

Puqing Jiang,¹ Xin Qian,¹ Ronggui Yang,^{1,*} and Lucas Lindsay^{2,†}

¹Department of Mechanical Engineering, University of Colorado, Boulder, Colorado 80309, USA

²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA



(Received 1 May 2018; published 26 June 2018)

Hexagonal boron nitride (h-BN) has received great interest in recent years as a wide band-gap analog of graphene-derived systems along with its potential in a wide range of applications, for example, as the dielectric layer for graphene devices. However, the thermal transport properties of h-BN, which can be critical for device reliability and functionality, are little studied both experimentally and theoretically. The primary challenge in the experimental measurements of the anisotropic thermal conductivity of h-BN is that typically the sample size of h-BN single crystals is too small for conventional measurement techniques, as state-of-the-art technologies synthesize h-BN single crystals with lateral sizes only up to 2.5 mm and thicknesses up to 200 μm . Recently developed time-domain thermoreflectance (TDTR) techniques are suitable to measure the anisotropic thermal conductivity of such small samples, as it only requires a small area of $50 \times 50 \mu\text{m}^2$ for the measurements. Accurate atomistic modeling of thermal transport in bulk h-BN is also challenging due to the highly anisotropic layered structure. Here we conduct an integrated experimental and theoretical study on the anisotropic thermal conductivity of bulk h-BN single crystals over the temperature range of 100–500 K using TDTR measurements with multiple modulation frequencies and a full-scale numerical calculation of the phonon Boltzmann transport equation starting from first principles. Our experimental and numerical results compare favorably for both the in-plane and the through-plane thermal conductivities. We observe unusual temperature dependence and phonon-isotope scattering in the through-plane thermal conductivity of h-BN and elucidate their origins. This paper not only provides an important benchmark of the anisotropic thermal conductivity of h-BN, but also develops fundamental insight into the nature of phonon transport in this highly anisotropic layered material.

DOI: [10.1103/PhysRevMaterials.2.064005](https://doi.org/10.1103/PhysRevMaterials.2.064005)

I. INTRODUCTION

Hexagonal boron nitride (h-BN), a layered two-dimensional (2D) material with a similar lattice structure as graphite, has been frequently used as an ultraviolet light emitter [1,2], as a solid lubricant in harsh environments [3], and as a thermally conductive and electrically insulating filler in composites [4] due to its unique physical properties. More recently, there is increasing interest in using h-BN as a substrate for graphene electronics [5]. Many unique features of h-BN, including its atomically smooth surface (free of dangling bonds and charge traps), very high-frequency optical phonon modes, large electronic band gap, and especially similar lattice constants to graphene, make it an ideal substrate for graphene electronics. Graphene devices on h-BN substrates are shown to have the mobility and carrier homogeneity that are almost an order of magnitude better than graphene devices on SiO_2 substrates [5]. Moreover, graphene/h-BN heterostructures have exhibited many interesting phenomena [6–11] and have been proposed for a wide range of applications including field-effect transistors [12–14], quantum tunneling transistors [15], high-frequency oscillators [16,17], tunneling diodes [18], light-emitting diodes [19], and solar cells [20]. Thermal management is critical in many of these BN-related applications; it

is therefore of fundamental importance to develop a detailed understanding of the thermal transport properties of h-BN.

The anisotropic thermal conductivity of bulk h-BN single crystals, however, remains little studied to date, either experimentally or theoretically. When the in-plane thermal conductivity of bulk h-BN is referred to in the literature [21,22], the data of a pyrolytic compression annealed h-BN sample measured by Sichel *et al.* [23] with a value of $390 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature measured using a steady-state technique are often cited. The data of Sichel *et al.*, however, are almost twice as high as the data measured by Simpson and Stuckes [24] using a flash technique also with a pyrolytic compression annealed h-BN sample. It is unclear whether the difference between these two studies is due to inconsistencies in sample quality or measurement methods. The only measured data of through-plane thermal conductivity of bulk h-BN available in the literature is from Simpson and Stuckes [24] who reported it to be $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. The primary challenge in measuring the thermal conductivity of h-BN single crystals is that the typical size of the single crystals is not large enough for many characterization techniques [25], including the steady-state technique used by Sichel *et al.* [23] and the flash technique by Simpson and Stuckes [24]. State-of-the-art synthesis techniques produce h-BN single crystals with lateral sizes only up to 2.5 mm and thicknesses up to 200 μm [26,27]. As such, the samples measured by Sichel *et al.* [23] and Simpson and Stuckes [24] 40 years ago were prepared into a centimeter size by hot pressing and annealing and thus were

