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Theoretical studies on the strong phonon coherence in the type-5 penta-PbN₈ sheet†

Asghar Hussain, Chenxin Zhang, Peng-Hu Du,  Qiang Sun * and Qian Wang *

Inspired by the recent prediction of the stable penta-PbN₈ sheet, which realizes the mathematical model known as the type-5 pentagonal tiling pattern from the perspective of materials, we have explored its lattice thermal transport properties. Using first-principles calculations combined with the unified theory of thermal transport, we found that penta-PbN₈ possesses a low lattice thermal conductivity at room temperature with the value of 4.61 (5.23) W m⁻¹ K⁻¹ along the x(y)-direction and a dominant contribution of 3.32 (3.84) W m⁻¹ K⁻¹ from the corresponding phonon coherence. Based on a detailed study of the phonon dispersion, phonon–phonon scattering, and phonon coherence, we further demonstrated that the intrinsic strong anharmonicity caused by the unique atomic configuration with a buckled geometry and the large atomic mass differences in this type-5 penta-sheet significantly enhance the phonon scattering rate and phonon coherent lifetime, leading to low lattice thermal conductivity with a high proportion contributed by phonon coherence. Our study demonstrates that the diverse patterns in the penta-sheet family lead to rich features in phonon transport.

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1. Introduction

Penta-graphene^{1,2} provides a novel structural model for the design and synthesis of pentagon-based two-dimensional (2D) materials going beyond the conventional ones, based on which more than 170 new pentagonal sheets have been theoretically identified.³ Several of these compounds, such as penta-PdSe₂,^{4,5} penta-PdS₂,⁶ and penta-NiN₂,⁷ have been synthesized following their theoretical predictions.^{8,9} These 2D materials exhibit fascinating characteristics and hold potential for various applications, including auxetics,^{1,10} nonlinear optics,^{11,12} piezoelectricity,^{13–15} thermal transport,^{16–18} thermoelectricity,^{19,20} photodetectors,²¹ photodiodes,²² and gas sensors.²³ However, almost all these pentagon-based 2D structures belong to the type-2, type-4 or type-1 pentagonal tiling pattern.³ For instance, penta-graphene,¹ penta-GeP₂,²⁴ penta-ZnS₂,¹¹ and the synthesized penta-NiN₂ sheet⁷ exhibit the type-4 pentagonal tiling pattern, whereas the synthesized penta-PdSe₂^{4,5} and penta-PdS₂⁶ sheets show the type-2 pentagonal tiling pattern. The penta-SrP₂ sheet previously reported by us is the first pentagonal material with the type-1 tiling.²⁵ Despite these advances, there exist a total of 15 mathematically known pentagonal tiling patterns,³ each capable of tiling the Euclidean plane with only identical copies of irregular pentagons, leaving

no gaps and overlaps. This opens up the possibility for designing and synthesizing 2D structures using tiling patterns other than the type-1, type-2, and type-4 patterns, thereby enriching the family of 2D materials. Recently, the first material realization of the type-5 mathematical model in 2D lattices was reported,²⁶ where penta-MN₈ (M = Mg, Ca, Sr, Ba; Sn, Pb; Cd; Mo, W) sheets with the type-5 pentagonal tiling pattern have been proposed by assembling the newly synthesized N₁₈ macrocycles with the metal or transition metal atoms, and Hückel aromaticity and 18-electron rules can be applied for understanding the stable pentagonal metal polynitrides.²⁶

Although these reported penta-sheets have different geometric structures and tiling patterns, they share common features, namely, the unique geometries with pentagons as their building units result in large intrinsic stress and low symmetry, which can induce strong anharmonicity and phonon–phonon interactions, making the study on the lattice thermal transport particularly interesting, as is the case with the reported type-2 and type-4 pentagonal systems.³ For instance, the lattice thermal conductivity of the type-4 sheet, penta-NiN₂, was found to be 11.67 W m⁻¹ K⁻¹ at room temperature when including the four-phonon scattering, which is reduced by 89.32% as compared to the value obtained by only considering the three-phonon scattering process.¹⁶ The lattice thermal conductivity of the penta-PdSe₂ sheet with the type-2 pentagonal tiling is 3.60 and 6.40 W m⁻¹ K⁻¹ in the *x* and *y* directions, respectively,²⁷ exhibiting strong anisotropy. These penta-sheets with type-2 or type-4 tiling patterns³ have the following features: (1) mixed

