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Temperature Dependence of Anisotropic Thermal-Conductivity Tensor of Bulk Black Phosphorus

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Thermal transport in layered, 2D black phosphorus (BP) is of great interest, not only due to its importance in the designs of BP devices,^[1] but also because it provides a unique platform to study the physics of heat transport in highly anisotropic materials.^[2] BP belongs to the orthorhombic Cmca point group,^[3] with its puckered honeycomb basal planes weakly bonded together by interlaver van der Waals' forces. Due to the nature of its crystal structure, second order tensors (e.g., the thermal conductivity tensor Λ) of BP have three independent components along the principal axes of zigzag (ZZ), armchair (AC), and through-plane (TP), see Figure 1a, and the thermal conductivity tensor is strongly anisotropic along these axes.^[4] (In this paper, we use $\Lambda_{\rm ZZ}$, $\Lambda_{\rm AC}$, and $\Lambda_{\rm TP}$ to denote the three independent components of the thermal conductivity tensor.) Here, we accurately measured and report the anisotropic thermal conductivity tensor ($\Lambda_{7,7}$, Λ_{AC} , and Λ_{TP}) of bulk BP in a temperature range of $80 \le T \le 300$ K. Our temperature dependence measurements provide a crucial benchmark for future studies of anisotropic heat transport in BP and phosphorene.

To date, there are only few experimental studies on anisotropic thermal conductivity of BP, even at 300 K. Luo et al.^[5] and Lee et al.^[6] measured BP flakes with a thickness of 9–30 and 60–310 nm using the optothermal Raman method and the microbridge technique, respectively, and reported $\Lambda_{ZZ} = 11-45$ W m⁻¹ K⁻¹ and $\Lambda_{AC} = 5-22$ W m⁻¹ K⁻¹ at room temperature. These values of Λ_{ZZ} and Λ_{AC} are substantially lower than predictions by first-principles calculations^[4,7,8] for bulk BP and phosphorene. While these low values of thermal conductivity were attributed to additional boundary scattering of phonons in the thin flakes,^[5,6] we note that

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scattering of phonons along the basal planes by the interfaces is rather weak^[9] and thus this explanation might not be satisfactory. The low values could also originate from degradation of the BP flakes by oxidation,^[10] as the BP flakes in both studies were exposed to the air for a substantial amount of time during sample preparation and measurements. With the degradation, the reported thermal conductivity is probably not intrinsic. Jang et al.^[11] encapsulated their BP flakes of thickness of 138-552 nm with a 3 nm Al₂O₃ overlayer, and obtained $\Lambda_{ZZ} = 63-86$ W m⁻¹ K⁻¹, $\Lambda_{AC} = 26-34$ W m⁻¹ K⁻¹, and $\Lambda_{TP} = 3.2-4.5$ W m⁻¹ K⁻¹ from their time-domain thermoreflectance (TDTR) measurements. Zhu et al.^[4] derived $\Lambda_{ZZ} = 84-101 \text{ W m}^{-1} \text{ K}^{-1}, \Lambda_{AC} = 26-36 \text{ W m}^{-1} \text{ K}^{-1}, \text{ and}$ $\Lambda_{\rm TP}$ = 4.3–5.5 W m⁻¹ K⁻¹ from their measurements on BP of thickness of 30-50 µm using time-resolved magneto-optic Kerr effect. Although Jang et al.'s and Zhu et al.'s samples were not seriously oxidized, their pump-probe measurements in the through-plane direction might be lower than the intrinsic $\Lambda_{\rm TP}$ because the mean-free-paths (ℓ) of a substantial portion of heat-carrying phonons are much longer than the characteristic length scales of their measurements (<500 nm), i.e., the thickness of the samples or the thermal penetration depth d.^[12–14] In fact, we obtained a $\Lambda_{\rm TP}$ value \approx 25% higher than Zhu et al.'s and Jang et al.'s measurements,^[4,11] when we used a much lower modulation frequency in our measurements to achieve a larger thermal penetration depth.

