## Low lattice thermal conductivity of pentadiamond

Cite as: J. Appl. Phys. **129**, 215107 (2021); https://doi.org/10.1063/5.0052267 Submitted: 30 March 2021 . Accepted: 17 May 2021 . Published Online: 04 June 2021

Yanyan Chen, Jie Sun, Tingwei Li, ២ Qian Wang, et al.

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J. Appl. Phys. 129, 215107 (2021); https://doi.org/10.1063/5.0052267

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Yanyan Chen, Jie Sun, Tingwei Li, and Qian Wang<sup>a)</sup> 厄

#### AFFILIATIONS

School of Materials Science and Engineering, CAPT, HEDPS, BKL-MEMD, Peking University, Beijing 100871, China

<sup>a)</sup>Author to whom correspondence should be addressed: qianwang2@pku.edu.cn

#### ABSTRACT

The lattice thermal conductivity of carbon materials is particularly interesting because it can vary within a range spanning five orders of magnitude depending on the atomic configuration. Herein, we systematically study the lattice thermal conductivity and phonon transport properties of pentadiamond, a new three-dimensional carbon allotrope consisting of pentagonal carbon rings. Based on first-principles calculations and an iterative solution to the linearized Boltzmann transport equation, the intrinsic lattice thermal conductivity ( $k_l$ ) is found to be 490.88 W/mK at room temperature, much lower than 2664.93 W/mK of diamond. A detailed analysis of both harmonic and anharmonic properties reveals that the low  $k_l$  of pentadiamond essentially originates from its large phonon phase space, short phonon relaxation time resulting from strong overlap between the acoustic and low-lying optical phonon branches, and the low phonon group velocity. The distinct thermal transport behavior exhibited in pentadiamond further shows the diversity and complexity in lattice thermal conductivity of carbon allotropes.

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#### I. INTRODUCTION

Carbon, one of the most abundant elements on the earth with its flexibility in bonding and orbital hybridization, can form diverse allotropes, including zero dimensional fullerenes,<sup>1</sup> one-dimensional carbon nanotubes,<sup>2</sup> two-dimensional (2D) graphene<sup>3</sup> and graphdiyne,<sup>4,5</sup> and three-dimensional (3D) graphite and diamond. Among them, diamond is one of the holy grails because of its exceptional physical properties, such as the unparallelable hardness, extraordinary strength, low friction, and ultrahigh thermal conductivity. With the development of synthetic diamonds, the applications of diamond have expanded from traditional mechanical processing to many other fields, including microdevices,<sup>6</sup> photosensors,<sup>7</sup> electrochemical oxidation,<sup>8</sup> supercapacitors,<sup>9</sup> and biomedical devices.<sup>10</sup> For example, 3D porous diamond foams have been found to possess even higher efficient heat dissipation than Cu foams,<sup>11</sup> and borondoped diamond electrodes exhibit excellent electrocatalytic oxidation performance in organic wastewater treatment.<sup>8</sup> These studies show that the properties of diamond are valued much more than its fascinating beauty. However, natural diamonds are extremely rare and expensive. Therefore, the design and synthesis of diamond-like materials have been a long-standing quest, stimulating the research of seeking for the new cousins of diamond.

To design new carbon allotropes, finding proper structure building blocks is essential. Carbon five-membered rings and six-membered rings are two basic building blocks of carbon materials. For instance,  $C_{60}$  fullerene is composed of 12 pentagons separated by 20 hexagons. In 2015, we proposed a new 2D carbon allotrope, penta-graphene,<sup>12</sup> which is solely composed of carbon pentagons. Penta-graphene has received considerable attention because of its novel geometric structure and properties. Thereafter, many other pure pentagon-based structures have been predicted, and some of them have been synthesized (see our Database for Pentagon-Based Sheets<sup>13</sup> for details), demonstrating that pure pentagon can also be used as building block.