Peking University, Beijing, China. E-mail: sunqiang@pku.edu.cn, qianwang2@pku.edu.cn

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three-fold and four-fold coordination; (2) typically in a square lattice. However, the type-5 penta-MN₈ sheet contains both three-fold and six-fold coordination. Because of the high coordination with buckling, the central atom M in the N₁₈ ring is more susceptible to thermal disturbances at finite temperatures. Moreover, in the penta-MN₈ family, penta-PbN₈ is of special interest: it has the largest mass difference in the series of Mg, Ca, Sr, Ba, Sn, Cd, Mo, W and Pb with N, making the penta-PbN₈ sheet in a sinusoidal-like undulating configuration,²⁶ which would significantly affect the phonon transport and thermal conductivity. However, despite the extensive studies on the lattice thermal properties of type-2 and type-4 penta-sheets, no investigations have been conducted on the lattice thermal transport properties of the newly proposed type-5 penta-sheets. This work bridges the gap by studying the thermal conductivity of penta-PbN₈ using the unified theory of thermal transport.²⁸ We demonstrate that phonon coherence, a key factor influencing the thermal transport properties, plays a significant role in determining the thermal conductivity of penta-PbN₈. The results show that penta-PbN₈ exhibits enhanced thermal conductivity and phonon coherence, highlighting its potential for applications that require efficient thermal management.

2. Computational methods

First-principles calculations have been carried out within the density functional theory (DFT) framework implemented in the Vienna *ab initio* simulation package (VASP) package.²⁹ The projector-augmented wave (PAW) method is employed to treat the interactions between ion cores and valence electrons.^{30,31} The exchange–correlation interaction between electrons is described with the Perdew–Burke–Ernzerhof (PBE) functional,³² for geometry optimization. The kinetic energy cut-off is set as 700 eV for the wave function. For geometrical optimization, the Brillouin zone is sampled with a $9 \times 9 \times 1$ Gamma-centered *k*-point mesh. The convergence criterion values for force and energy are 10^{-8} eV and 10^{-6} eV Å⁻¹, respectively. To prevent interactions with the periodic images of the penta-PbN₈ sheet, a 17.25 Å vacuum space is included perpendicular to the sheet.

According to the unified theory of thermal transport,^{28,33–35} the total lattice thermal conductivity κ_L is the sum of the thermal conductivity κ_L^P and κ_L^C contributed by phonon scattering (particle-like) and phonon coherence, respectively:

$$\kappa_L = \kappa_L^P + \kappa_L^C. \quad (1)$$

κ_L^P can be obtained from the Boltzmann transport equation (BTE),³⁶ within the framework of three-phonon and four-phonon scattering, as follows:

$$\kappa_L^{P,\alpha\beta} = \frac{1}{k_B T^2 \Omega N} \sum_{\mathbf{q}} \sum_i \bar{N}(\mathbf{q})_i (\bar{N}(\mathbf{q})_i + 1) (\hbar \omega(\mathbf{q})_i)^2 V^\alpha(\mathbf{q})_i V^\beta(\mathbf{q})_i \tau(\mathbf{q})_i. \quad (2)$$

where α and β denote the Cartesian coordinates, and k_B , T , Ω , N , and $\hbar$ represent the Boltzmann constant, absolute temperature,

volume of the unit cell, number of discrete $\mathbf{q}$ points in the Brillouin zone, and the reduced Planck constant, respectively. Additionally, $\omega(\mathbf{q})_i$ and $\bar{N}(\mathbf{q})_i$ represent the angular frequencies and the equilibrium Bose–Einstein distribution, respectively, indexed by wave vector $\mathbf{q}$ and branch i . $\tau(\mathbf{q})_i$ is the phonon lifetime. The calculation for κ_L^P is conducted with the ShengBTE package,³⁷ where the harmonic (second order) and anharmonic (third and fourth order) interatomic force constants (IFCs) are provided as inputs for the calculations of thermal conductivity. For the penta-PbN₈ sheet, its phonon dispersion spectrum is obtained from PHONOPY,³⁸ using the finite displacement method with a $3 \times 2 \times 1$ supercell and a $3 \times 3 \times 1$ *k*-point mesh. The structures required for calculating third and fourth-order IFCs are generated using the Monte-Carlo random displacement method coded in the HIPHIVE package.³⁹ The cut-off distance for the second-order IFCs is set to 8.17 Å, while for the third and fourth-order IFCs, cut-off distances of 5.00 and 4.00 Å are applied, respectively. The thickness of the penta-PbN₈ sheet is maintained at 4.26 Å during the calculations of lattice thermal conductivity, which is determined by considering the buckling of this sheet and the van der Waals radius.^{40,41} The $\mathbf{q}$ -mesh used for convergent ShengBTE calculations is set as $51 \times 25 \times 1$ and $9 \times 5 \times 1$ for the third- and fourth-order calculations, as shown in Fig. S1 in the ESI.† Additionally, detailed convergence tests for the fitting of interatomic force constants are shown in Fig. S2 in the ESI.†