*Ronggui.Yang@Colorado.Edu

†lindsaylr@ornl.gov

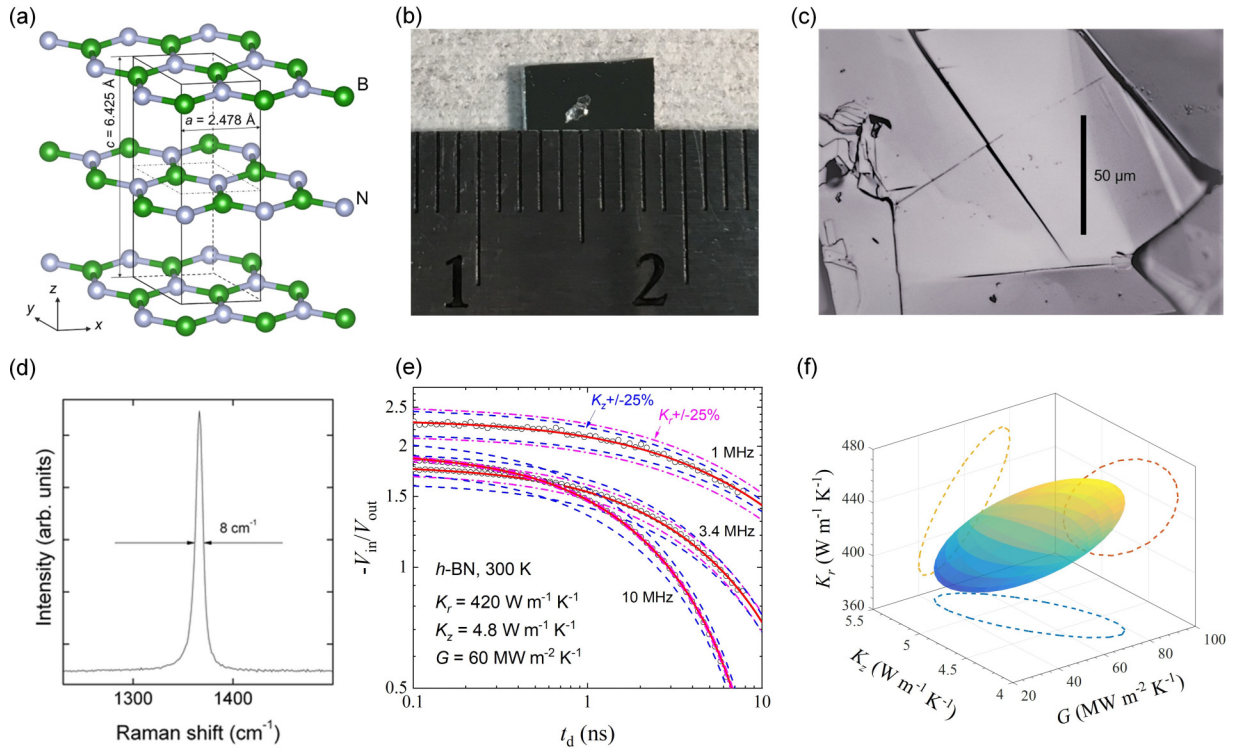


FIG. 1. (a) Layered crystalline structure of h-BN. The interlayer spacing is 3.213 \AA , and the in-plane lattice constant is equal to 2.478 \AA from our first-principles calculations, which are 1% and 3.5% smaller than measurements [54], respectively. (b) and (c) Optical images of a h-BN sample sitting on a silicon substrate. (d) Raman spectrum of h-BN. (e) Representative data fitting of TDTR measurements of h-BN at 300 K using a laser spot size $w_0 = 10 \mu\text{m}$ and multiple modulation frequencies between 1 and 10 MHz. A single set of parameters K_r , K_z , and G can be used to fit the measured data at all the modulated frequencies. (The data measured at 2.1 and 5.1 MHz can be fitted equally well but are not shown here for clarity.) The dashed curves and dashed-dotted curves are 25% bounds on the best-fitted K_z and K_r values, respectively, as a guide to the reading of the sensitivity of the signals. (f) Confidence ranges of K_r , K_z , and G when these parameters are simultaneously determined from the multiple-frequency TDTR measurements of h-BN as presented in (e).

not single crystals in a strict sense but with porosity. On the other hand, the recent advancement of an ultrafast laser-based time-domain thermoreflectance (TDTR) method has made it possible to measure anisotropic thermal conductivity of very small-scale samples.

Likewise, it is a surprise that theoretical modeling of the thermal conductivity of bulk h-BN is lacking, likely due to the challenges in accurate modeling of phonon-phonon interactions in highly anisotropic materials. Strong in-plane covalent bonding of light boron (B) and nitrogen (N) atoms give very high acoustic velocities and high-frequency phonon modes of h-BN along the planar direction, whereas weak interplanar bonding gives low acoustic velocities and low-frequency modes perpendicular to the planes (see dispersion in Fig. 2). *Ab initio* calculations based on Boltzmann transport theory [28–30] in combination with density functional theory (DFT) [31,32] have demonstrated accuracy in describing thermal conductivity of a variety of bulk materials [33–35] and 2D structures [36–40]. Yet, anisotropic layered materials, including h-BN, have not been studied as intensively [41–44].

In this paper, we present an integrated study of the anisotropic thermal conductivity of bulk h-BN single crystals from both experiments and first-principles-based calculations over the temperature range of 100–500 K. Both the in-plane and the through-plane thermal conductivities of bulk h-BN single crystals were measured by TDTR using multiple modulation

frequencies and calculated from a full numerical solution of the Peierls-Boltzmann phonon transport equation. Our measurements and calculations agree favorably with each other. We also develop fundamental insight into the nature of phonon transport in this highly anisotropic layered 2D material.

II. METHODOLOGIES

A. Experimental details

The h-BN single-crystal (grade A) samples, which were purchased from SPI Supplies®, are 1-mm-sized flakes with a thickness of $>10 \mu\text{m}$ [see Fig. 1(b) for an optical image of a typical sample]. Microscopic images of the samples demonstrate atomically flat surfaces and large domain sizes of $>50 \mu\text{m}$ [see Fig. 1(c)]. The h-BN samples are of high purity, as confirmed by the sharp peak in the Raman spectrum provided by the vendor [see Fig. 1(d)]. To prepare the samples for measurements, the small h-BN crystals were first attached to a large Si wafer using a carbon tape. The first few layers of h-BN were then removed by exfoliation with scotch tape immediately before the deposition of a 100-nm-thick Al film using an electron-beam evaporator. The Al film serves as a transducer for the thermal conductivity measurements [45].