With the relatively few published works on the thermal properties of BP, knowledge of anisotropic heat transport in BP and other layered materials (e.g., the mean-free-paths of phonons in the through-plane and in-plane directions) is still incomplete. Even for the most well-studied graphite, the consensus has yet been achieved. For example, while Zhang et al.^[15] reported that the through-plane thermal conductivity converges when the thickness of graphite film is above 500 nm, Fu et al.[16] found that the thermal conductivity of a 700 nm thin film is still 27% lower than the bulk value. In this work, we use frequencydependent TDTR measurements^[12,17] and the first-principles calculations to determine the distribution of phonon meanfree-paths in bulk BP along the through-plane direction. We find that at 300 K, the span of phonon mean-free-paths along the TP axis is surprisingly broad from sub-10 nm to 1 μ m. Also, we find that frequency-dependent phonon relaxation times are mostly isotropic in direction when both the vibrations and the propagation directions of phonons are in-plane, but are significantly suppressed when either the vibrations or the propagation directions of phonons are out-of-plane.

Our samples are 3 mm-sized bulk BP samples, see Figure 1b. The largest sample, denoted by BP-1, with a dimension of

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Figure 1. Characterization of black phosphorus. a) Crystal structure of black phosphorus, in perspective, top and front views, respectively. Only two stacked layers are shown. b) Optical image of our black phosphorus samples, the left was purchased from HQ-Graphene (BP-1), while the middle (BP-2) and the right (BP-3) were home-grown. BP-2 was coated with an Al thin film in the image. c) Polarized Raman spectra of BP-1 showing the outof-plane A_g^1 mode and in-plane B_{2g} and A_g^2 modes, acquired using the parallel-polarization configuration. The sample was rotated so that the angle between incident laser polarization and initial orientation of BP-1 ranges from 0° to 90°, as noted in the plot. Each plot is shifted by 3×10^4 counts W^{-1} s⁻¹ from previous measurement for clarity. d) Angle dependence of the integrated intensity of the B_{2g} peak shown in (c) (red circles), and when the measurements were repeated after we rotated the samples by 2° (blue squares). The black line is a fit of sin²(2 θ) to the intensity of the B_{2g} peak. e) θ -2 θ XRD scan of BP-1.

 $\approx 8 \text{ mm} \times 5 \text{ mm} \times 0.3 \text{ mm}$, was purchased from HQ Graphene. The other two smaller samples, BP-2 and BP-3, with a dimension of 5 mm \times 1.5 mm \times 0.1 mm and 5 mm \times 1 mm \times 0.1 mm, were home-grown. All three BP samples were grown by a mineralizer-assisted gas-phase transformation method,^[18] through a short way transport reaction of red phosphorus with Sn/SnI4 as the mineralization additive. Sizes of several millimeters to centimeters are realized by controlling the cooling speed during the growth process. Details of our sample preparation are presented in the Experimental Section. To prepare the samples for measurements, we mounted BP-2 and BP-3 on Si substrates for easier handling. (BP-1 is exempted from this step since it is large and thick enough.) We then exfoliated the top layers of the BP samples to expose the fresh BP surfaces, and immediately loaded the samples into an ultrahigh vacuum thermal evaporation chamber for deposition of a 100 nm thick Al film. The Al film acts as the transducer for our measurements, and also passivates the fresh BP surfaces. We ensure that the total time that the BP samples were exposed to air is less than 1 min to minimize oxidation of BP.

Before thermal measurements, we identify the crystallographic orientations of the BP samples by polarized Raman spectroscopy,^[19] see Figure 1c. To improve the accuracy of our determination of the crystallographic orientations of BP, we conduct the polarized Raman measurements for multiples of 15°, and fit the measurements with a $\sin^2(2\theta)$ function to determine ZZ and AC axes, see Figure 1d and the Experimental Section. We also ensure that the basal planes are perpendicular to the sample surface via X-ray diffraction (XRD) scan of the BP-1 sample. In the XRD spectrum, we observed only (0 n 0) peaks, where n = 4, 6, and 8, as expected, see Figure 1e.