On the other hand, the phonon coherence (κ_L^C) is calculated based on the phonon coherence equation.^{35,42}

$$\begin{aligned} \kappa_L^{C,\alpha\beta} = & \frac{\hbar^2}{k_B T^2 \Omega N} \sum_{\mathbf{q}} \sum_{i \neq j} \frac{\omega(\mathbf{q})_i + \omega(\mathbf{q})_j}{2} V^\alpha(\mathbf{q})_{ij} V^\beta(\mathbf{q})_{ji} \\ & \times \frac{\omega(\mathbf{q})_i \bar{N}(\mathbf{q})_i (\bar{N}(\mathbf{q})_i + 1) + \omega(\mathbf{q})_j \bar{N}(\mathbf{q})_j (\bar{N}(\mathbf{q})_j + 1)}{4(\omega(\mathbf{q})_i - \omega(\mathbf{q})_j)^2 + (\Gamma(\mathbf{q})_i + \Gamma(\mathbf{q})_j)^2} \\ & \times (\Gamma(\mathbf{q})_i + \Gamma(\mathbf{q})_j), \end{aligned} \quad (3)$$

where $\Gamma(\mathbf{q})_i = 1/\tau(\mathbf{q})_i$ is the phonon linewidth (scattering rate) of each phonon mode. $\omega(\mathbf{q})_i$ is given by the second-order IFCs, and the phonon scattering rates $\Gamma(\mathbf{q})_i$ are obtained by including the three-phonon (τ_3^{-1}) and four-phonon scattering rates (τ_4^{-1}): $\Gamma(\mathbf{q})_i = \tau_3^{-1} + \tau_4^{-1}$. In addition, $V(\mathbf{q})_{ij}$ and $\tau(\mathbf{q})_{ij}$ denote the off-diagonal velocity matrix and the lifetime matrix, respectively, which can be derived using the following equations:

$$V(\mathbf{q})_{ij} = \frac{1}{\omega(\mathbf{q})_i + \omega(\mathbf{q})_j} \left\langle e(\mathbf{q})_i \left| \frac{\partial D(\mathbf{q})}{\partial \mathbf{q}} \right| e(\mathbf{q})_j \right\rangle, \quad (4)$$

$$\tau(\mathbf{q})_{ij} = \frac{2(\Gamma(\mathbf{q})_i + \Gamma(\mathbf{q})_j)}{4(\omega(\mathbf{q})_i - \omega(\mathbf{q})_j)^2 + (\Gamma(\mathbf{q})_i + \Gamma(\mathbf{q})_j)^2}. \quad (5)$$

where $e(\mathbf{q})_i$ is the eigenvector of the phonon mode i , and $D(\mathbf{q})$ is the dynamical matrix of the crystal with an eigenvalue of $\omega^2(\mathbf{q})_i$. The calculation for κ_L^C is performed using our in-house code.