Very recently, a 3D new carbon allotrope purely composed of pentagonal structural units, pentadiamond, has been theoretically predicted and was found to be light as graphite and semiconducting as silicon.<sup>14</sup> Although the mechanical properties of pentadiamond are not comparable to those of diamond,<sup>15</sup> its atomic configuration is novel, and it is thermally, dynamically, and mechanically stable. Thus, several follow-up studies have been conducted to further explore its optical, mechanical, and heat transport properties.<sup>16,17</sup> Based on the atomic configuration, a pentadiamond-like metallic carbon nitride has been predicted.<sup>18</sup> The lattice thermal conductivity  $k_l$  of pentadiamond was calculated by using the machine-learning interatomic potentials and found to be 427 W/mK at room temperature.<sup>17</sup> However, the thermal transport properties and phonon scattering processes of pentadiamond have not been

well studied yet, and the mechanism for low lattice thermal conductivity remains uncovered.

Lattice thermal conductivity  $k_l$  of a material is one of the most fundamental physical properties and is of particular interest for carbon materials because it can vary in an extremely large range from less than 0.01 W/mK for amorphous carbons<sup>19</sup> to greater than 2000 W/mK for diamond.<sup>20</sup> In this work, to illustrate above issue and how the structural unit changes the properties of carbon materials, the thermal transport properties of pentadiamond are systematically studied by using first-principles calculations combined with solving exactly the linearized phonon Boltzmann transport equation (BTE). Specifically, the underlying physical mechanisms are uncovered by carefully analyzing the bonding strength, phonon spectra, group velocity, three-phonon scattering rate, phase space, and Grüneisen parameter.

#### **II. COMPUTATIONAL METHODS**

All calculations are performed based on density functional theory (DFT) with the projector augmented wave (PAW) method<sup>21,22</sup> as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>23</sup> We use the Perdew–Burke–Ernzerhof (PBE) functional<sup>24</sup> within the generalized gradient approximation (GGA)<sup>25</sup> to treat the exchange-correlation interaction of electrons. The kinetic energy cutoff for wave function is set to 520 eV, and the Monkhorst–Pack<sup>26</sup> *k*-point with a grid density of  $2\pi \times 0.02$  Å<sup>-1</sup> is used to sample the Brillouin zone for integrations in reciprocal space. The convergence criteria for energy and force are chosen to be  $10^{-8}$  eV and  $10^{-6}$  eV/Å for the total energy and force, respectively.

The calculation of lattice thermal conductivity  $k_l$  is carried out by solving the phonon Boltzmann transport equation (BTE)<sup>27</sup> as implemented in the ShengBTE package.<sup>28</sup> Phonons dominate the heat transport in semiconductors, and the intrinsic  $k_l$  can be expressed as follows:

$$k_l^{\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\lambda} f_0 (f_0 + 1) (\hbar \omega_{\lambda})^2 v_{\lambda}^{\alpha} F_{\lambda}^{\beta}, \qquad (1)$$

where  $\alpha$  and  $\beta$  denote the directions of the Cartesian coordinate system and  $\lambda$  is the phonon mode consisting of both wave vector qand phonon branch index *j*.  $k_B$ , *T*, *N*,  $\Omega$ , and  $\hbar$  represent the Boltzmann constant, temperature, the number of q points uniformly space in the Brillouin zone, the volume of unit cell, and the reduced Planck constant, respectively.  $f_0$  refers to the Bose–Einstein distribution function at thermodynamic equilibrium, while  $\omega_{\lambda}$  and  $v_{\lambda}$  are phonon frequency and phonon velocity, respectively.  $F_{\lambda}^{\beta}$  is the phonon mean free displacement formulated as  $F_{\lambda}^{\beta} = \tau_{\lambda}^{0}(v_{\beta,\lambda} + \Delta_{\lambda})$ , where  $\tau_{\lambda}^{0}$  is the phonon lifetime under relaxation time approximation (RTA),<sup>29</sup> and the  $\Delta_{\lambda}$  is used to correct the inaccuracy of RTA via solving the BTE iteratively. In addition, Eq. (1) can be also rewritten in the form of volumetric phonon specific heat  $(C_{\rm ph})^{30}$  as

$$k_l^{\alpha\beta} = \frac{1}{N} \sum_{\lambda} C_{ph\lambda} v_{\alpha\lambda} v_{\beta\lambda} \tau_{\lambda}.$$
(2)