We measure the through-plane thermal conductivity Λ_{TP} of the BP samples by frequency-dependent TDTR,^[12,20] and the two in-plane thermal conductivities Λ_{ZZ} and Λ_{AC} by the beam-offset TDTR method.^[21] Details of our implementation, data analysis, and signal processing of the TDTR and beamoffset TDTR methods are presented in the Experimental Section and the Supporting Information. In both methods, two parameters must be carefully considered: the $1/e^2$ radii w_0 of the laser beams and the modulation frequency f of the pump beam. (The modulation frequency f affects heat diffusion during the measurements, which is characterized by a parameter called the thermal penetration depth *d*; $d = \sqrt{\Lambda/\pi Cf}$, where Λ is thermal conductivity and C is volumetric heat capacity.) For accurate measurements of Λ_{TP} , we employed a large w_0 (25 μ m) and a low *f* (0.5 MHz), and ensure that heat diffusion is mainly 1D in the through-plane direction. The low *f* is crucial to ensure that our TDTR measurements approach the intrinsic $\Lambda_{\rm TP}$, since TDTR is not sensitive to heat transport by ballistic phonons with mean-free-path $\ell >> 2d.^{[12,13,22]}$ (Interpretation of the frequency dependence of TDTR measurements is discussed below.) For the beam-offset TDTR method, we employed a low

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offset (um)

Figure 2. Beam-offset TDTR measurements of BP-1 along the ZZ and AC axes. a) at 300 K using $w_0 = 2.5 \,\mu\text{m}$ and $f = 0.5 \,\text{MHz}$, and c) at 80 K using $w_0 = 5 \,\mu\text{m}$ and $f = 0.5 \,\text{MHz}$. Three sets of measurements are plotted concurrently: one measured when the angle between ZZ axis and horizontal scan direction is 0° (red squares), one measured after the sample was rotated by 90° (blue triangles), and one after the sample was stored under ambient conditions for six months (black circles). The green lines are fits of an isotropic thermal model. b,d) Thermal conductivity of black phosphorus at 300 K (b) and 80 K (d) derived from the beam-offset TDTR measurements on BP-1 (black circles), BP-2 (red triangles), and BP-3 (blue diamonds), as a function of the angle between the beam-offset scanning direction and the ZZ axis of the BP samples. The green lines are amplitudes of the orthogonal components of the thermal conductivity tensor under rotation about the TP axis, with the major and minor axes of 83 and 28 W m⁻¹ K⁻¹ at 300 K, and of 360 and 130 W m⁻¹ K⁻¹ at 80 K, respectively.

f = 0.5 MHz and a small w_0 (as small as 2.5 µm), to ensure that heat mainly spreads along the basal planes and is predominantly determined by $\Lambda_{\rm ZZ}$ and $\Lambda_{\rm AC}$. At f = 0.5 MHz and T = 80 K, heat diffuses up to 50 µm in either side of the pump beam, see **Figure 2**c. Thus, for accurate measurements of the intrinsic thermal conductivity tensor of bulk BP at 80 K, the lateral dimension of the BP samples should be >100 µm.

To ensure the accuracy and consistency of our beam-offset measurements, we systematically performed multiple measurements on our BP samples: i) We rotated our BP sample by 90° and performed the beam-offset measurements when the ZZ axis of the sample was horizontal and when it was vertical, relative to the optical table. We obtained identical results. ii) We performed an additional measurement six months after the

initial sample preparation, to check for any degradation of our BP samples. No observable degradation was found. iii) We rotated our samples by $\pm 30^{\circ}$ and performed measurements along different crystallographic orientations. We achieved excellent agreement for all these measurements, see Figure 2 and more detailed discussion in the Experimental Section.

We performed multiple measurements on three BP samples and obtained similar values for Λ_{ZZ} , Λ_{AC} , and Λ_{TP} , see **Table 1** for a summary of the average values of our measurements performed using different modulation frequency f and laser spot size w_0 at room temperature. On average, we obtained $\Lambda_{ZZ} = 83 \pm 10 \text{ W m}^{-1} \text{ K}^{-1}$, $\Lambda_{AC} = 28 \pm 5 \text{ W m}^{-1} \text{ K}^{-1}$, and $\Lambda_{TP} =$ $6.5 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature. For Λ_{ZZ} and Λ_{AC} , our values are similar to the values obtained by Jang et al.^[11] and Zhu et al.^[4] For Λ_{TP} , our value is >25% higher than the prior reported Λ_{TP} measured at a higher f of 9–10 MHz.^[4,11] We believe that prior Λ_{TP} is artificially low because with the high f, a substantial portion of phonons remain non-equilibrium within a region of $2d \approx 600 \text{ nm}$ and heat transport by these non-equilibrium phonons are not registered in TDTR measurements, see

270

Table 1. Summary of all the measurements at 300 K. The unit is W m^{-1} K⁻¹.