We measure the anisotropic thermal conductivities of h-BN using ultrafast laser-based time-domain thermoreflectance [46]. In our TDTR measurements, a train of laser

pulses at an 81-MHz repetition rate is split into a pump path and a probe path. The pump pulses are modulated at a frequency in the range of 1–10 MHz using an electro-optic modulator, whereas the probe pulses are delayed with respect to the pump via a mechanical delay stage. Both the pump and the probe beams are then directed into an objective lens and focused on the sample surface. The modulated pump beam induces heating on the sample surface, with the resulting temperature change being detected by the probe beam via thermoreflectance $\Delta R = (dR/dT)\Delta T$. A fast-response photodiode detector collects the reflected probe beam and converts the optical signals into electrical signals. A radio-frequency lock-in amplifier picks up the thermal signal, which contains an in-phase component V_{in} and an out-of-phase component V_{out} . The ratio of V_{in} and V_{out} , $R = -V_{\text{in}}/V_{\text{out}}$, recorded as a function of delay time, is used to extract thermal properties of the sample through the best fit of the model with the measured signals. The thermal transport model for TDTR experiments is briefly discussed in Appendix A to assist the understanding of the data reduction procedure. More details of the model can also be found in Refs. [47,48].

TDTR can measure both the in-plane and the through-plane thermal conductivities of the sample under different heat transfer configurations, achieved by changing the relative sizes of the laser spot w_0 and the in-plane thermal penetration depth $d_{p,r}$, defined as $d_{p,r} = \sqrt{K_r/\pi f C}$, where K_r and C are the in-plane thermal conductivity and volumetric heat capacity of the sample and f is the modulation frequency. When TDTR experiments are conducted under the condition of $w_0 \gg d_{p,r}$, the heat flow is mainly one dimensional along the through-plane direction, and the TDTR signals are mainly affected by the through-plane thermal conductivity K_z of the sample. When TDTR experiments are conducted under the condition of $w_0 \leq d_{p,r}$, the heat flow is three dimensional, and the TDTR signals depend on both K_r and K_z of the sample. Note that w_0 here is the root-mean-square average of the $1/e^2$ radii of the pump and probe spots on the sample surface. Previously, we developed a variable spot size TDTR approach to measure anisotropic thermal conductivity [46]. In the variable spot size TDTR approach, different heat transfer regimes are achieved by varying the laser spot size w_0 and fixing the modulation frequency f (and consequently $d_{p,r}$) to avoid potential artifacts from frequency-dependent K_z of the sample [46]. Several materials have been found to have frequency-dependent K_z , notably some layered 2D materials, such as MoS₂ [49], black phosphorus [50], and some semiconductor alloys [51,52]. However, not all layered 2D materials are found to have frequency-dependent K_z with h-BN and graphite as two such examples [46].

In this paper, a fixed laser spot size of $w_0 = 10 \mu\text{m}$ and multiple modulation frequencies from 1 to 10 MHz were used to measure the anisotropic thermal conductivity of h-BN using TDTR (specifically, the five frequencies of 1, 2.1, 3.4, 5.1, and 10 MHz were chosen). Although the TDTR signals are consistently sensitive to K_z of h-BN at all the modulation frequencies, the TDTR signals are highly sensitive to K_r only at low modulation frequencies as depicted by the 25% bound curves shown in Fig. 1(e). We found that thermal model predictions using a single set of parameters (K_r and K_z of h-BN and Al/h-BN interfacial thermal conductance G) can

fit the TDTR signals at multiple frequencies very well, as shown in Fig. 1(e), which indicates no modulation frequency dependence as reported previously on some other materials [49,51,52]. From this set of TDTR data, the thermal properties are extracted to be $K_r = 420$, $K_z = 4.8 \text{ W m}^{-1} \text{ K}^{-1}$, and $G = 60 \text{ MW m}^{-2} \text{ K}^{-1}$ for single-crystalline h-BN at room temperature.

Such a lack of frequency dependence is consistently evident in TDTR measurements of h-BN at other temperatures as well, which makes the data reduction much simpler. The multiple-frequency TDTR measurements of h-BN were repeated over a temperature range from 100 to 400 K. A least-squares algorithm developed by Yang *et al.* [53] is used to simultaneously determine K_r , K_z , and G and estimate their uncertainties at each temperature. Figure 1(f) shows the confidence ranges of K_r , K_z , and G of h-BN at room temperature when these parameters are simultaneously determined from the TDTR data at multiple frequencies. The uncertainties of K_r , K_z , and G of h-BN at room temperature are found to be 11%, 13%, and 33%, respectively.

B. Computational details

Our calculations are based on a full solution of the Peierls-Boltzmann transport equation [28–30] with harmonic (for phonon frequencies) and anharmonic (for phonon interactions) interatomic force constants (IFCs) calculated from DFT [31,32]. More specifically, we used the plane-wave-based QUANTUM ESPRESSO package [55,56] within the local-density approximation (LDA) using Perdew-Zunger exchange correlation [57] and norm-conserving von Barth–Car pseudopotentials [58] to represent the core electrons. The bulk h-BN system was relaxed with the AA' layer stacking configuration [see Fig. 1(a)] using $12 \times 12 \times 8$ electronic integration grids and a 110-Ry energy cutoff. This gives structural lattice constants $a = 2.478$ and $c = 6.425 \text{ \AA}$. These parameters are 1% and 3.5% smaller than measurements [54], respectively, as LDA calculations typically overbind the atoms [59]. DFT van der Waals corrections were not included as LDA calculations of the phonon dispersions agree well with measured data (see Fig. 2). The harmonic IFCs, high-frequency dielectric tensor, and Born effective charges used to construct the dynamical matrices that determine phonon frequencies were calculated from density functional perturbation theory [60] using an $8 \times 8 \times 6$ integration mesh. Third-order anharmonic IFCs were built from numerical derivatives of the interatomic forces from Γ -point-only electronic structure calculations of perturbed 200 atom supercells with interactions restricted to unit-cell atom neighbors within 2.8 \AA for atoms on the same plane and within 4.2 \AA for atoms in neighboring layers.

