First-principles study of the anisotropic thermal expansion and thermal transport properties in *h*-BN

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ABSTRACT The thermal expansion coefficient (TEC) and thermal conductivity (k) of thermal fillers are key factors for designing thermal management and thermal protection composite materials. Due to its unique advantages, hexagonal boron nitride (*h*-BN) is one of the most commonly used thermal fillers. However, its TEC and k values are still unclear due to the inconsistency of characterization techniques and sample preparations. In this work, these disputes were addressed using the quasi-harmonic approximation (QHA) method and phonon Boltzmann transport equation (BTE) theory based on the density functional theory (DFT), respectively. The accuracy of our calculated TEC and k values was confirmed by previously reported experimental results, and the underlying physical principles were analyzed from the phonon behaviors. Our TEC results show that the *h*-BN has small in-plane negative value and large cross-plane positive value, which are -2.4×10^{-6} and $36.4 \times 10^{-6} \text{ K}^{-1}$ at 300 K, respectively. And the anisotropic TEC is mainly determined by the anisotropic isothermal bulk modulus and the low-frequency out-of-plane longitudinal phonon modes. We found that the convergence of cutoff radius and q -grid size have significant effect on the accuracy of k of *h*-BN. Our results show that the in-plane k is much higher than the cross-plane k , and the values at 300 K are 286.6 and $2.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The anisotropic phonon group velocity arising from the vibration behaviors of acoustic phonon modes should be primarily responsible for the anisotropic k . Our calculated TEC and k values will provide important references for the design of *h*-BN composite materials.

Keywords: *h*-BN, thermal expansion coefficient, thermal conductivity, phonon behaviors, density functional theory

INTRODUCTION

Hexagonal boron nitride (*h*-BN), also known as “white graphite”, has attracted considerable attention because of its typically lamellar structure and anisotropic properties [1–5]. It is one of the most promising thermal conductive fillers in high-thermal-conductivity materials for electronic devices due to its high in-plane (a/b -axis) thermal conductivity (k) and excellent dielectric properties [6,7]. Meanwhile, *h*-BN composite ceramics have been widely used as thermal protective materials because of their low cross-plane (c -axis) thermal conductivity and high sublimation temperature near 3000°C [8,9]. In order to maximize the performance of *h*-BN according to different application backgrounds, orienting the *h*-BN grains along or away the heat flow direction is widely adopted to acquire composite materials with higher or lower thermal conductivity [10–14]. Nevertheless, *h*-BN also shows significant anisotropy in the thermal expansion coefficient (TEC), which is much higher along the in-plane (a/b -axis) direction than that along the cross-plane (c -axis) direction. Hence, the orientation of *h*-BN grain will cause severe stress concentration and even thermal failure of the composite materials at high temperatures when the matrix shows poor TEC mismatch [15]. Therefore, clear knowledge of the anisotropic thermal properties (such as TEC, thermal conductivity (k), etc.) of *h*-BN at different temperatures, as well as their underlying physical principles, is essential for the design of *h*-BN composite materials.

For anisotropic TEC of *h*-BN, there are a few experimental measurements. The in-plane TEC of *h*-BN tested by Pease [16] using X-ray diffraction (XRD) method shows that it rises from $-2.9 \times 10^{-6} \text{ K}^{-1}$ to zero with in-

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creasing testing temperature from 293 to 1043 K. While, Paszkowicz *et al.* [17] reported that *h*-BN presents an in-plane TEC of $-2.72 \times 10^{-6} \text{ K}^{-1}$ at room-temperature also using the XRD method, which is larger than that of Pease [16]. The cross-plane TEC of *h*-BN tested by Pease [16] increases linearly with a mean value of $40.5 \times 10^{-6} \text{ K}^{-1}$ in the range of 296–1073 K. And Paszkowicz *et al.* [17] reported that it shows a nonlinear increase with maximum value of $37.7 \times 10^{-6} \text{ K}^{-1}$ below 297.5 K. While Yates *et al.* [18] found that the cross-plane TEC of *h*-BN decreases gradually in the range of 105–780 K by the interferometry method. Therefore, due to the differences in testing methods and samples in the previous work, the TEC values of *h*-BN still have conflicts, especially for cross-plane TEC. The simulation results can not only understand the origin of these differences, but also reveal the underlying physical principles. However, as far as we know, there is rare report on the study of thermal expansion properties of *h*-BN by simulation methods so far.