	$w_0 = 2.5 \ \mu m, f = 0.5 \ MHz$		$w_0 = 5 \ \mu m, f = 0.5 \ MHz$		$w_0 = 25 \ \mu m, f = 0.5 \ MHz$
	$\Lambda_{\sf ZZ}$	$\Lambda_{\sf AC}$	$\Lambda_{\sf ZZ}$	$\Lambda_{\sf AC}$	Λ_{TP}
BP-1	80.4 ± 10	26.4 ± 5	84 ± 11	28 ± 6	$\textbf{6.5} \pm \textbf{0.8}$
BP-2	85 ± 10	28 ± 5	86 ± 11	30 ± 6	
BP-3	79.2 ± 10	27.6 ± 5			

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the discussion below on the frequency dependence of TDTR measurements. We note that we derived an apparent through-plane thermal conductivity of 5.4 W m⁻¹ K⁻¹ when we applied f = 10 MHz, similar to what Zhu et al. reported.^[4] In our measurements, the diameters of our laser beams vary from 5 to 50 µm, much larger than the mean-free-paths of phonons in BP (see Figure 5b and Figure S11 in the Supporting Information). Thus, our results do not depend on the size of the laser beams, see Table 1. Our values thus represent the intrinsic thermal conductivity tensor of bulk BP.

We compare the derived $\Lambda_{\rm TP}$, Λ_{ZZ} , and $\Lambda_{\rm AC}$ in the temperature range of 80–300 K to first-principles calculations of the thermal conductivity of bulk BP by Zhu et al.^[4] and of phosphorene by Li and co-workers,^[7] Jain and McGaughey,^[8] and Zhu et al.^[4] in **Figure 3**. We find that within the temperature range, all three components of the measured thermal conductivity tensor are inversely proportional to *T*, which agrees well with the predictions from the first-principles calculations. The *T*⁻¹ dependence suggests that, in all crystallographic orientations, heat is carried mainly by phonons that are all



Figure 3. Temperature dependence of the anisotropic thermal conductivity tensor of black phosphorus. Solid symbols represent data derived from measurements on BP-1 (black circles) and BP-2 (red triangles). All measurements were performed using f = 0.5 MHz. For measurements of $\Lambda_{\rm TP}$, we used $w_0 = 25 \,\mu$ m, while for measurements of $\Lambda_{\rm ZZ}$ and $\Lambda_{\rm AC}$, we used $w_0 = 5 \,\mu$ m. For comparison, prior measurements of polycrystalline BP by Slack^[30] (blue open circles), of a 170 nm thick BP nanoribbon by Lee et al.^[6] in ZZ and AC directions (up and down open triangles) and of graphite by Nihira and Iwata^[31] (orange open diamonds) are also plotted. Solid lines and dashed lines are the first-principles calculations of the thermal conductivity tensor of bulk BP and phosphorene, respectively, by Li and co-workers^[7] (blue), Jain and McGaughey^[8] (green), and Zhu et al.^[4] (magenta).

predominantly scattered by Umklapp processes, despite the anisotropy that we observed in the thermal conductivity. Our measured Λ_{AC} and Λ_{TP} are similar to the first-principles calculations of bulk BP by Zhu et al.,^[4] while the measured Λ_{77} is ≈20% lower than the first-principles prediction. Comparing to phosphorene, our Λ_{ZZ} (Λ_{AC}) is 30% (9%) lower than the firstprinciples predictions by Jain and McGaughey.^[8] The difference could be attributed to reduction in Λ_{ZZ} and Λ_{AC} of bulk BP due to enhanced scattering of out-of-plane TA1 phonons in bulk BP compared to that in phosphorene, similar to enhanced scattering of TA1 phonons in graphite compared to that in graphene.^[23] (We used TA1 and TA2 to denote the lower and higher energy branches of the transverse phonons, respectively, see the phonon dispersion in Figure S8 in the Supporting Information. Along the basal planes (e.g., ZZ and AC), TA1 and TA2 refers to out-of-plane ZA and in-plane vibration modes.)