III. RESULTS AND DISCUSSION

Figure 3 summarizes the in-plane and the through-plane thermal conductivities of single-crystalline h-BN from both TDTR measurements and first-principles predictions over the temperature range of 100–500 K, along with the literature data from Sichel *et al.* [23] and Simpson and Stuckes [24] for comparison. Calculations of both isotopically pure and natural h-BN are presented to demonstrate the effect of

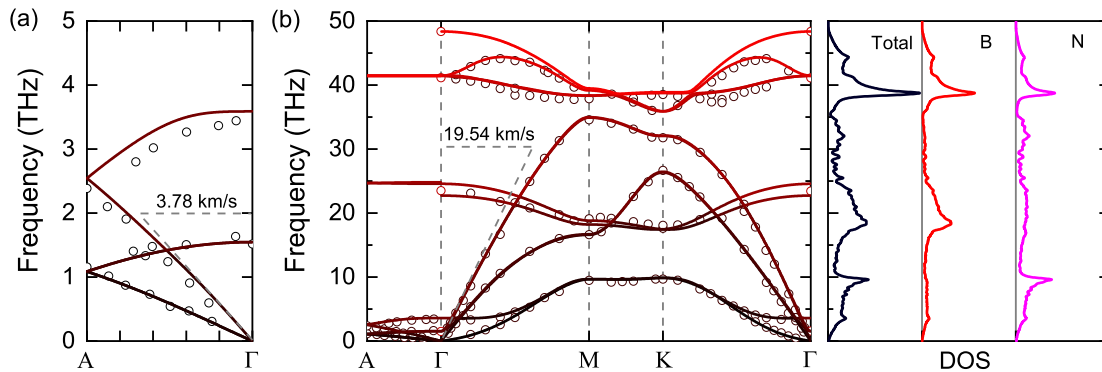


FIG. 2. (a) and the left panel of (b): calculated phonon dispersions of h-BN in high-symmetry directions, which agree well with literature measurements [61–63]. Right panel of (b): total density of states (DOS) and projected density of states on B and on N sites.

phonon-isotope scattering in determining the thermal conductivity. All measurements were performed on natural h-BN crystal samples from SPI Supplies. The measured results and the theoretical calculations compare relatively well. At room temperature, the TDTR measurements give $K_r = 420 \pm 46$ and $K_z = 4.8 \pm 0.6 \text{ W m}^{-1} \text{ K}^{-1}$, whereas the first-principles method predicts $K_r = 537$ and $K_z = 4.1 \text{ W m}^{-1} \text{ K}^{-1}$ for nat-

ural h-BN. Our measured K_r of h-BN compare favorably with the measurements by Sichel *et al.* [23] over the entire temperature range; however, both K_r and K_z are nearly twice larger than those measured by Simpson and Stuckes [24]. Decreasing in temperature from 400 K, both measurements and calculations demonstrate typical increasing K_r as intrinsic phonon-phonon interactions become weaker. However, the measured K_r value peaks at ~ 200 K and begins to decrease with decreasing temperature, whereas calculations continue to increase with $1/T$ behavior. This discrepancy is likely due to extrinsic scattering (e.g., defects, inclusions, grain boundaries, etc.) that provide relatively stronger thermal resistance at lower temperatures as intrinsic scattering becomes weak.

An interesting phenomenon is revealed by the temperature dependence of K_z of h-BN in Fig. 3. Whereas K_r of h-BN exhibits a $1/T$ dependence as expected in the high-temperature range of >300 K [64], the K_z temperature dependence is relatively flat, not following the usual trend, in both our measurements and calculations. Furthermore, calculated results in Fig. 3 show a significant reduction in K_z due to phonon-isotope scattering at higher temperatures of >300 K (increased spacing between the pure and the natural h-BN curves) than observed at lower temperatures. The opposite behavior (stronger phonon-isotope scattering at lower temperatures) is expected and seen in the temperature dependence of K_r . These unusual behaviors of K_z of h-BN can be understood in terms of the relative importance of the high-frequency phonons in determining the overall through-plane conductivity of h-BN, as discussed in detail below.

Figure 4 gives the conductivity contributions from the six highest-frequency branches and separately the six lowest-frequency branches to K_r and K_z of h-BN as a function of temperature for both isotopically pure and natural h-BN. Note that some acoustic modes with frequencies of >25 THz [see Fig. 2(b)] give contributions to the high-frequency grouping. For both K_r and K_z of h-BN, the low-frequency contributions decrease as $1/T$ whereas the high-frequency contributions increase with increasing temperature. As temperature increases, more high-frequency phonons are thermally excited, resulting in enhanced scattering of the low-frequency modes and with relatively increased contributions from high-frequency modes themselves as well. Note that, at very high

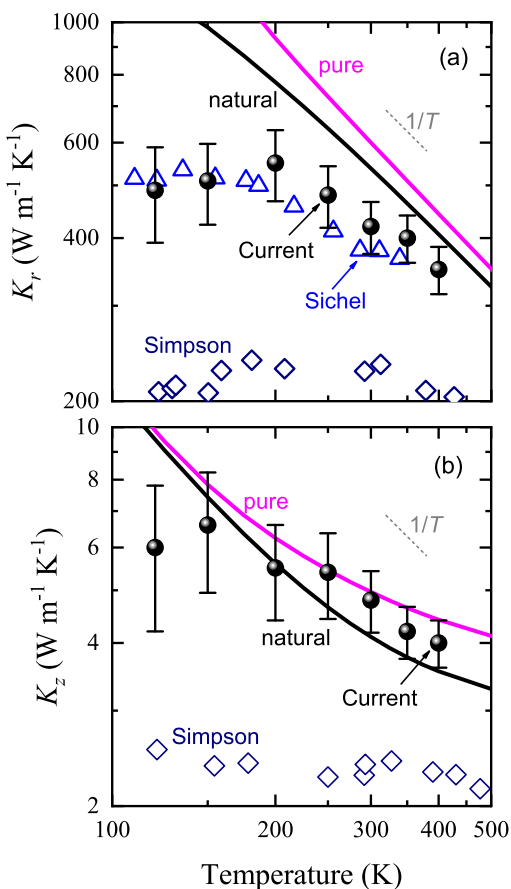


FIG. 3. (a) In-plane and (b) through-plane thermal conductivities of h-BN from both our measurements (solid symbols) and first-principles calculations (solid curves) as a function of temperature, compared with the measurements by Sichel *et al.* [23] and Simpson and Stuckes [24] from the literature.