For *k* of *h*-BN, its anisotropic property has been studied using both experimental and simulation methods [19–21]. Simpson and Stuckes [19] found that the in-plane *k* of *h*-BN has a maximum value of about $250 \text{ W m}^{-1} \text{ K}^{-1}$ at 235 K and the cross-plane *k* decreases from $2.5 \text{ W m}^{-1} \text{ K}^{-1}$ at 100 K to $1.7 \text{ W m}^{-1} \text{ K}^{-1}$ at 800 K. While the in-plane *k* below 350 K measured by Sichel *et al.* [20] using steady-state technique is almost twice as high as that of Simpson *et al.* [19] using flash technique. Jiang *et al.* [21] simulated the anisotropic *k* of *h*-BN using first-principles-based calculations in the temperature range of 100–500 K, and compared that with the experimental result by time-domain thermoreflectance technique. However, when calculating the third-order anharmonic interatomic force constants (IFCs), this simulation only took the 7th nearest neighbor atoms into account. As a result, the calculated results show certain deviation with the experimental results.

Therefore, due to the inconsistencies of different characterization techniques and the differences between the experimental and calculation results, it is still unclear about the accurate TEC and *k* of *h*-BN, especially the values at high temperatures. In this work, we solved these disputes by accurately determining the anisotropic TEC and *k* values of *h*-BN below 2000 K by the quasi-harmonic approximation (QHA) method and phonon Boltzmann transport equation (BTE) theory based on the density functional theory (DFT). The accuracy of our calculation results was confirmed by previously reported experimental results, and the underlying physical mechanism of the anisotropic TEC and *k* of *h*-BN was sys-

tematically studied from the phonon behaviors.

COMPUTATIONAL DETAILS

Calculation based on DFT

The first principles calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) based on the DFT [22,23]. The interactions between ion cores and valence electrons were modeled by the projector-augmented wave potentials (PAW) [24]. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) was employed to treat the exchange-correlation energy [25]. And a plan wave cutoff energy of 600 eV was used. The optimizing of initial cell used the $30 \times 30 \times 12$ Γ -centered Monkhorst-Pack *k*-mesh. The relaxation convergence criterion of electronic and ion are 10^{-8} eV and $10^{-6} \text{ eV/\AA}$, respectively. And the van der Waals interaction was considered between adjacent layers of *h*-BN. For the calculation of thermodynamic properties, a reciprocal-grid density of $\approx \frac{20}{a} \times \frac{20}{b} \times \frac{20}{c}$ Γ -centered Monkhorst-Pack *k*-mesh were used, where, *a*, *b* and *c* are the lattice constants of the supercell scaled by the unit of $\text{\AA}$, and the convergence thresholds for the electronic energy is 10^{-7} eV .

TEC based on QHA method

The temperature-dependent TEC ($\varphi(T)$) can be calculated using Equation (1):

$$\varphi(T) = \frac{1}{a(T)} \frac{da(T)}{dT}, \quad (1)$$

where *a*(*T*) and *T* are the temperature-dependent lattice constant and temperature in Kelvin, respectively. The *a*(*T*) can be obtained from the temperature-dependent volume (*V*(*T*)). And the *V*(*T*) was determined using the QHA method by fitting the Vinet equation of state (EOS) to the minimum Helmholtz free energy (Equation (2)) at any temperature [26].

$$\begin{aligned} F(V, T) &= E_0 + F_{\text{vib}}(T) \\ &= E_0 + \frac{1}{2} \sum_{q,v} \hbar \omega_{q,v} \\ &\quad + k_B T \sum_{q,v} \ln \left[1 - \exp \left(-\frac{\hbar \omega_{q,v}}{k_B T} \right) \right], \end{aligned} \quad (2)$$

where E_0 is the ground-state energy, $F_{\text{vib}}(T)$ is the vibrational free energy, *q*, *v*, $\hbar$, k_B , *V* and *T* are the wave vector, band index, reduced Planck constant, Boltzmann constant, volume and temperature, respectively, $\omega_{q,v}$ is the phonon frequency at *q* and *v*. During the fitting process,

twelve different lattice constants with the same spacing around the optimized lattice constant (a_0 or c_0) were considered (0.995 a_0 to 1.006 a_0 for the calculation of in-plane TEC, and 0.90 c_0 and 1.12 c_0 for the cross-plane TEC). And the phonon vibrational properties required in Equation (2) were calculated using the density functional perturbation theory (DFPT) as implemented in Phonopy code [26], where 5×5×3 supercell was used.

