Strongly anisotropic in-plane thermal transport in single-layer black phosphorene

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Using first principles calculations, we predict the thermal conductivity of the two-dimensional materials black phosphorene and blue phosphorene. Black phosphorene has an unprecedented thermal conductivity anisotropy ratio of three, with predicted values of 110 W/m-K and 36 W/m-K along its armchair and zigzag directions at a temperature of 300 K. For blue phosphorene, which is isotropic with a zigzag structure, the predicted value is 78 W/m-K. The two allotropes show strikingly different thermal conductivity accumulation, with phonons of mean free paths between 10 nm and 1 μm dominating in black phosphorene, while a much narrower band of mean free paths (50–200 nm) dominate in blue phosphorene. Black phosphorene shows intriguing potential for strain-tuning of its thermal conductivity tensor.

Two-dimensional (2D) materials (e.g., graphene, MoS₂, silicene) are a focus of intense research because of their rich physics and potential for integration into next-generation electronic and energy conversion devices1–4. As opposed to their bulk counterparts, the optical, electronic, mechanical, and thermal properties of 2D materials can be easily tailored through the application of external strain, by introducing defects, or by stacking multiple layers of the same or different 2D materials. For example, the thermal conductivity of freely-suspended single-layer graphene is reduced from 3000–5000 W/m-K to 600 W/m-K by depositing it on amorphous SiO₂5.

Recently, a new and promising 2D semiconductor, black phosphorene, was fabricated by exfoliating a few layers from bulk black phosphorus6,7. Similar to graphene, black phosphorene has a honeycomb-like structure, but it is non-planar [Fig. 1(a)]. Single-layer black phosphorene is a direct-gap semiconductor with a predicted band gap of 2 eV6. The band gap decreases with an increasing number of layers and is 0.3 eV for the bulk phase. Performance characteristics similar to or better than other 2D materials have been achieved for a black phosphorene-based transistor7. What distinguishes black phosphorene from other 2D materials is its anisotropic structure, which leads to direction-dependent optical and electronic properties that vary by as much as 50%8,9.

Our objective is to study the lattice thermal conductivity of single-layer black phosphorene, for which there is no existing experimental or theoretical data available. Ong et al. investigated the effect of strain on the ballistic thermal conductance of black phosphorene using non-equilibrium Green’s functions based on harmonic lattice dynamics calculations10. Our aim is to predict the thermal conductivity of black phosphorene by including anharmonic phonon-phonon scattering. Thermal transport characterization is important for application in most devices, where large electrical currents can lead to Joule heating, non-radiative recombination, and potentially high operating temperatures. We find that the in-plane thermal transport in black phosphorene is strongly anisotropic, with thermal conductivity varying by a factor of three over the two orthogonal directions. While strong anisotropy in thermal conductivity is observed for van der Waals layered materials when comparing the in-plane and cross-plane directions (e.g., two orders of magnitude in graphite11), no other covalently-bonded 2D or 3D materials show the in-plane anisotropy we predict for black phosphorene.

We also investigate the thermal transport in blue phosphorene, another single-layered allotrope of phosphorus [Fig. 1(b)], which was recently predicted to be nearly as stable as black phosphorene12. First principles calculations predict a band gap in blue phosphorene in excess of 2 eV12, but unlike black phosphorene, blue phosphorene is isotropic.

Methods

Thermal transport in semiconductors like black phosphorene and blue phosphorene is dominated by atomic vibrations whose energy is quantized as phonons. The phonon contribution to thermal conductivity in the \( l \) direction can be calculated using a solution to the...
The phonon dispersion in the high-symmetry directions for (a) black phosphorene and (b) blue phosphorene. The slope of the longitudinal acoustic phonon branches at the Gamma point (shown as dashed straight lines), which represents the sound velocity, is anisotropic for black phosphorene and isotropic for blue phosphorene.

**Results**

**Phonon Dispersion.** The phonon dispersion in the high-symmetry directions of the first Brillouin zone for black phosphorene and blue phosphorene are plotted in Figs. 2(a) and 2(b) and closely match those reported by Zhu et al.\(^1^2\). Black (blue) phosphorene has a four (two)-atom unit cell, resulting in twelve (six) dispersion branches. The maximum phonon frequency is similar in both allotropes (14.0 THz in black and 16.3 THz in blue), but the phonon band gap in blue phosphorene (4.9 THz) is almost double that in black phosphorene (2.5 THz). The longitudinal acoustic phonon group velocity close to the \(\Gamma\) point (i.e., the sound speed), is 7.733 m/s in the \(\Gamma - Y\) (armchair) direction and 4.168 m/s in the \(\Gamma - X\) (zigzag) direction for black phosphorene, an indication of anisotropic phonon transport. For blue phosphorene, the sound velocity is 8.287 m/s in both the \(\Gamma - M\) and \(\Gamma - K\) directions.