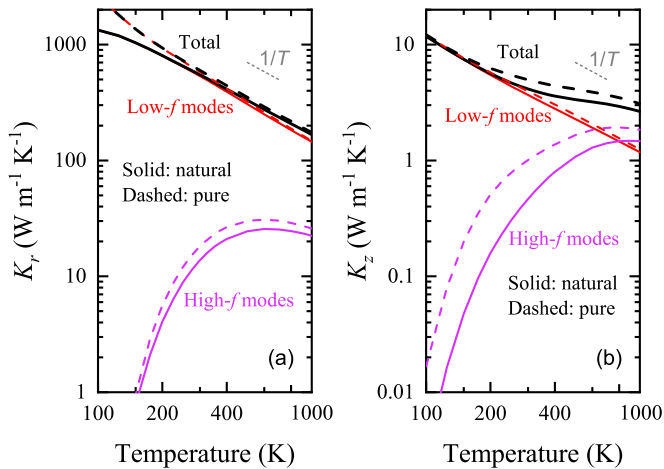


FIG. 4. Calculated contributions to K_r and K_z from the six lowest-frequency branches (red curves) and the six highest-frequency branches (pink curves) [see Fig. 2(b) for phonon branches] as a function of temperature. The dashed curves give conductivity contributions to isotopically pure h-BN, whereas the solid curves give contributions to h-BN with naturally occurring isotope concentrations.

temperatures, the high-frequency conductivity contributions also decay as $1/T$ [see the peak behavior in high-frequency contributions in Fig. 4(a)]. Across the entire temperature range of 100–1000 K, K_r is dominated by the contributions from the low-frequency modes. On the other hand, the low-frequency modes give comparable or even lower contributions to K_z than those of the high-frequency modes at higher temperatures (see Appendix B for details). As the high-frequency modes become more important in K_z at high temperatures, so does the phonon-isotope scattering that these modes are more susceptible to (considering the fourth power frequency dependence of the phonon-isotope scattering rate $1/\tau_{ph-iso} \sim \omega^4$). Therefore, the unusual temperature and isotope behaviors of K_z of h-BN at high temperatures of >300 K are due to the relatively small and decreasing conductivity contributions from the low-frequency modes and the increasing contributions of the high-frequency modes as temperature increases.

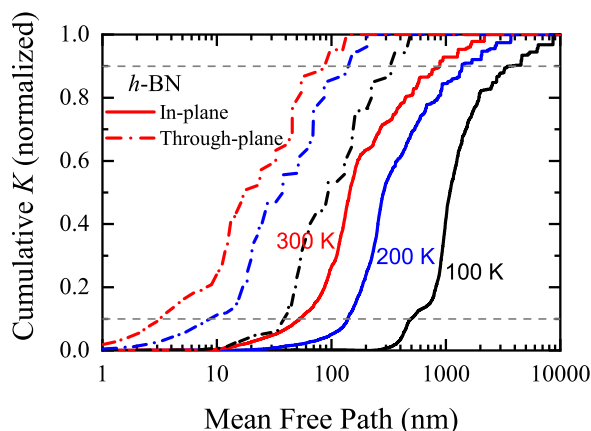


FIG. 5. Normalized calculated cumulative thermal conductivity of h-BN as a function of phonon mean-free path at 100, 200, and 300 K.

For a wide variety of applications of h-BN in nanodevices, feature size relative to the heat-carrier mean-free paths (MFPs) is of practical importance as it affects the effective thermal conductivity of nanosized h-BN. Figure 5 gives the normalized cumulative thermal conductivity of h-BN for both the in-plane and the through-plane directions as a function of phonon MFP at different temperatures: 100, 200, and 300 K. At room temperature (300 K), phonons with MFPs in the range of 3–90 nm contribute $\sim 80\%$ of the total through-plane thermal conductivity (this corresponds to the accumulation curve between the horizontal dashed lines in Fig. 5). These MFPs in the through-plane direction are an order of magnitude smaller than the MFPs of phonons in the in-plane direction. Based on this MFP spectrum for h-BN, we expect that the room-temperature K_z of h-BN films depend on the film thickness for systems with thicknesses of <100 nm and the K_r of h-BN crystals should be reduced from the intrinsic value with grain sizes of $<1 \mu\text{m}$.

IV. CONCLUSION

To summarize, this paper presents an integrated study of the anisotropic thermal conductivity of bulk h-BN single crystals using both time-domain thermoreflectance techniques and first-principles calculations over the temperature range of 100–500 K. The TDTR measurements were conducted with multiple modulation frequencies, and the calculations were from a full numerical solution of the Peierls-Boltzmann phonon transport equation with interatomic forces from density functional theory calculations as input. Our measured and calculated temperature-dependent anisotropic thermal conductivities agree favorably well. We observed unusual behaviors in the temperature-dependent K_z of h-BN at high temperatures of >300 K, which are attributed to the relatively low contributions from low-frequency modes in the through-plane thermal conductivity of h-BN at high temperatures. This paper not only provides an important benchmark of the anisotropic thermal conductivity of h-BN, but also develops fundamental insight into the nature of phonon transport in this highly anisotropic layered material.

ACKNOWLEDGMENTS

P.J., X.Q., and R.Y. acknowledge support from NSF Grant No. 1511195 and DOE Grant No. DE-AR0000743. L. L. acknowledges support from the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division.

APPENDIX A: THERMAL TRANSPORT MODEL FOR TDTR EXPERIMENTS

Here, the thermal transport model for TDTR experiments is briefly described to assist with the understanding of the data fitting and experimental results presented in this paper. More detailed derivations of the model can be found in previous work [47,48].