Lattice thermal conductivity based on phonon BTE

As an insulating material, the thermal conductivity of *h*-BN is determined by the lattice thermal conductivity (k). The anharmonic lattice dynamics method based on phonon BTE theory is one of the most characteristic methods to obtain k , which involves the calculations of harmonic second-order and anharmonic third-order IFCs. In this work, the phonon BTE was solved to obtain k according to Equation (3) using the ShengBTE code [27].

$$k^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0(f_0 + 1) (\hbar \omega_{\lambda})^2 v_{\lambda}^{\alpha} \tau_{\lambda}^0 (v_{\lambda}^{\beta} + \Delta_{\lambda}^{\beta}), \quad (3)$$

where $k^{\alpha\beta}$ is thermal conductivity matrix, Ω and N are the volume of the unit cell and total number of q points in the Brillouin zone (BZ), respectively, f_0 is the Bose-Einstein statistic, ω_{λ} and τ_{λ}^0 are the angular frequency and the relaxation time obtained from perturbation theory of the phonon mode λ , Δ_{λ}^{β} is the measure of how much the population of a specific phonon mode deviates from the relaxation time approximation prediction, and v_{λ} is the group velocity. More detailed information on the workflow of ShengBTE can be found in Ref. [27]. The harmonic second-order IFCs were obtained from the DFPT calculation mentioned above. And a 4×4×3 supercell was constructed to calculate the anharmonic third-order IFCs

using thirdorder.py [27].

RESULTS AND DISCUSSION

Phonon spectrum and thermal vibrational properties

The *h*-BN shows a typical layered structure, as shown in Fig. 1a, where boron and nitrogen atoms are bonded by covalent bonds in the layer and the adjacent layers are interacted through van der Waals force. The optimized structural lattice constants are $a = b = 2.507$ Å and $c = 6.555$ Å, which are very close to the data ($a = b = 2.500$ Å and $c = 6.660$ Å) reported by Zhang *et al.* [29].

A detailed knowledge of the vibrational states of phonon is the basis of understanding the thermal properties [30]. The calculated phonon spectra of *h*-BN together with the vibrational density of states (DOS) along high symmetry directions of the first BZ are shown in Fig. 1b. There is no imaginary frequency in the phonon spectrum, indicating the dynamical stability of the structure, and the results agree well with the previous reports [31,32]. Because the unit cell of *h*-BN contains four atoms, the phonon dispersion contains twelve phonon modes, which include three acoustic phonon modes (ZA, LA and TA) and nine optical phonon modes (three ZO, three LO and three TO). “A” and “O” represent the acoustic and optical modes, and “Z”, “L”, and “T” stand for out-of-plane longitudinal, in-plane longitudinal and in-plane transverse vibrations, respectively. The phonon dispersion curves of different phonon models are represented in Fig. 1b, where one of the TO and LO modes almost overlap with the TA and LA modes, respectively, and a ZO mode with the lowest frequency is labeled as ZO'. It can be seen from the phonon DOS that the ZA and ZO' modes are mainly derived from the vibration of N atoms, while both B and N play a role in the medium and high frequency optical modes.

The atomic displacement patterns calculated from the

Figure 1 (a) The unit cell of *h*-BN; (b) the phonon spectrum of *h*-BN and the vibrational DOS along high symmetry directions. Inset shows the BZ with high-symmetry k -points indicative of hexagonal lattice [28].

phonon spectrum of different phonon modes at M point are shown in Fig. 2. Consistent with DOS results, the vibration of B atoms becomes stronger with increasing vibration frequency. Different with the ZA mode where B and N atoms in each layer move collectively in the same direction along the c axis, the B and N atoms in the ZO' and ZO mode move in the opposite directions. Therefore, higher temperature is required to excite the ZO' and ZO mode due to the van der Waals force between adjacent layers, which will reduce their influence on the thermal properties compared with the ZA mode. Since the out-of-plane bending of B–N bonds is softer than the in-plane bending, the out-of-plane phonon modes show lower frequencies than the in-plane phonon models. Similar to other layered materials, the ZA mode exhibits a quadratic dispersion (q^2) around the Γ point, while the LA and TA modes show linear dispersions [33]. As discussed below, these differences in vibration modes along different directions will lead to the anisotropy in thermal properties of h -BN.