The inputs for thermal conductivity are the second-order (harmonic) and third-order (anharmonic) interatomic force constants (IFCs), which are calculated using PHONOPY<sup>31</sup> and thirdorder.py.<sup>28</sup> A  $3 \times 3 \times 3$  supercell is used for the calculations of the harmonic and anharmonic IFCs for pentadiamond as it has a large primitive cell, while a  $6 \times 6 \times 6$  supercell is used for diamond. For calculating the anharmonic IFCs, we include the interactions up to the 10th nearest neighbor atoms with the cutoff radii of 6.45 and 5.75 Å for pentadiamond and diamond, respectively. In solving the Boltzmann transport equation for phonons, the *q*-grids of  $15 \times 15 \times 15$  and  $60 \times 60 \times 60$ are, respectively, adopted for pentadiamond and diamond, while the scale broad parameter of 0.1 is chosen for both of them.

#### **III. RESULTS AND DISCUSSION**

#### A. Geometric structure and mechanical properties

The optimized geometry of pentadiamond with the lattice parameter of 9.19 Å is schematically presented in Fig. 1(a), which crystallizes in the orthogonal space group  $Fm\bar{3}m$  (No. 225) with a point group of  $O_h^5$ . Its primitive cell consists of 22 carbon atoms that occupy the Wyckoff positions of 8c (0.250, 0.250, 0.250), 32f (0.152, 0.152, 0.152), and 48h (0.198, 0.198, 0.000), forming the covalent network with pentagonal units by sharing their edges. These three kinds of chemically nonequivalent carbon atoms are labeled as C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>, as shown in Fig. 1(c), where C<sub>1</sub> and C<sub>2</sub> atoms are in  $sp^3$  hybridization, while C<sub>3</sub> atoms are in  $sp^2$  hybridization. For comparison, the geometric structure of diamond is also given in Fig. 1. Obviously, different from diamond, where all the carbon atoms are in  $sp^3$  hybridization and each one is bonded covalently with its four neighboring atoms, forming a densely packed structure with a mass density ( $\rho$ ) of 3.49 g/cm<sup>3</sup>, pentadiamond has a more complex crystal structure with the mixed  $sp^2 - sp^3$  bonding and a lower mass density of 2.26 g/cm<sup>3</sup>, which would lead to a low lattice thermal conductivity according to the Slack criteria.<sup>32</sup>



**FIG. 1.** (a) and (b) Optimized geometry and (c) and (d) the structural unit of pentadiamond and diamond. The three chemically nonequivalent carbon atoms in pentadiamond are labelled as  $C_1$ ,  $C_2$ , and  $C_3$ .

Phase	Pentadiamond (this work)	Diamond (this work)	Pentadiamond (Brazhkin et al. <sup>15</sup> )	Diamond (Li et al. <sup>36</sup> )
C <sub>11</sub>	539.22	1080.27	537	1051.1
C <sub>12</sub>	105.55	141.95	106	127.7
C <sub>44</sub>	141.00	574.67	143	560.6
В	250.14	454.72	249	435.1
G	167.66	529.85	169	518.7
Ε	411.13	1144.87	413	1113.7
V	0.23	0.08	0.22	0.07
B/G	1.49	0.86	1.47 <sup>a</sup>	0.84 <sup>a</sup>

TABLE I. Calculated elastic parameters C<sub>ij</sub> (in GPa), bulk modulus B (in GPa), shear modulus G (in GPa), Young's modulus E (in GPa), Poisson's ratio v, and Paugh ratio B/G for pentadiamond and diamond.

<sup>a</sup>Deduced from raw data in the corresponding literature.