In TDTR experiments, when the temperature rise is low such that the heat transport equations are linear and time

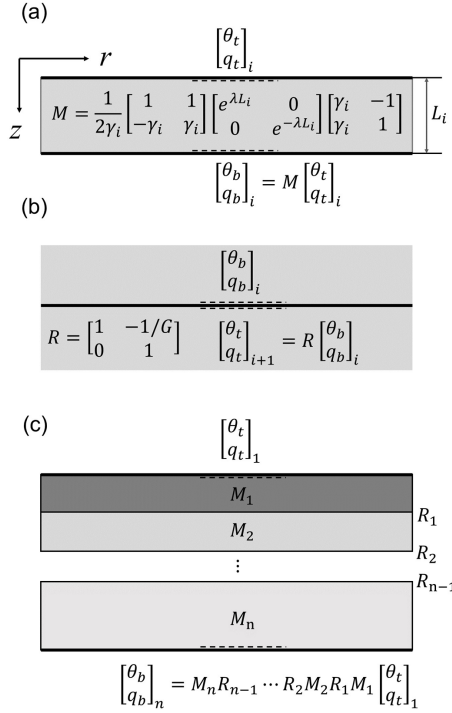


FIG. 6. Schematic of thermal transport model for deriving the frequency-domain solution of heat diffusion in an anisotropic multilayered system. θ and q represent the temperature and heat flux in the frequency domain, and the subscripts t and b denote the top and bottom, respectively.

invariant, the measured in-phase and out-of-phase signals can be written as

$$V_{\text{in}} = \frac{1}{2} \sum_{n=-\infty}^{\infty} [\Delta T(\omega_0 + n\omega_s) + \Delta T(-\omega_0 + n\omega_s)] \exp(in\omega_s t_d), \quad (\text{A1})$$

$$V_{\text{out}} = -\frac{i}{2} \sum_{n=-\infty}^{\infty} [\Delta T(\omega_0 + n\omega_s) - \Delta T(-\omega_0 + n\omega_s)] \exp(in\omega_s t_d), \quad (\text{A2})$$

where $\omega_0 = 2\pi f$ is the modulation frequency, $\omega_s = 2\pi f_{\text{rep}}$ is the laser repetition rate, and t_d is the delay time. The frequency-domain temperature response $\Delta T(\omega)$ is defined as

$$\Delta T(\omega) = A_1 \int_0^{\infty} \hat{G}(k, \omega) \exp(-\pi^2 k^2 w_0^2) 2\pi k dk, \quad (\text{A3})$$

where A_1 is the pump power, k is a Hankel transform variable, w_0 is the root-mean-square average of the pump and probe laser spot radii, and $\hat{G}(k, \omega)$ is the Green's function for the temperature response due to a unit heat flux, the derivation of which involves the solution of an anisotropic heat diffusion problem in a multilayered stack. As illustrated in Fig. 6, the temperature and the heat flux on the top surface of the multilayer stack are related to those at the bottom of the

substrate as

$$\begin{aligned} \begin{bmatrix} \theta_b \\ q_b \end{bmatrix}_n &= M_n R_{n-1} \cdots R_2 M_2 R_1 M_1 \begin{bmatrix} \theta_t \\ q_t \end{bmatrix}_1 \\ &= \begin{bmatrix} A & B \\ C & D \end{bmatrix} \begin{bmatrix} \theta_t \\ q_t \end{bmatrix}_1, \end{aligned} \quad (\text{A4})$$

with matrices M and R defined as

$$M = \frac{1}{2\gamma} \begin{bmatrix} 1 & 1 \\ -\gamma & \gamma \end{bmatrix} \begin{bmatrix} e^{\lambda L} & 0 \\ 0 & e^{-\lambda L} \end{bmatrix} \begin{bmatrix} \gamma & -1 \\ \gamma & 1 \end{bmatrix}, \quad (\text{A5})$$

$$R = \begin{bmatrix} 1 & -1/G \\ 0 & 1 \end{bmatrix}, \quad (\text{A6})$$

where $\lambda = \sqrt{(4\pi^2 k^2 K_r + i\omega C)/K_z}$, $\gamma = K_z \lambda$, L is the thickness of the layer, and G is the interface thermal conductance.

Applying the boundary condition $q_{b,n} = 0$ at the bottom of the substrate yields $0 = C\theta_{t,1} + Dq_{t,1}$. The Green's function \hat{G} can thus be solved as

$$\hat{G}(k, \omega) = \frac{\theta_{t,1}}{q_{t,1}} = -\frac{D}{C}. \quad (\text{A7})$$

Generally, the integral in Eq. (A3) should be evaluated numerically.

APPENDIX B: SPECTRAL CONTRIBUTIONS TO THE ANISOTROPIC THERMAL CONDUCTIVITY OF h-BN

The similar or even higher contributions to K_z from the high-frequency modes compared to those of the low-frequency modes at high temperatures is unusual, as the high-frequency phonons, often of optic modes, typically have smaller group velocities and thus contribute little to thermal transport. In fact, the high-frequency branches in the through-plane direction in Fig. 2(b) are nearly flat, suggesting that these modes should not give large contributions to K_z . However, Fig. 2(b) only shows the highly symmetric directions, not fully representing the entire Brillouin zone. Furthermore, every phonon mode has both a through-plane and an in-plane component, and thus every phonon contributes to transport in both directions. To better elucidate the origin of the comparatively high contributions of the high-frequency phonons to K_z , we plot the calculated phonon lifetimes, group velocities, and spectral thermal conductivities for each phonon mode considered in h-BN at 300 K along the in-plane and through-plane directions as a function of phonon frequency in Fig. 7. We can see that the phonon lifetimes in h-BN do not have a strong frequency dependence; the group velocities of the high-frequency phonons, especially some modes near 20 and 40 THz, are not small either when compared to the low-frequency phonons in the through-plane direction. The high-frequency modes thus have similar contributions to K_z compared to the low-frequency modes as revealed by Fig. 7(c). The reduced thermal conductivity in the through-plane direction compared to the in-plane direction mainly comes from the phonons of an intermediate frequency from 3 to 20 THz. Due to the weak interlayer bonding, the soft through-plane phonons have much reduced lifetimes and group velocities compared to the stiff in-plane phonons, and thus their contributions to the thermal conductivity are much reduced in the through-plane direction.