It is well known that thermal expansion properties are related to the anharmonicity of lattice vibration. The relationship between the anharmonic effect and the non-linear vibration of the atoms can be reflected by the mode Grüneisen parameter (γ), which can be obtained as follows [34]:

$$\gamma = -\frac{1}{\omega_{q,\lambda}} \frac{\partial \omega_{q,\lambda}}{\partial \varepsilon}, \quad (4)$$

where $\omega_{q,\lambda}$ is the frequency of phonon mode with polarization λ and wave vector q , and ε is the stress. The relationship between γ at selected high symmetry points of the phonon spectrum and the vibrational frequency is shown in the Fig. 3, where some γ points of the TA and LA modes overlap with those of the optical phonon modes. It is worth noting that the low-frequency ZA and ZO' modes show large negative γ values along the in-plane direction and small positive values along the cross-plane direction, while the high-frequency modes show γ values around zero. It is consistent with the well-known phenomenon that the out-of-plane longitudinal phonon

modes in layered materials are similar to the bending vibration on a continuum membrane. And the in-plane tensile strain can stiffen this bending vibration resulting in a large negative γ due to the strong B–N bonds, while the cross-plane tensile strain can soften the vibration thereby generating small positive γ due to the weak van der Waals force [30,35]. The negative (positive) γ will lead to negative (positive) TEC (φ) according to Equation (5) [36]:

$$\varphi = \frac{\gamma C_V}{B_T V}, \quad (5)$$

because the C_V (specific heat capacity), B_T (isothermal bulk modulus) and V (volume) are all positive values. Therefore, the sign of TEC along different directions is mainly determined by ZA and ZO' modes. Besides, it also affects the k because larger γ value leads to more phonon-phonon Umklapp scattering ($1/\tau$) according to $\tau \propto 1/\gamma^2$ [37].

Anisotropy in thermal expansion property

The calculated TEC in the temperature range of 0–2000 K along the in-plane and cross-plane directions and the previous experimental results are shown in Fig. 4a and b. The in-plane TEC shows a sudden decline to the maximum negative value of $-2.50 \times 10^{-6} \text{ K}^{-1}$ around 230 K followed by an increase to zero around 1370 K, which is consistent with the changing trend of the in-plane TEC of two-dimensional BN [37,38]. The cross-plane TEC presents upward positive values over the entire temperature range, which increases sharply to $35.3 \times 10^{-6} \text{ K}^{-1}$ around 230 K, and then goes up slowly to $47.1 \times 10^{-6} \text{ K}^{-1}$ around 2000 K.

As shown in Fig. 4a, our simulated in-plane TEC compares favorably with the experimental result by Paszkowicz *et al.* [17] in the temperature range below 200 K, and shows a similar changing trend with the experimental result by Yates *et al.* [18]. It is worth noting that the two experimental results were tested from bulk h -BN and the h -BN grains may not be in perfect alignment, which might be the reason that our simulation results are

Figure 2 The atomic displacement patterns of different phonon modes at M point.

Figure 3 (a) In-plane and (b) cross-plane mode Grüneisen parameters of *h*-BN.

larger than the experimental results. And the plateau in the temperature range of 200–300 K of the result by Paszkowicz *et al.* [17] might due to the experimental uncertainty. As shown in Fig. 4b, the calculated cross-plane TEC is basically consistent with the result by Paszkowicz *et al.* [17], which increases gradually from 0 to 297.5 K with maximum value of $37.7 \times 10^{-6} \text{ K}^{-1}$. And Pease [16] reported that the cross-plane TEC of *h*-BN increases linearly above 296 K by XRD method, which also agrees well with our result. However, the experimental cross-plane TEC result by Yates *et al.* [18] is quite different from our result, which shows decreasing values in the range of 105–780 K. While the cross-plane TEC of graphite that shows similar crystal structure with *h*-BN also exhibits increasing tendency above 290 K [39], which is consistent with our and Pease's results. Therefore, the decreasing cross-plane TEC in the temperature range of 105–780 K by Yates *et al.* [18] might not be reliable. And based on the above discussion, we can conclude that the

anisotropic TEC of *h*-BN is accurately calculated using QHA method in this work.