Next, we study the mechanical properties to explore the bonding strength of the two carbon allotropes as analyzing mechanical properties is one of the efficient ways to estimate the bonding strength.<sup>33,34</sup> Usually stiffer bonds lead to a higher phonon group velocity and thus a higher thermal conductivity.35 The calculated results of the elastic parameters C<sub>ij</sub>, bulk modulus B, shear modulus G, Young's modulus E, and Poisson's ratio v are summarized in Table I, which are consistent with those of previous studies,<sup>15</sup> showing the accuracy and reliability of our calculations. We note that the calculated elastic constants of pentadiamond and diamond satisfy the well-known Born stability criteria for cubic structures,<sup>37</sup> confirming the mechanical stability of these two structures. Young's modulus and the shear modulus of pentadiamond are much smaller than those of diamond, implying that the average C-C bond strength of pentadiamond is much weaker than that of diamond. In general, the materials with low Young's modulus and shear modulus possess "soft bonding" feature, which would lead to low phonon group velocity and Debye temperature.<sup>39,40</sup> In addition, Paugh ratio G/B, the ratio of bulk modulus (B) to shear modulus (G), can be used to distinguish whether a material is brittle (B/G < 1.75) or ductile (B/G > 1.75),<sup>41</sup> which is found to be 1.49 and 0.86 for pentadiamond and diamond, respectively, indicating that both pentadiamond and

diamond exhibit brittle behavior. However, the lower Paugh of diamond characterizes the stronger chemical bonding. Based on the mechanical data in Table I, one can expect that the  $k_l$  of pentadiamond should be lower than that of diamond.

#### B. Phonon spectra and lattice thermal conductivity

We then calculate the phonon spectra and corresponding phonon density of states (PhDOS) of pentadiamond and diamond. The results are plotted in Figs. 2(a) and 2(b), respectively, where the acoustic modes are highlighted in red as they play an important role in the processes of heat transport. Figure 2(a) shows that there is a small bandgap of ~10 THz in the high frequency region with the highest vibrational frequency of 49 THz, while that for the perfectly  $sp^3$  bonded diamond is 40 THz, as shown in Fig. 2(b). According to the PhDOS, the high frequencies of pentadiamond mainly come from the  $sp^2$  hybridized C<sub>3</sub> atoms, suggesting that the large PhDOS above 40 THz are contributed from the C<sub>3</sub>-C<sub>3</sub> bonds. The bond length of C<sub>3</sub>-C<sub>3</sub> is 1.352 Å, showing the double bond character, which would lead to small bandgap in the phonon spectra of pentadiamond, similar to that in C<sub>20</sub>-T carbon.<sup>42</sup> In addition, different from diamond, the most remarkable feature of



FIG. 2. Phonon spectra and corresponding PhDOS of (a) pentadiamond and (b) diamond.

Phase	Pentadiamond (this work)	Diamond (this work)	Diamond (Kou <i>et al.</i> <sup>44</sup> )
$v_l$	14 477.43	18 240.57	17 936.49
$v_t$	8 613.12	12 321.50	12 213.63
$v_m$	9 535.99	13 446.55	13 314.42
$ heta_D$	1 373	2 240	2 230

**TABLE II.** Sound velocity (longitudinal  $v_h$ , transverse  $v_t$ , and average  $v_a$ ) (in m/s) and Debye temperature  $\theta_D$  (in K) of pentadiamond and diamond.

the phonon dispersions in pentadiamond is the strong overlapping between the acoustic and low-lying optical branches. Due to the overlap, the acoustic phonons, which is dominant in the heat transport, will be strongly scattered by the low-frequency optical phonons, thus leading to lower thermal conductivity, as is the case with skutterudite FeSb<sub>3</sub>.<sup>43</sup> In addition, the acoustic branches of pentadiamond are significantly softened as compared to those of diamond, which would lead to a low Debye temperature ( $\theta_D$ ) that corresponds to the highest normal mode of vibration for a crystal. We calculate  $\theta_D$  by using the formula:  $\theta_D = (\hbar/k_B) \cdot (6\pi^2/\Omega)^{1/3} \cdot v_a$ , where  $\Omega$  is the volume of the unit cell, and  $v_a$  is the average sound velocity defined as  $v_a = [(1/v_l^3 + 2/v_t^3)/3]^{-1/3}$ , where  $v_l$  and  $v_t$  are the longitudinal and transverse sound velocities, respectively, and are calculated using the equations:  $v_l = \sqrt{(3B + 4G/3)/\rho}$  and  $v_t = \sqrt{G/\rho}$  (B is bulk modulus, G is shear modulus, and  $\rho$  is mass density). The calculated results are listed in Table II, showing that the Debye temperature of pentadiamond is 1373 K, which is much lower than that of diamond (2240 K). The low Debye temperature of pentadiamond implies its low lattice thermal conductivity.