We notice that at low temperatures, $\Lambda_{ZZ}/\Lambda_{AC}$ of BP nanoribbons measured by Lee et al.^[6] approaches ≈ 1 contrary to our measurements of strong anisotropy, see Figure 3. We think that even if the mean-free-paths of phonons are limited by the sample size due to strong boundary scattering, heat transport should still be anisotropic for BP nanoribbons due to the anisotropy in the speeds of sounds, see discussions below. Thus, low temperature measurements of Lee et al.^[6] might indicate that their BP nanoribbons could be seriously oxidized, resulting in isotropic speeds of sounds.

We present the thermal conductance (*G*) of Al/BP interfaces in **Figure 4**. From the temperature dependence, we confirm that heat is mainly carried by phonons across the BP interface. At 300 K, we find that G = 72 MW m⁻² K⁻¹; this value of *G* is stable over a period of greater than six months, indicating that our BP samples did not degrade over time. *G* of Al/BP is nearly twice of *G* of NbV/AlO_x/BP^[11] and TbFe/BP,^[4] and is significantly higher than that of Al/graphite.^[24] We attribute this observation to a better match of the Debye temperature between Al and BP,^[25] compared to Al and graphite.



Figure 4. Temperature dependence of interfacial thermal conductance of AI/BP. Our values (black circles) are nearly twice as large as that of TbFe/ BP^[4] (solid triangle (indicated)) and NbV/AIO_x/BP^[11] (solid square). For comparison, we also plot thermal conductance of AI/HOPG^[24] (open diamonds), Al/single-layer-graphene(SLG)/Cu^[32] (open circles), and Al/ $MoS_2^{[33]}$ (inverted open triangle). HOPG refers to highly oriented pyrolytic graphite.

www.advmat.de To further understand the physics of anisotropic heat transport in BP, we employ the frequency-dependent TDTR measurements^[12,17] and first-principles-based phonon Boltzmann transport equation (BTE) calculations,^[26] two powerful tools that were recently developed to study phonon mean-free-paths. Frequency dependence of TDTR measurements has been developed into a convenient approach to probe the mean-free-paths of phonons,^[12,17] even though questions on how to accurately interpret the measurements (e.g., how to handle the non-equilibrium heat transfer across the interfaces^[27]) still remain. In this work, we use a simple approximation, presented below, to analyze our frequency-dependent TDTR measurements. We do not employ the more sophisticated approaches such as solving the BTE on the sample geometry^[13] or reconstruction of phonon mean-free-paths using a complex optimization procedure,^[28] because 1) the main source of uncertainty in modeling is how to handle the transmission, reflection, and scattering of phonons at the interface, which is not mitigated in these more sophisticated approaches; and 2) our simple analysis below might underestimate, if any, the distribution of phonon meanfree-paths. Thus, the conclusion that we derived from our frequency-dependent measurements - the distribution of the mean-free-paths of phonons along the through-plane direction is rather broad - should remain valid even if the more sophisticated analyses are applied.



Thus, we instead rely on the conclusions that we derived from our previous solution of the BTE on a semi-infinite solid using a boundary condition relevant to TDTR and frequency-domain thermoreflectance (FDTR). Our previous BTE calculations showed that as long as the distribution of phonon mean-free-path is sufficiently wide (e.g., in alloys when heat is carried mainly by low-energy phonons^[27]), the apparent thermal conductivity measured by TDTR could be crudely approximated by assuming an additional boundary scattering at a characteristic length of $L_c = 2d$.^[13] Since the phonon meanfree-paths in BP span more than two orders of magnitude according to our first-principles calculations, see below, the use of the criterion $L_c = 2d$ should be acceptable. We emphasize again that the thermal conductivity accumulation function derived using this simplified approach only gives a crude approximation to the distribution of phonon mean-free-paths in BP.