The cross-plane TEC shows much larger values than the in-plane TEC, and both present a turning point around 230 K. The cross-plane TEC and the in-plane TEC have the values of 36.4×10^{-6} and $-2.4 \times 10^{-6} \text{ K}^{-1}$ at 300 K, respectively. According to Equation (5), the TEC is related to the mode Grüneisen parameters (γ), specific heat capacity (C_V) and isothermal bulk modulus (B_T). The C_V was calculated using Equation (6) [39]:

$$C_V = -T \left(\frac{\partial^2 F_{\text{vib}}(T)}{\partial T^2} \right)_V. \quad (6)$$

And the B_T was obtained using Equation (7) [40]:

$$B_T = V \frac{\partial^2 E_0}{\partial V^2} + V \left(\frac{\partial^2 F_{\text{vib}}(T)}{\partial V^2} \right)_T. \quad (7)$$

The calculated C_V and B_T are shown in Fig. 4c and d. The C_V follows the Debye T^3 law below ~ 230 K, and then gradually approaches to a fixed value with rising temperature, which is consistent with the Dulong-Petit law [41]. The B_T decreases almost linearly with increasing temperature, while the in-plane B_T is much higher than cross-plane B_T due to the strong in-plane B–N bonds and weak cross-plane van der Waals forces. At low temperatures, only low-frequency phonon modes can be excited, and other modes will be excited in succession as the temperature increases. As mentioned above, the low-frequency ZA and ZO' modes show large negative γ values along the in-plane directions, while the high-frequency phonon modes show γ values around or even greater than zero. Therefore, with the increase of temperature, the in-plane TEC first decreases rapidly due to the rapid increasing C_V , decreasing B_T and large negative γ values, and then increases gradually due to the subsequent excitation of high-frequency phonon modes with small γ . The same is true for the variation rule of the cross-plane TEC, and the much higher TEC values is due to the much lower cross-plane B_T than that along the in-plane direction.

Anisotropy in thermal transport property

Calculation of thermal conductivity (k) using the phonon BTE method needs the second-order IFCs and the third-order anharmonic IFCs. All neighbor atoms may contribute to the values of third-order IFCs. In practice, a cutoff radius (r^{cutoff}) is chosen and all interactions inside r^{cutoff} are included while the interactions outside r^{cutoff} are ignored. If the r^{cutoff} is not large enough, the calculated value of k will be relatively larger than the real one [42].

Figure 4 (a) In-plane and (b) cross-plane TEC of *h*-BN compared with previous results of Paszkowicz *et al.* [17] and Yates *et al.* [18]. Calculated (c) C_V and (d) B_T along different directions.

Since the computing time and resources increase exponentially with the r^{cutoff} , too large r^{cutoff} should be avoided. Meanwhile, the determination of q -grid size is also an important factor that affects the calculation accuracy when using the ShengBTE code [27]. Therefore, the convergence tests of r^{cutoff} and q -grid size are necessary to quickly and accurately obtain k . In this work, the r^{cutoff} is determined by analyzing the root mean square (RMS) of the elements of the second-order IFCs according to the work of Qin and Hu [43], as follows:

$$\text{RMS}(\Phi_{ij}) = \left[\frac{1}{9} \sum_{\alpha, \beta} (\Phi_{ij}^{\alpha\beta})^2 \right]^{\frac{1}{2}}, \quad (8)$$

where Φ_{ij} is the second-order IFCs between atom i and j , and $\Phi_{ij}^{\alpha\beta}$ is the harmonic response of the force acting on atom i (α -direction) resulting from the displacement of atom j (β -direction). As shown in Fig. 5a, the in-plane atomic interactions are much larger than those in the cross-plane directions. And as the distance increases, the interactions in the plane decrease monotonically while the cross-plane interactions decrease with fluctuations because the cross-plane B-B interactions are greater than