Since pentadiamond is semiconducting with a gap of 2.52 eV,<sup>14</sup> phonons are the major heat carriers; therefore, we focus on the  $k_l$  of pentadiamond. The temperature-dependent  $k_l$  of pentadiamond and diamond is calculated using the phonon BTE, as shown in Fig. 3(a). The calculated  $k_l$  of pentadiamond and diamond is 490.88 and 2664.93 W/mK at room temperature, respectively, which agrees well with the previous studies.<sup>17,45,46</sup> The  $k_l$  of pentadiamond is higher than that of many carbon allotropes, such as 3D graphene (150 W/ mK at 300 K<sup>4/</sup> and T-carbon (33 W/mK at 300 K),<sup>48</sup> but it is significantly reduced as compared to that of diamond. Apart from that, the cumulative  $k_l$  as a function of frequency is calculated and plotted in Fig. 3(b), which shows that the phonons with their frequencies lower than 25 THz contribute more than 90% to the thermal conductivities in the two carbon materials. The percentage contributions of the three acoustic and optical phonon branches are also plotted to understand the contributions of different phonon branches. As shown in Fig. 3(c), in mid-and-high temperature, pentadiamond and diamond exhibit quite different behaviors; the optical branches contribute more than 30% to the overall  $k_l$  in pentadiamond, while the optical branches contribute less than 10% to the overall  $k_l$  in diamond. Usually, acoustic phonons are considered as the major heatingcarrying phonons since optical phonons have small group velocities, just like that in diamond. While in pentadiamond, there are optical phonon modes with frequency around 10-20 THz with group velocities similar to that of acoustic modes [Fig. 4(a)], which makes their contribution comparable to that of acoustic phonons.

To explore why the  $k_l$  of pentadiamond is only one-fifth that of diamond, we focus on the critical factors that determine the lattice thermal conductivity based on Eq. (2), namely, the phonon specific heat  $C_{ph}$ , phonon group velocity  $v_{g}$ , and phonon relaxation time  $\tau$ . The calculated specific heats of pentadiamond and diamond are plotted in Fig. 3(d), from which one can see that there is no much difference in  $C_{ph}$  between pentadiamond and diamond. Therefore, the specific heat is not the main reason for the difference in thermal conductivity between these two carbon allotropes.

The frequency-dependent phonon group velocity  $v_g$  and phonon relaxation time  $\tau$  are calculated, and the results are plotted in Fig. 4. The group velocity  $v_g$  of pentadiamond is significantly lower than that of diamond in the range from 0 to 40 THz, while it is higher than that of diamond in the high frequency range (40-50 THz). Considering the high-frequency phonons (higher than 40 THz) contribute less to the total  $k_l$ , we conclude that the average group velocity of diamond is slightly higher than that of pentadiamond, and the group velocity cannot adequately explain the big difference in  $k_l$  between pentadiamond and diamond. In addition, according to Figs. 4(c) and 4(d), the relaxation time of both pentadiamond and diamond decreases with frequency, confirming that the phonons with low frequency would make more contributions to the total  $k_i$ . More importantly, the magnitude of relaxation time of pentadiamond is obviously smaller compared to diamond. Based on the above discussions, it is clear that the significant reduction of the lattice thermal conductivity of pentadiamond is mainly attributed to the reduced phonon relaxation time resulting from the strong phonon-phonon scattering.

#### C. Phonon scattering processes

In order to illustrate the mechanism of the difference in phonon relaxation time between pentadiamond and diamond, we further investigate the scattering mechanism of phonon modes to provide physical insight. The three-phonon scattering processes depends on two factors: the number of existing scattering channels for various phonons and the strength of each scattering channel, which can be described by using weighted phase space  $(WP_3)$  and mode Grüneisen parameter  $(\gamma)$ , respectively.  $WP_3$ qualitatively characterizes the number of available scattering channels that satisfy the selection rules of energy and momentum conservations in heat transfer, and a less restricted WP<sub>3</sub> can result in a large scattering rate (the reciprocal of the phonon relaxation time of  $1/\tau$ ), leading to low  $k_l$ . The calculated results of weighted phase space plotted in Figs. 5(a) and 5(b) show that the WP<sub>3</sub> of pentadiamond is considerably larger than that of diamond throughout the whole frequency region. The less restricted WP<sub>3</sub> indicates more available three phonon scattering processes in pentadiamond, leading to a large scattering rate and low thermal conductivity eventually. It is known that  $WP_3$  is entirely determined by the phonon dispersion of a material, and the large  $WP_3$  of pentadiamond might arise from its complex crystal structure, large number of atoms per primitive cell, and the strong acoustic-optical interactions. Thus, the phonon scattering space plays a key role in suppressing the thermal conductivity of pentadiamond.