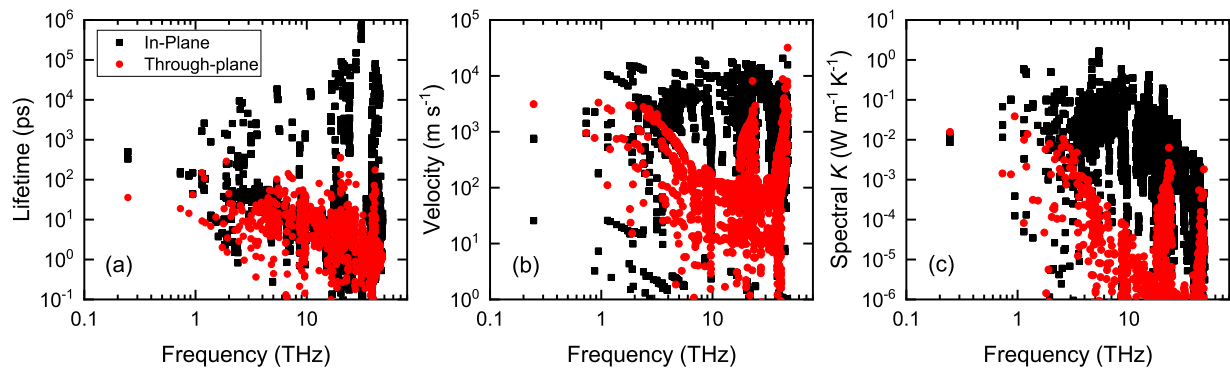


FIG. 7. (a) Phonon lifetimes, (b) group velocities, and (c) spectral thermal conductivities for phonons in h-BN at 300 K for both in-plane and through-plane directions as a function of phonon frequency from the full solution of the Peierls-Boltzmann transport equation.

- [1] K. Watanabe, T. Taniguchi, T. Niiyama, K. Miya, and M. Taniguchi, *Nat. Photonics* **3**, 591 (2009).
- [2] Y. Kubota, K. Watanabe, O. Tsuda, and T. Taniguchi, *Science* **317**, 932 (2007).
- [3] Y. Kimura, T. Wakabayashi, K. Okada, T. Wada, and H. Nishikawa, *Wear* **232**, 199 (1999).
- [4] C. Zhi, Y. Bando, T. Terao, C. Tang, H. Kuwahara, and D. Golberg, *Adv. Funct. Mater.* **19**, 1857 (2009).
- [5] C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, and J. Hone, *Nat. Nanotechnol.* **5**, 722 (2010).
- [6] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, M. I. Katsnelson, L. Eaves, S. V. Morozov, A. S. Mayorov, N. M. Peres, A. H. Neto, J. Leist, A. K. Geim, L. A. Ponomarenko, and K. S. Novoselov, *Nano Lett.* **12**, 1707 (2012).
- [7] J. I. A. Li, T. Taniguchi, K. Watanabe, J. Hone, A. Levchenko, and C. R. Dean, *Phys. Rev. Lett.* **117**, 046802 (2016).
- [8] B. Amorim, J. Schiefele, F. Sols, and F. Guinea, *Phys. Rev. B* **86**, 125448 (2012).
- [9] D. Golla, A. Brasington, B. J. LeRoy, and A. Sandhu, *APL Materials* **5**, 056101 (2017).
- [10] B. Zhao and Z. M. Zhang, *J. Heat Transfer* **139**, 022701 (2016).
- [11] J. Wu, B. Wang, Y. Wei, R. Yang, and M. Dresselhaus, *Mater. Res. Lett.* **1**, 200 (2013).
- [12] S. Kang, B. Fallahzad, K. Lee, H. Movva, K. Kim, C. M. Corbet, T. Taniguchi, K. Watanabe, L. Colombo, and L. F. Register, *IEEE Electron Device Lett.* **36**, 405 (2015).
- [13] I. Meric, C. R. Dean, N. Petrone, L. Wang, J. Hone, P. Kim, and K. L. Shepard, *Proc. IEEE* **101**, 1609 (2013).
- [14] G.-H. Lee, Y.-J. Yu, X. Cui, N. Petrone, C.-H. Lee, M. S. Choi, D.-Y. Lee, C. Lee, W. J. Yoo, and K. Watanabe, *ACS Nano* **7**, 7931 (2013).
- [15] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, and S. V. Morozov, *Science* **335**, 947 (2012).
- [16] J. Gaskell, L. Eaves, K. S. Novoselov, A. Mishchenko, A. K. Geim, T. M. Fromhold, and M. T. Greenaway, *Appl. Phys. Lett.* **107**, 103105 (2015).
- [17] S. C. de la Barrera and R. M. Feenstra, *Appl. Phys. Lett.* **106**, 093115 (2015).
- [18] S. H. Lee, M. S. Choi, J. Lee, C. H. Ra, X. Liu, E. Hwang, J. H. Choi, J. Zhong, W. Chen, and W. J. Yoo, *Appl. Phys. Lett.* **104**, 053103 (2014).
- [19] F. Withers, O. Del Pozo-Zamudio, A. Mishchenko, A. P. Rooney, A. Gholinia, K. Watanabe, T. Taniguchi, S. J. Haigh, A. K. Geim, A. I. Tartakovskii, and K. S. Novoselov, *Nature Mater.* **14**, 301 (2015).
- [20] X. Li, S. Lin, X. Lin, Z. Xu, P. Wang, S. Zhang, H. Zhong, W. Xu, Z. Wu, and W. Fang, *Opt. Express* **24**, 134 (2016).
- [21] L. Lindsay and D. A. Broido, *Phys. Rev. B* **84**, 155421 (2011).
- [22] I. Jo, M. T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, and L. Shi, *Nano Lett.* **13**, 550 (2013).
- [23] E. K. Sichel, R. E. Miller, M. S. Abrahams, and C. J. Buiocchi, *Phys. Rev. B* **13**, 4607 (1976).
- [24] A. Simpson and A. D. Stuckes, *J. Phys. C: Solid State Phys.* **4**, 1710 (1971).
- [25] D. Zhao, X. Qian, X. Gu, S. A. Jajja, and R. Yang, *J. Electron. Packag.* **138**, 040802 (2016).
- [26] N. D. Zhigadlo, *J. Cryst. Growth* **402**, 308 (2014).
- [27] S. Liu, R. He, Z. Ye, X. Du, J. Lin, H. Jiang, B. Liu, and J. H. Edgar, *Cryst. Growth Des.* **17**, 4932 (2017).
- [28] J. M. Ziman, *Electrons and Phonons: The Theory of Transport Phenomena in Solids* (Clarendon, New York, 1960).
- [29] G. P. Srivastava, *The Physics of Phonons* (Taylor & Francis, New York, 1990).
- [30] L. Lindsay, *Nanoscale Microscale Thermophy. Eng.* **20**, 67 (2016).
- [31] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- [32] W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- [33] D. A. Broido, M. Malorny, G. Birner, N. Mingo, and D. A. Stewart, *Appl. Phys. Lett.* **91**, 231922 (2007).
- [34] J. Shiomi, K. Esfarjani, and G. Chen, *Phys. Rev. B* **84**, 104302 (2011).
- [35] L. Lindsay, D. A. Broido, and T. L. Reinecke, *Phys. Rev. B* **87**, 165201 (2013).
- [36] A. Cepellotti, G. Fugallo, L. Paulatto, M. Lazzeri, F. Mauri, and N. Marzari, *Nat. Commun.* **6**, 6400 (2015).
- [37] W. Li, J. Carrete, and N. Mingo, *Appl. Phys. Lett.* **103**, 253103 (2013).
- [38] A. Jain and A. J. McGaughey, *Sci. Rep.* **5**, 8501 (2015).