B-N interactions. We chose the r^{cutoff} of 4.37 Å (9th nearest neighbor atoms), 5.04 Å (11th nearest neighbor atoms) and 5.44 Å (13th nearest neighbor atoms) combined with different q -grid sizes to make the convergence tests of k . As shown in Fig. 5b and c, compared with r^{cutoff} from 4.37 to 5.04 Å, the change in in-plane k caused by increasing r^{cutoff} from 5.04 to 5.44 Å is very small, and this phenomenon is more obvious for the cross-plane k . Considering the results of $\text{RMS}(\Phi_{ij})$ and convergence tests and the computational cost, at least a r^{cutoff} of 5.44 Å is required for obtaining converged k of *h*-BN. It can also be seen that the in-plane and cross-plane q -grid sizes should be larger than 20×20 and 14, respectively. Therefore, the anisotropic k of *h*-BN was calculated with a r^{cutoff} of 5.44 Å and a q -grid size of $20 \times 20 \times 14$ in this work.

A comparison of the calculated results in the temperature range of 100–2000 K with previously reported results is shown in Fig. 6. Our calculated results are slightly smaller than the experimental results of Sichel *et al.* [20] and Jiang *et al.* [21] at low temperatures. And both the current in-plane and cross-plane k values compare well with the experimental results of Simpson and Stuckes [19] in the temperature range of 260–860 K. The

Figure 5 (a) The RMS(Φ_{ij}) vs. r_{cutoff} for h-BN, where the spacing of cutoff distance (the top x axis) is unequal. Effects of r_{cutoff} (9th nearest neighbor atoms, black line; 11th nearest neighbor atoms, red line; 13th nearest neighbor atoms, blue line) and q-grid size on the anisotropic k of h-BN: (b) in-plane and (c) cross-plane.

differences between different experimental results may be due to the inconsistencies in sample quality or measurement methods. The calculation results cannot be verified at higher temperatures due to the lack of experimental results. It can be seen that, compared with the simulation results of Jiang *et al.* [21], which only considered the 7th nearest neighbor atoms when calculating the third-order anharmonic IFCs, our simulation results are relatively in better agreement with the experimental results. The calculated in-plane and cross-plane k values at 300 K are 286.6 and 2.7 W m⁻¹ K⁻¹, respectively.

It shows that the in-plane k of h-BN is much higher

than that along the cross-plane direction, and both of them decrease gradually with rising temperature. According to the Debye heat conduction theory, k of solid materials can be estimated from the following formula [42]:

$$k = \frac{1}{3} C_V v l = \frac{1}{3} C_V v^2 \tau, \quad (9)$$

where C_V is the specific heat, v , l and τ are the phonon group velocity, mean free path (MFP) and relaxation time, respectively. Fig. 7 shows the phonon group velocity and relaxation time along the in-plane and cross-plane directions at 300 K. The group velocity can be obtained from the slope of phonon dispersion along each BZ direction according to Equation (10) [44]:

$$v = \frac{\partial \omega_i}{\partial q}. \quad (10)$$

The optical phonon modes, as shown in Fig. 1b, are nearly flat, indicating that these modes contribute little to the k . And the in-plane acoustic phonon modes (LA and TA) show higher slope values than the out-of-plane acoustic phonon mode (ZA). Therefore, the group velocity along the in-plane direction is larger than that along the cross-plane direction as shown in Fig. 7a. As shown in Fig. 7b, the cross-plane phonons show relatively low relaxation time compared with the in-plane phonons. It is well known that the phonon relaxation time is dominated by two factors: phonon-phonon scattering phase space and strength [45]. The three-phonon scattering phase spaces of the phonons are shown in Fig. 7c, which shows little difference along different directions. The scattering strength can be reflected by the Grüneisen parameter (γ). As shown in Fig. 3, the LA and TA modes show larger γ along the cross-plane direction than that along the in-plane direction. Therefore, the in-plane phonons show relatively larger relaxation time compared with the cross-plane phonons. Together with the anisotropic group velocities, these will cause the much lower cross-plane k than that along the in-plane direction. It can also be seen that the phonon relaxation time decreases with increasing frequency, which is caused by the enhanced phonon scattering at high frequencies [46], and therefore, both the in-plane and cross-plane k decrease with rising temperature. Actually, the excited defects at high temperatures will also reduce the phonon relaxation time and result in the decrease of k [47], which was not considered in our calculation process.