The mode Grüneisen parameter ( $\gamma$ ) can measure the strength of three-phonon scattering processes and qualitatively characterize



FIG. 3. (a) Temperature-dependent lattice thermal conductivities of pentadiamond and diamond. (b) Variation of the normalized cumulative lattice thermal conductivity with frequency for pentadiamond and diamond. (c) Contributions from the phonon branches and (d) heat capacity of pentadiamond and diamond at different temperatures.

the anharmonicity of lattice vibrations. A larger  $|\gamma|$  implies a higher anharmonicity and lower lattice thermal conductivity. Considering the isotropy of both pentadiamond and diamond, we calculate  $\gamma$ along the  $\Gamma$ -X high symmetry line using  $\gamma = (A/\omega_{\lambda})$  ( $\partial \omega_{\lambda}/\partial A$ ), where A is the volume of the cell and  $\omega_{\lambda}$  is the angular frequency. Larger  $|\gamma|$  is found in pentadiamond, showing stronger anharmonicity as compared to diamond. These results are in good agreement with the statement that strong anharmonicity can be observed in either soft lattices or the lattices that are not well packed.<sup>34</sup> In addition, the atomic displacement parameter (ADP) is also calculated. As shown in Fig. 5(d), the calculated values of ADP for diamond are extremely small (<0.002 Å<sup>2</sup>), while the corresponding values for pentadiamond are larger. The high Grüneisen parameter and ADP are responsible for the low thermal conductivity of pentadiamond, as compared to diamond.

Based on the above analysis, we conclude that the low thermal conductivity of pentadiamond essentially originates from the large scattering phase space because of its large, complex unit cell and



FIG. 4. (a) and (b) Variation of group velocity and (c) and (d) relaxation time with frequency at 300 K for pentadiamond and diamond.

the strong interactions between the acoustic and low-lying optical branches and is also attributed to the large Grüneisen parameter and low Debye temperature.

It is interesting to note that pentadiamond and penta-graphene have some similarities in their reduced lattice thermal conductivities, as compared to diamond and graphene, respectively. It is well known that the lattice thermal conductivity of graphene is ultrahigh with a value of 3717 W/mK at 300 K,<sup>49</sup> while that of penta-graphene is 645 W/mK at the same temperature.<sup>50</sup> The underlying reasons for

the similar trend of reduced lattice thermal conductivity are due to the following basic facts: (1) Both pentadiamond and pentagraphene are energetically metastable as respectively compared with diamond and graphene, where the reduced bond strength leads to reduced phonon velocity. (2) The non-compact geometric feature in both pentadiamond and penta-graphene results in stronger anharmonicity than that of diamond and graphene. (3) The carbon atoms in both pentadiamond and penta-graphene are in mixed  $sp^2$  and  $sp^3$  hybridizations, while the atoms in diamond and graphene



FIG. 5. (a) and (b) Weighted three phonon phase space as a function of frequency, (c) Grüneisen parameter along the  $\Gamma$ -X high symmetry path, and (d) the variation of calculated ADP with temperature for pentadiamond and diamond.

are purely  $sp^3$  and  $sp^2$  hybridized, respectively. The heterogeneity in chemical bonds enhances the anharmonicity.<sup>51</sup>