**Thermal Conductivity.** The thermal conductivities of black phosphorene and blue phosphorene for temperatures between 200 and 500 K are plotted in Fig. 3(a). For black phosphorene, thermal transport is anisotropic and we plot the thermal conductivity in both the armchair and zigzag directions [see Fig. 1(a)]. Predicting the thermal conductivity of a 2D material requires specification of the layer thickness. We choose the bulk layer separation, which is 5.25 Å for black phosphorus\(^\text{19}\) and 5.63 Å for blue phosphorus\(^\text{12}\). As the thermal conductivity scales linearly with the layer thickness, the values reported here can be easily modified for other choices.

Thermal conductivity decreases with increasing temperature, as expected for a phonon-dominated crystalline material. At a temperature of 300 K, the predicted thermal conductivities are 110 W/mK (zigzag) and 36 W/m-K (armchair) for black phosphorene and 78 W/m-K for blue phosphorene. For black phosphorene, the thermal conductivity in the zigzag direction is three times higher than that in the armchair direction. This anisotropy could be useful in the design of heat channeling in micro- and nano-devices. We attribute this anisotropy in thermal conductivity to the anisotropic phonon dispersion, which leads to direction-dependent group velocities [Fig. 2(a)].

Based simply on the zone-center longitudinal acoustic group velocities, Eqn. 1 predicts a thermal conductivity anisotropy of...
Figure 3 | (a) Temperature-dependent thermal conductivity of black phosphorene and blue phosphorene. The thermal conductivities are obtained using an iterative solution of the linearized BTE. The predictions (symbols) are connected using lines to guide the eye. (b) Thermal conductivity accumulation functions for black phosphorene and blue phosphorene at a temperature of 300 K.

3.5, which is comparable to that from the full calculation. For blue phosphorene, the thermal conductivity is isotropic and is up to 1.8 times lower than the zigzag direction thermal conductivity of black phosphorene.

Our thermal conductivities are obtained using an iterative solution of the linearized BTE. For single-layer graphene, Lindsay et al. showed that the commonly used relaxation time approximation (RTA) of the BTE under-predicts the thermal conductivity by more than a factor of five at a temperature of 300 K. We find that the RTA under-predicts the thermal conductivity by up to a factor of 1.3 for black phosphorene and 2.0 for blue phosphorene at a temperature of 300 K (see SI).

The thermal conductivity of black phosphorene has recently also been predicted by other researchers. Zhu et al. used the RTA to predict values of 84 W/m-K (24 W/m-K) in the zigzag (armchair) direction. These values closely match our RTA predictions of 81 W/m-K (30 W/m-K) (see SI). Qin et al. predict black phosphorene thermal conductivities a factor of three lower than our values. This difference may be due to (i) their use of the RTA, (ii) their choice of the cubic force constant cutoff, and/or (iii) the implementation of a translational invariance constraint on the third-order force constants. Our predictions of the effects of these factors on thermal conductivity are presented in the SI.

In Fig. 3(b), we plot the thermal conductivity accumulation functions for black phosphorene and blue phosphorene at a temperature of 300 K. The thermal conductivity accumulation function describes the contribution of different mean free path phonons towards the total thermal conductivity of a material. Phonons with mean free paths spanning over two orders of magnitude (10 nm to 1 μm) contribute towards the thermal conductivity in black phosphorene. For blue phosphorene, however, the accumulation function closely resembles a step function, with the major contribution coming from phonons with mean free paths between 50 and 200 nm. This steep thermal conductivity accumulation in blue phosphorene is similar to that in silicene (which also has buckled hexagonal structure), where phonons with mean free path between 5 and 20 nm contribute more than 80% to the thermal conductivity. The thermal conductivity accumulation functions indicate that, unlike in graphene, where thermal conductivity is predicted to increase with sample sizes even greater than 10 μm, changing the sample size beyond 10 μm will have a minimal effect on the thermal conductivity of either phosphorene allotrope at a temperature of 300 K.

As mentioned above, the structure of blue phosphorene is similar to that of silicene. Blue phosphorene, however, has a thermal conductivity of 78 W/m-K at a temperature of 300 K, which is more than eight times higher than that predicted for silicene (9.4 W/m-K). This higher thermal conductivity of blue phosphorene is the result of a larger sound velocity and the larger frequency gap in its phonon dispersion [Fig. 2(b)].


dataset

| Material          | Total thermal conductivity (W/m-K) | LA (%) | TA (%) | ZA (%) | Optical (%) |
|-------------------|----------------------------------|-------|-------|-------|-------------|
| Black phosphorene (zigzag) | 110                              | 32    | 22    | 31    | 15          |
| Black phosphorene (armchair) | 36                               | 28    | 33    | 12    | 27          |
| Blue phosphorene  | 78                               | 26    | 27    | 44    | 3           |
| MoS$_2$          | 108                               | 28    | 24    | 39    | 9           |
| Graphene         | 3600                             | 8     | 15    | 76    | 1           |

As a result, the predicted contribution of ZA phonons to thermal conductivity in the phosphorene allotropes varies from 12–
44% as compared to 76% in graphene at a temperature of 300 K, as presented in Table 1. We note that the thermal conductivity contributions of the different acoustic phonon branches in black phosphorene and blue phosphorene are similar to those predicted for MoS$_2$, which also has a non-planar structure. More information is provided in the SI.