The MFP of phonon shows great practical importance in nanodevices because it can affect the effective k of the nanosized structures [48]. The normalized cumulative k

Figure 6 (a) Comparison of our calculated in-plane (a) and cross-plane (b) k with previously reported results, including the measured results of Simpson and Stuckes [19], Jiang *et al.* [21] and Sichel *et al.* [20], and the simulation results of Jiang *et al.* [21].

Figure 7 (a) In-plane and through-plane phonon group velocities; (b) phonon relaxation time; (c) three-phonon scattering phase space of *h*-BN at 300 K as a function of phonon frequency; (d) normalized cumulative k of *h*-BN as a function of phonon MFP at different temperatures.

of *h*-BN at 100, 500, 1000, 1500 and 2000 K as a function of the MFP are shown in Fig. 7d. The MFPs decrease gradually with the increasing temperatures and the in-plane MFPs are much larger than those along the cross-plane direction, which are consistent with the results of

group velocities and relaxation time of the phonons. Based on the MFP spectrum, we can select different *h*-BN powders for the composite materials according to different application backgrounds. For example, the *h*-BN powder with thicknesses of >50 nm and grain size of

>100 nm should be selected if we expect the composite material show high k .

CONCLUSIONS

In this work, the disputes of TEC and k values of h -BN reported in previous studies were addressed using the QHA method and phonon BTE theory based on DFT, respectively. The accuracy of our calculation results was verified by comparing with the previously reported experimental results. And the underlying physical principles were analyzed from the phonon behaviors. The TEC shows strong anisotropy with small in-plane negative value and large cross-plane positive value of -2.4×10^{-6} and $36.4 \times 10^{-6} \text{ K}^{-1}$ at 300 K, respectively. The analysis shows that the sign of TEC of h -BN along different directions is mainly determined by the vibration behaviors of ZA and ZO' modes, and the much higher in-plane TEC values are due to the much higher in-plane B_T than that along the cross-plane direction. The convergence tests of r^{cutoff} and q -grid size were performed to ensure the calculation accuracy of k , and at least a r^{cutoff} of 5.44 Å and a q -grid size of $20 \times 20 \times 14$ should be used to quickly and accurately obtain k . The results show that the in-plane k of h -BN is much higher than cross-plane k , and the values at 300 K are 286.6 and $2.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The anisotropic phonon group velocities arising from the vibration behaviors of ZA, LA and TA modes should be principally responsible for the anisotropic k . The in-plane MFPs are much larger than those along the cross-plane direction, which further indicates the significant anisotropy in k of h -BN. Our calculated thermal expansion and thermal transport properties in h -BN will provide important references for the design of h -BN composite materials.

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Conflict of interest The authors declare that they have no conflict of interest.

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h-BN各向异性热膨胀和热输运特性的第一性原理研究

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摘要 热填料的热膨胀系数和热导率是设计热管理和热防护复合材料的关键参考因素. 六方氮化硼(*h*-BN)由于其独特的优点是最常用的热填料之一. 但由于不同测试方法和测试样品的不一致性, 其热膨胀系数和热导率的精确数值尚不清楚. 本文分别用基于密度泛函理论的准谐近似方法和声子玻耳兹曼输运方程理论精确计算了*h*-BN沿层间和层内方向的热膨胀系数和热导率, 通过与已有实验结果的对比较验证了计算结果的准确性, 并通过对声子行为的分析研究了其基本物理原理. 结果表明, *h*-BN的热膨胀系数沿层内方向为较小的负值, 沿层间方向为较大的正值, 在300 K时分别为 -2.4×10^{-6} 和 $36.4 \times 10^{-6} \text{ K}^{-1}$. 研究表明, *h*-BN各向异性的热膨胀系数主要由其各向异性的等温体积模量和低频面外纵向声学支和光学支的振动特性所引起. 为了确保*h*-BN热导率的快速准确预测, 本文首次进行了原子间交互作用截断半径和 q 网格尺寸的收敛性测试. 计算结果表明, *h*-BN平面内的热导率远大于沿平面间方向的热导率, 在300 K时分别为286.6和2.7 $\text{W m}^{-1} \text{ K}^{-1}$. 声子行为分析表明, 由面外纵向声学支、面内纵向声学支和横向声学支的振动特性引起的各向异性声子群速度是造成*h*-BN各向异性热导率的主要原因. 本文的计算结果对*h*-BN复合材料的设计具有重要的参考价值.