#### **IV. CONCLUSIONS**

In this work, we have studied the lattice thermal conductivity and phonon scattering processes of pentadiamond by using first-principles calculations combined with an iterative solution of the BTE and found that the intrinsic  $k_l$  of pentadiamond is 490.88 W/mK at room temperature, much lower than that of diamond (2664.93 W/mK). The low  $k_l$  of pentadiamond can be attributed to the following factors: (1) more scattering channels arising from the strong crossing and interaction between the acoustic branches and low-lying optical branches; (2) the low group velocity and Debye temperature originating from the existence of "soft bonding" feature, which is characterized by the low Young's modulus and shear modulus; (3) the strong anharmonicity caused by the unique geometric characteristics of pentadiamond distinguishing

from those of diamond, such as complexities in structure and bonding. These findings indicate that pentadiamond behaves very differently in lattice thermal conductivity from its cousin, diamond, further demonstrating the flexibility in turning the thermal conductivity of carbon materials in a large range for diverse device applications by changing atomic configurations.

#### ACKNOWLEDGMENTS

This work was partially supported by grants from the National Natural Science Foundation of China (NNSFC) (Grant Nos. NSFC-21773004 and NSFC-11974028) and the National Key Research and Development Program of the Ministry of Science and technology of China (Grant No. 2017YFA0205003) and was supported by the High-Performance Computing Platform of Peking University, China. There are no conflicts to declare.

#### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

#### REFERENCES

<sup>1</sup>H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Nature 318, 162 (1985).

<sup>2</sup>S. Iijima, Nature 354, 56 (1991).

<sup>3</sup>K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).

<sup>4</sup>G. Li, Y. Li, H. Liu, Y. Guo, Y. Li, and D. Zhu, Chem. Commun. 46, 3256 (2010).

<sup>5</sup>X. Gao, Y. Zhu, D. Yi, J. Zhou, S. Zhang, C. Yin, F. Ding, S. Zhang, X. Yi, J. Wang, L. Tong, Y. Han, Z. Liu, and J. Zhang, Sci. Adv. 4, eaat6378 (2018).

<sup>6</sup>O. Auciello and A. V. Sumant, Diamond Relat. Mater. 19, 699 (2010).

7A. A. Altukhov, M. S. Afanas'ev, V. B. Kvaskov, V. E. Lyubchenko, A. Yu. Mityagin, E. N. Murav'ev, L. A. Pomortsev, V. A. Potapov, and B. V. Spitsyn, Inorg. Mater. 40, S50 (2004).

<sup>8</sup>R. Mei, Q. Wei, C. Zhu, W. Ye, B. Zhou, L. Ma, Z. Yu, and K. Zhou, Appl. Catal. B 245, 420 (2019).

<sup>9</sup>J. Xu, N. Yang, S. Heuser, S. Yu, A. Schulte, H. Schönherr, and X. Jiang, Adv. Energy Mater. 9, 1803623 (2019).

<sup>10</sup>R. J. Narayan, R. D. Boehm, and A. V. Sumant, Mater. Today 14, 154 (2011).

11 L. Zhang, K. Zhou, Q. Wei, L. Ma, W. Ye, H. Li, B. Zhou, Z. Yu, C. Lin, J. Luo, and X. Gan, Appl. Energy 233-234, 208 (2019).

12S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe, and P. Jena, Proc. Natl. Acad. Sci. U.S.A. 112, 2372 (2015).

13Y. Shen and Q. Wang, Database, see http://www.pubsd.com/ for "Database for entagon-based sheets" (2020).

pentagon-based sneets (2020). <sup>14</sup>Y. Fujii, M. Maruyama, N. T. Cuong, and S. Okada, Phys. Rev. Lett. 125, 016001 (2020); 125, 079901(E) (2020).

- 15 V. V. Brazhkin, M. V. Kondrin, A. G. Kvashnin, E. Mazhnik, and A. R. Oganov, arXiv:2007.08912 (2020).
- <sup>16</sup>R. M. Tromer, L. C. Felix, C. F. Woellner, and D. S. Galvao, Chem. Phys. Lett. 763, 138210 (2021).
- 17B. Mortazavi, F. Shojaei, X. Zhuang, and L. F. C. Pereira, Carbon Trends 3, 100036 (2021).

18 Z. Li, Y. Wu, S. Zhang, Y. Zhang, Y. Gao, K. Luo, Z. Zhao, and J. He, J. Phys. Chem. C 124, 24978 (2020).

<sup>19</sup>A. A. Balandin, M. Shamsa, W. L. Liu, C. Casiraghi, and A. C. Ferrari, Appl. Phys. Lett. 93, 043115 (2008).