The thermal conductivity of freely-suspended single-layer graphene at a temperature of 300 K is reduced from 3000–5000 W/m-K to 600 W/m-K when it is deposited on amorphous SiO$_2$. This more than a factor of five reduction in the thermal conductivity is due to the increased scattering of ZA phonons in supported graphene. The results presented in this work are for suspended phosphorene. As can be seen in Table 1, the contribution of ZA phonons is 31% (12%) in the zigzag (armchair) direction in black phosphorene and 44% in blue phosphorene. We expect a comparable decrease in the thermal conductivity of supported phosphorene samples.

**Strain Tuning of Thermal Conductivity.** We now consider the possibility of strain-tuning the thermal conductivity of black phosphorene and blue phosphorene. In Fig. 4(a), we plot the stresses in both allotropes when they are subjected to a bi-axial tensile strain. For black phosphorene, the stress is anisotropic and is three times lower in the armchair direction compared to the zigzag direction. For blue phosphorene, which has a zigzag structure, the stress is isotropic and is 1.5 times larger than the stress in the zigzag direction of black phosphorene.

As can be seen from Eqn. 1, thermal conductivity scales as the square of the phonon group velocities. We plot the strain-dependence of the sound velocities in Fig. 4(b) for black phosphorene and blue phosphorene under the bi-axial strain conditions. The sound velocities are maximum at zero strain for both materials and decrease with increasing strain. Using this reduction as a guide, we estimate that the thermal conductivities of both allotropes may decrease by a factor of 1.7 at a strain of 8%. Similar calculations for uni-axial strains suggest the possibility for strain-tailoring the thermal conductivity anisotropy in black phosphorene. For example, the estimated anisotropy in the thermal conductivity of black phosphorene is a factor of 4.6 (2.2) for uni-axial strain of 6% along the armchair (zigzag) direction (see SI).

**Anisotropy.** To the best of our knowledge, no other 2D material displays anisotropic in-plane thermal transport. Furthermore, the thermal conductivity anisotropy in black phosphorene is striking when compared to that found in layered, wurtzite, and orthorhombic three-dimensional crystal structures, as compiled in Table 2. We quantify anisotropy, $r$, by the ratio of the maximum and minimum direction-dependent thermal conductivities. The maximum $r$ is in the layered structures graphite and hexagonal boron nitride. These layers are weakly bonded through van der Waals interactions compared to the strong covalent bonds within the layers, which results in poor interlayer heat transport. Of the remaining materials in Table 2, which are all covalently bonded, the maximum anisotropy is for our prediction for black phosphorene, which is twice as large as the next highest value.

**Summary**

We predicted the thermal conductivity of black phosphorene and blue phosphorene using first-principles-driven lattice dynamics calculations and a full (iterative) solution of the BTE. We found a factor of three anisotropy in the thermal conductivity of black phosphorene, which could potentially be tuned up to 4.6 using strain. At a temperature of 300 K, the predicted thermal conductivities of both phosphorene allotropes are larger than that of silicene, similar to that of MoS$_2$, and are up to two order of magnitude smaller than that of graphene.

![Figure 4](image_url)

**Figure 4** | (a) Stress and (b) sound velocity in black phosphorene and blue phosphorene under bi-axial strain. The predicted values (symbols) are connected using lines to guide the eye.

| Material       | $k_{\text{max}}$ (W/m-K) | $k_{\text{min}}$ (W/m-K) | $r$  |
|----------------|--------------------------|--------------------------|------|
| Graphite (exp$^{33}$) | (1000–2000)              | 6                        | −300 |
| h-BN (exp$^{33}$)     | (200–300)                | 2                        | −100 |
| **Black Phosphorene** | **110**                  | **36**                   | **3.1** |
| SnSe (exp$^{34}$)     | 0.70                     | 0.46                     | 1.52 |
| GaN (pred$^{14}$)     | 401                      | 385                      | 1.04 |
| AlN (pred$^{14}$)     | 322                      | 303                      | 1.06 |
| NdFeO$_3$ (pred$^{35}$) | 3.01                    | 2.68                     | 1.12 |
| NdAlO$_3$ (pred$^{35}$) | 6.61                    | 5.72                     | 1.16 |

Table 2 | Anisotropy in thermal conductivity for selected materials with layered, wurtzite, and orthorhombic crystal structure at a temperature of 300 K. ‘exp’ and ‘pred’ in the first column denote experimental measurements and simulation predictions.
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