- [39] L. Lindsay, W. Li, J. Carrete, N. Mingo, D. A. Broido, and T. L. Reinecke, *Phys. Rev. B* **89**, 155426 (2014).
- [40] Y. Hong, J. Zhang, and X. C. Zeng, *J. Phys. Chem. C* **120**, 26067 (2016).
- [41] G. Fugallo, A. Cepellotti, L. Paulatto, M. Lazzeri, N. Marzari, and F. Mauri, *Nano Lett.* **14**, 6109 (2014).
- [42] A. N. Gandi and U. Schwingenschlögl, *Europhys. Lett.* **113**, 36002 (2016).
- [43] D. O. Lindroth and P. Erhart, *Phys. Rev. B* **94**, 115205 (2016).
- [44] X. Gu, B. Li, and R. Yang, *J. Appl. Phys.* **119**, 085106 (2016).
- [45] R. B. Wilson, B. A. Apgar, L. W. Martin, and D. G. Cahill, *Opt. Express* **20**, 28829 (2012).
- [46] P. Jiang, X. Qian, and R. Yang, *Rev. Sci. Instrum.* **88**, 074901 (2017).
- [47] D. G. Cahill, *Rev. Sci. Instrum.* **75**, 5119 (2004).
- [48] A. J. Schmidt, X. Chen, and G. Chen, *Rev. Sci. Instrum.* **79**, 114902 (2008).
- [49] P. Jiang, X. Qian, X. Gu, and R. Yang, *Adv. Mater.* **29**, 1701068 (2017).
- [50] B. Sun, X. Gu, Q. Zeng, X. Huang, Y. Yan, Z. Liu, R. Yang, and Y. K. Koh, *Adv. Mater.* **29**, 1603297 (2017).
- [51] Y. K. Koh and D. G. Cahill, *Phys. Rev. B* **76**, 075207 (2007).
- [52] R. B. Wilson, J. P. Feser, G. T. Hohensee, and D. G. Cahill, *Phys. Rev. B* **88**, 144305 (2013).
- [53] J. Yang, E. Ziade, and A. J. Schmidt, *Rev. Sci. Instrum.* **87**, 014901 (2016).
- [54] W. Paszkowicz, J. B. Pelka, M. Knapp, T. Szyszko, and S. Podsiadlo, *Appl. Phys. A: Mater. Sci. Process.* **75**, 431 (2002).
- [55] <http://www.quantum-espresso.org>
- [56] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, *J. Phys.: Condens. Matter.* **21**, 395502 (2009).
- [57] J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [58] A. Dal Corso, S. Baroni, R. Resta, and S. de Gironcoli, *Phys. Rev. B* **47**, 3588 (1993).
- [59] P. Haas, F. Tran, and P. Blaha, *Phys. Rev. B* **79**, 085104 (2009).
- [60] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [61] R. J. Nemanich, S. A. Solin, and R. M. Martin, *Phys. Rev. B* **23**, 6348 (1981).
- [62] R. Geick, C. H. Perry, and G. Rupprecht, *Phys. Rev.* **146**, 543 (1966).
- [63] J. Serrano, A. Bosak, R. Arenal, M. Krisch, K. Watanabe, T. Taniguchi, H. Kanda, A. Rubio, and L. Wirtz, *Phys. Rev. Lett.* **98**, 095503 (2007).
- [64] C. Herring, *Phys. Rev.* **95**, 954 (1954).