20 L. Wei, P. K. Kuo, R. L. Thomas, T. R. Anthony, and W. F. Banholzer, Phys. Rev. Lett. 70, 3764 (1993).

<sup>21</sup>P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

<sup>22</sup>G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

23G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

<sup>24</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

- **25**Y. Liu and C. Storey, J. Optim. Theory Appl. **69**, 139 (1991).
- <sup>26</sup>H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).

<sup>27</sup>M. Omini and A. Sparavigna, Phys. B 212, 101 (1995).

28 W. Li, J. Carrete, N. A. Katcho, and N. Mingo, Comput. Phys. Commun. 185, 1747 (2014).

- <sup>29</sup>L. Lindsay, D. A. Broido, and T. L. Reinecke, Phys. Rev. B 87, 165201 (2013).
- <sup>30</sup>H. Liu, G. Qin, Y. Lin, and M. Hu, Nano Lett. 16, 3831 (2016).

<sup>31</sup>A. Togo and I. Tanaka, Scr. Mater. 108, 1 (2015).

<sup>32</sup>G. A. Slack, J. Phys. Chem. Solids 34, 321 (1973).

33S. K. Saha and G. Dutta, Phys. Rev. B 94, 125209 (2016).

34W. G. Zeier, A. Zevalkink, Z. M. Gibbs, G. Hautier, M. G. Kanatzidis, and G. J. Snyder, Angew. Chem. Int. Ed. 55, 6826 (2016).

<sup>35</sup>P. Chakraborty, G. Xiong, L. Cao, and Y. Wang, Carbon 139, 85 (2018).

- <sup>36</sup>Z. Li, F. Gao, and Z. Xu, Phys. Rev. B **85**, 144115 (2012).
- 37Z.-j. Wu, E.-j. Zhao, H.-p. Xiang, X.-f. Hao X.-j. Liu, and J. Meng, Phys. Rev. B 76, 054115 (2007).
- <sup>38</sup>F. Mouhat and F.-X. Coudert, Phys. Rev. B **90**, 224104 (2014).
- **39**Y. Shen, F. Q. Wang, and Q. Wang, Nano Energy **73**, 104822 (2020).

<sup>40</sup>D. Yang, W. Yao, Y. Yan, W. Qiu, L. Guo, X. Lu, C. Uher, X. Han, G. Wang, T. Yang, and X. Zhou, NPG Asia Mater. 9, e387 (2017).

<sup>41</sup>S. F. Pugh, Philos. Mag. 45, 823 (1954).

42 J.-Q. Wang, C.-X. Zhao, C.-Y. Niu, Q. Sun, and Y. Jia, J. Phys.: Condens. Matter 28, 475402 (2016).

<sup>43</sup>Y. Fu, D. J. Singh, W. Li, and L. Zhang, Phys. Rev. B **94**, 075122 (2016).

44J. Kou, Y. Zhou, K. Li, and L.-H. Gan, Comput. Mater. Sci. 182, 109758 (2020).

45 A. V. Inyushkin, A. N. Taldenkov, V. G. Ralchenko, A. P. Bolshakov,

A. V. Koliadin, and A. N. Katrusha, Phys. Rev. B 97, 144305 (2018).
 <sup>46</sup>F. Q. Wang, M. Hu, and Q. Wang, J. Mater. Chem. A 7, 6259 (2019).

47Y. Han, J.-Y. Yang, and M. Hu, Nanoscale 10, 5229 (2018).

48S.-Y. Yue, G. Qin, X. Zhang, X. Sheng, G. Su, and M. Hu, Phys. Rev. B 95, 085207 (2017).

- 49 B. Peng, H. Zhang, H. Shao, Y. Xu, G. Ni, R. Zhang, and H. Zhu, Phys. Rev. B 94, 245420 (2016).
- 50 F. Q. Wang, J. Yu, Q. Wang, Y. Kawazoe, and P. Jena, Carbon 105, 424 (2016). <sup>51</sup>K. Pal, Y. Xia, J. He, and C. Wolverton, Phys. Rev. Mater. 3, 085402 (2019).