We first compare the apparent through-plane thermal conductivity Λ_{TP} that we derived from our frequency-dependent TDTR measurements with a modulation frequency of $0.5 \le f \le 10$ MHz, to prior measurements on BP, see **Figure 5a**. We plot our frequency dependent Λ_{TP} at 80, 150, and 300 K as a function of $L_c = 2d$. We observe a considerable L_c dependence for the apparent Λ_{TP} at 300 K; Λ_{TP} does not converged even when $L_c = 1 \ \mu\text{m}$. From the L_c dependence, we expect that the



Figure 5. Anisotropy in the mean-free-paths of phonons in BP. a) Frequency-dependent TDTR measurements of the through-plane thermal conductivity (Λ_{TP}) (circles) at 80 K (hollow), 150 K (half filled), and 300 K (solid), compared to measurements on BP flakes with thickness of 138–552 nm by Jang et al.^[11] (squares), measurements of BP at 9.1 MHz by Zhu et al.^[4] (triangles), and our first-principles calculations on L_c -dependent Λ_{TP} at 80 K (dashed-dotted line), 150 K (dashed line), and 300 K (solid line). All measurements and calculations are normalized by the calculated Λ_{TP} of bulk BP of 6.5 W m⁻¹ K⁻¹ (300 K), 14 W m⁻¹ K⁻¹ (150 K), and 30 W m⁻¹ K⁻¹ (80 K), respectively. All measurements are plotted as a function of a characteristic length $L_c = 2d$ or flake thickness *h*, whichever smaller, as defined in main text. b) Thermal conductivity accumulation along through-plane (TP) directions at 300 K (solid line), 150 K (dashed line), and 80 K (dashed-dotted line) from our first-principles calculations. The accumulated thermal conductivity calculated from the first-principles calculations is normalized by the respective bulk thermal conductivity. c) The relaxation times (τ) of longitudinal (LA) and transverse (TA1 and TA2) phonon modes along the high-symmetry axes of BP, as a function of angular frequency (ω) of phonons.

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phonon mean-free-paths along through-plane direction are relatively long, although the thermal conductivity is low.

In the same figure, we also plot prior measurements of Λ_{TP} of BP flakes, as a function of either 2d or film thickness h, whichever smaller. While we find that prior measurements on BP flakes by Jang et al.^[11] and Zhu et al.^[4] generally agree with our frequency-dependent measurements, we notice that two data points from Jang et al. significantly deviate, see Figure 5a. We attribute the discrepancy to the higher-than-usual level of uncertainty for measurements by Jang et al. Unlike the standard analysis of our TDTR measurements with only two unknowns (the thermal conductance of Al/BP interface and Λ_{TP} of BP), there are four unknowns in the analysis of Jang et al.'s measurements including the thermal conductance of NbV/BP interfaces, the thickness of BP flakes that was not independently measured, the through-plane thermal conductivity of BP flakes, and the thermal conductance of BP/Si interface, see ref. [11] for details. Jang et al. performed two TDTR measurements to derive the four unknowns simultaneously. However, due to the larger number of unknowns in Jang et al.'s analysis, higher uncertainty is expected. Particularly, in the Supporting Information of ref. [11], Jang et al. reported that the derived thermal conductance of BP/Si interfaces varies by up to 50% for their BP samples. This could be a source of errors in their derived $\Lambda_{\rm TP}$ values.

To gain more insights on the L_c -dependent thermal conductivity in BP, we perform BTE calculations of heat conduction along the through-plane direction of BP by sandwiching BP between hot and cold reservoirs with a distance of L_c apart, which provides additional boundary scattering mentioned above. Details of first-principles calculations and the framework of phonon BTE are provided in Section S6 in the Supporting Information. We note that the current first-principles calculations render the same thermal conductivity values of bulk BP as reported by Zhu et al.;^[4] the difference is that in this work, we extend the prediction to L_c -dependent thermal conductivity of BP by adding a boundary scattering term. The calculated through-plane thermal conductivity with an additional boundary scattering at L_c , as shown in Figure 5a, agrees well with both our frequency-dependent measurements and prior reported measurements on BP, for all three temperatures. As seen from Figure 5a, the through-plane thermal conductivity corresponding to $L_c = 10$ nm, 100 nm, and 1 μ m is around 16%, 53%, and 87% of the bulk value, respectively, at 300 K. Our results thus provide a credible explanation to why Zhu et al.^{[4]} obtained a $\Lambda_{\rm TP}\approx\!\!25\%$ smaller than the intrinsic value, i.e., they performed the measurements using f = 9 MHz with the 2*d* only \approx 600 nm and thus heat transport by a substantial portion of non-equilibrium phonons were not measured in their experiments.

Since the L_c -dependent thermal conductivity comes from the long mean-free-path, in Figure 5b, we directly plot the thermal conductivity accumulation function^[29] along TP axis at 80, 150, and 300 K, calculated from our first-principles model, as a function of phonon mean-free-path ℓ . (The accumulation functions along other axes are presented in the Supporting Information.) The accumulation functions are normalized by their corresponding bulk thermal conductivity.^[4] The mean-free-path distribution at 300 K spans from several nanometers to several

microns. Phonons with long mean-free-paths along TP direction should be related to low frequency acoustic phonons. For example, the mean-free-path of the longitudinal (LA) phonon mode along TP direction with a frequency of 1 THz is around 1.6 μ m, considering the sound velocity is around 4600 m s⁻¹ from the calculated phonon dispersion and a phonon lifetime of 400 ps, as discussed below.

To understand the origins of the anisotropy in the thermal conductivity of BP, we first examine the phonon dispersion of BP along the principal axes (ZZ, AC, and TP) as shown in Figure S8 in the Supporting Information. The sound velocity (group velocity of low-frequency LA modes) is 8300, 4800, 4600 m s⁻¹ along the three directions, showing anisotropicity. The large difference of group velocity between ZZ and AC directions should be an important origin of the anisotropy of their thermal conductivity. We also notice that the difference of the sound velocity along AC and TP directions are small. However, from the phonon dispersion, the phonon branches other than LA branch along TP directions. Therefore, the group velocity should be responsible for the anisotropy between TP direction and basal-plane directions to some extent.

Since thermal conductivity is also dependent on the phonon relaxation time (lifetime), we plot the phonon lifetime τ of the LA and transverse (TA1 and TA2) phonons in BP along the principal axes (ZZ, AC, and TP) in Figure 5c. Interestingly, we find that τ roughly scales with ω^2 for LA and TA2 phonons but roughly scales with ω for TA1 phonons along all principal axes in the frequency range we calculated, but with different scattering strengths. We also observe that when both the vibrations and the propagation directions of phonons are within the basal planes (i.e., LA and TA2 phonons along ZZ and AC axes), the relaxation times of the phonon modes are rather isotropic in direction and are determined primarily by phonon frequency ω , see Figure 5c. The scattering of these in-plane vibration modes is relatively weaker. On the other hand, when either the vibrations or the propagation directions of phonons are out-of-plane (e.g., TA1 phonons, and phonons along the TP axis), phonons are much strongly scattered with clear anisotropy. The results thus suggest that the anisotropy of Λ_{ZZ} and Λ_{AC} in the basal planes is mainly due to anisotropy in the phonon dispersion, while the anisotropy of $\Lambda_{\rm TP}$ and basal-plane thermal conductivity is due to both phonon dispersion and relaxation time.

In summary, we performed both frequency-dependent and beam offset TDTR measurements and the first-principles calculations on the thermal conductivity tensor of bulk BP in the temperature range of 80-300 K. Our measurements and calculations provide consistent results. We derive the following important conclusions. 1) We observe a T^{-1} dependence for the all three components of the thermal conductivity tensor and thus conclude that phonons are mainly scattered by the Umklapp processes in all crystallographic orientations in BP. 2) We obtain the intrinsic through-plane thermal conductivity of BP through frequency-dependent TDTR measurements and observe a considerable frequency dependence in the throughplane thermal conductivity measurements. Our measurements suggest that the phonon mean-free-paths are rather long in the through-plane direction. 3) From our first-principles calculations, we find that in BP, approximately, $\tau \propto \omega^2$ for LA and TA2

phonons, but $\tau \propto \omega$ for TA1 phonons in the frequency range we studied. Also, τ is mostly isotropic in direction when both the vibrations and the propagation directions of phonons are in-plane (LA and TA2 phonons along ZZ and AC axes), but the scattering is strongly enhanced when either the vibrations or the propagation directions of phonons are out-of-plane (e.g., TA1 phonons, and phonons along the TP axis). We thus conclude that the anisotropy in the relaxation times only contributes to the anisotropy in the through-plane thermal conductivity, but not the anisotropy in the thermal conductivities along the basal planes. Our experimental and theoretical studies advance the fundamental understanding on heat transport in layered and highly anisotropic materials.

Experimental Section

Growth of Black Phosphorus: BP-2 and BP-3 were prepared using the following method. 20 mg of Sn, 10 mg of SnI₄, and 500 mg of red phosphorus were weighed in a silica glass ampoule of 10 cm length, an inner diameter of 1.0 cm, and a wall thickness of 0.25 cm. The ampoule was evacuated and placed horizontally in a dual zone split tube furnace, with the starting material mixture located in the hot zone and the empty ampoule side in the colder zone. The reaction temperature was set to be 650 and 600 °C for hot zone and colder zone, respectively, and held for 1 h, and then cooled to 300 °C during 24 h for both zones.

Polarized Raman Spectroscopy: Polarized Raman spectroscopy was conducted using a home-built micro-Raman setup. In the polarized Raman measurements, a p-polarized 532 nm continuous wave laser was used to excite the Raman spectra, and a linear polarizer was employed before the spectrometer to collect only Raman-scattered light with polarization parallel to the polarization of the incident laser (i.e., the parallel-polarization configuration). The laser power was 3 mW and the spectrometer integration time was set to 2 s in all the measurements. More discussions on the Raman measurements can be found in the Supporting Information.

In polarized Raman spectra, the B_{2g} mode shows a simple angular dependence, see Figure 1c, and is insensitive to laser wavelength and sample thickness;^[11] thus, the B_{2g} peak is used to accurately determine the crystallographic orientations of BP. In previous studies,[11] the ZZ (or AC) axis was determined through continuous monitoring of the height of the B_{2g} peak till the height was minimum. However, accurately pinpointing the minimum height is difficult. Instead, the polarized Raman measurements were conducted for multiples of 15° and the integrated intensity of the $B_{2g}\xspace$ peaks as a function of rotation angle was plotted, see the red circles in Figure 1d. Then, the measurements were fitted with $\sin^2(2(\theta+\alpha))$, where θ is the rotation angle and α is the correction angle (see Section S1 in the Supporting Information). The fitted α is usually small (in Figure 1d, $\alpha = 0$) and could be used to accurately determine ZZ (or AC) axes. The uncertainty of the approach is $\approx 2^{\circ}$, see the blue squares in Figure 1d. Then, images of identifiable features on samples (e.g., the orientation of edges) were captured by an in situ bright-field microscope, to assist determination of the crystallographic orientations during thermal measurements (Section S2 in the Supporting Information).

TDTR and Beam-Offset TDTR: In the beam-offset TDTR measurements, a pump beam with a small w_0 was modulated at a low frequency *f*, resulting in a wide in-plane heat spreading. To profile the temperature distribution generated by the pump beam, a probe beam was systematically offset in either the horizontal or the vertical directions while the out-of-phase signals at -100 ps were recorded, akin to measurements of laser spot sizes by autocorrelation,^[13] see Figure 2a,c. (In most measurements, the horizontal and vertical directions corresponded to the ZZ and AC axes of BP, respectively.) The in-plane thermal conductivity was then derived from the full-width-half-maximum (FWHM) of the beam-offset measurements by comparing the FWHM to

calculations of an anisotropic thermal model,^[13] see Section S5 in the Supporting Information for the iteration approach applied to derive Λ_{ZZ} and Λ_{AC} . As an internal consistency check, two sets of measurements on BP-1 were compared, one performed when ZZ axis was horizontal and when it was vertical. An excellent agreement was achieved for both measurements, see Figure 2a,c. In addition, to ensure that the BP samples were properly passivated, another set of experiments was also performed six months after the initial sample preparation. No changes in the beam-offset data were observed, see Figure 2a,c, indicating that with the Al passivation, the BP samples did not deteriorate over time.

It was ensured that the approach to determine the crystallographic orientations by polarized Raman spectroscopy was accurate. The samples were intentionally rotated by as large as $\pm 30^{\circ}$ and the derived thermal conductivity was plotted as a function of the angle relative to the ZZ axis, see Figure 2b,d. It was found that the measurements formed a symmetric ellipse with the major and minor axes of 83 and 28 W m⁻¹ K⁻¹ at 300 K, as well as of 360 and 130 W m⁻¹ K⁻¹ at 80 K, as expected from the rotation of the thermal conductivity tensor of BP.

More details on TDTR and beam-offset TDTR measurements and data analysis are presented in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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