3. Results and discussion

3.1 Geometric structure and stability

Fig. 1a shows the top and side views of the fully optimized penta-PbN₈ sheet with a buckling of 0.86 Å and lattice parameters of $a = 5.95$ Å and $b = 11.88$ Å. This structure possesses $P2_1/C$ symmetry (no. 13 space group). Its unit cell contains 18 atoms with 16 N and 2 Pb atoms, occupying five non-equivalent Wyckoff positions, namely, $4g_1$ (0.482, 0.374, 0.502), $4g_2$ (0.562, 0.089, 0.495), $4g_3$ (0.705, 0.535, 0.492), $4g_4$ (0.583, 0.333, 0.496), and $2e$ (0.250, −0.000, 0.520). The Pb–N and N–N bond lengths are measured to be 2.36 Å and 1.31 Å, respectively. Our computational results are consistent with the previous study.²⁶ To check the thermodynamic stability of penta-PbN₈, we calculated its formation enthalpy ΔH and compared it with those of other Pb_xN_{1-x} systems based on the equation $\Delta H = H(Pb_xN_{1-x}) - xH(Pb) - (1 - x)H(N)$, here $H(Pb_xN_{1-x})$, $xH(Pb)$, and $H(N)$ are the enthalpies of the Pb_xN_{1-x} systems, Pb and N on the per-atom basis, respectively. The calculated convex-hull diagram is plotted in Fig. S3 (ESI†). ΔH of penta-PbN₈ is calculated to be 29 meV per atom, which is 61 meV per atom lower than that of the synthesized bulk PbN₆,⁴³ indicating that penta-PbN₈ is metastable but realizable under appropriate synthesis conditions.

Next, to examine the dynamical stability of the penta-PbN₈ sheet, we calculated its phonon spectrum. As presented in Fig. 1b, there are no imaginary phonon modes across the first Brillouin zone, confirming its dynamical stability. For comparison, the phonon band structure obtained from the HiPhive is also plotted using the dashed blue lines, which coincides well with the result from Phonopy, indicating the reliability of IFC fitting. According to the phonon density of states (PhDOS), Pb vibrations predominantly contribute to the acoustic phonon and low-frequency optical modes. In contrast, the high-frequency optical phonon modes mainly originate from both Pb and N vibrations. This mismatch is attributed to the mass difference between Pb and N atoms, which contributes to significant mass disorder scattering, further shortening the phonon lifetimes.⁴⁴ The highest frequency of the acoustic phonon remains relatively low (< 3 THz). The low-frequency acoustic modes are enlarged in the inset of Fig. 1b, and the three acoustic phonon branches are highlighted in the red color, including the out-of-plane transverse acoustic (ZA), in-plane transverse acoustic (TA), and in-plane longitudinal acoustic (LA)

branches along the high symmetric paths. The LA and TA branches remain linear when the wave vector $\mathbf{q}$ is near the Γ point. In contrast, the out-of-plane acoustic (ZA) branch displays parabolic dispersion, characteristic of a monolayer 2D material, as illustrated for low-buckled penta-graphene.¹ Furthermore, a significant overlap exists between the acoustic and low-frequency optical branches. Due to the overlap, the acoustic phonons, which dominate heat transport, would be strongly scattered by the low-frequency optical phonons.

In addition, we performed *ab initio* molecular dynamics (AIMD) simulations from 300 K to 700 K for 10 ps with a time step of 1 fs to confirm the thermal stability of the penta-PbN₈ sheet using a $3 \times 2 \times 1$ supercell. The total potential energies fluctuate around constant values, as plotted in Fig. 1c, confirming that the penta-PbN₈ sheet is thermally stable at high temperatures up to 700 K. To study the mechanical stability properties of the penta-PbN₈ sheet, we calculated the stiffness tensor components, C_{ij} ($i, j = 1, 2, 6$) using the finite distortion method.⁴⁵ The independent elastic constants are $C_{11} = 79.48$, $C_{22} = 34.91$, $C_{66} = 0.27$, $C_{12} = 70.05$, $C_{16} = 0.29$, and $C_{26} = 0.24$ N m^{−1}, which satisfy the Born–Huang criteria for a monoclinic 2D material.⁴⁶ Therefore, the penta-PbN₈ sheet is mechanically stable. Additional information about the calculation of stiffness tensor components can be found in the ESI.†

3.2 Lattice thermal conductivity from phonon scattering

To study the lattice thermal transport properties of the penta-PbN₈ sheet, we calculated its lattice thermal conductivity κ_L within the unified theory of thermal transport^{28,35} by including the contributions from both phonon scattering and phonon coherence. κ_L shows an increasing trend with temperature as shown in Fig. 2a, which is similar to the trend observed in previously reported studies on Ag₈SnS₆⁴⁷ and bilayer twisted penta-NiN₂.¹⁸ κ_L is found to be 4.61 W m^{−1} K^{−1} along the x -direction and 5.23 W m^{−1} K^{−1} along the y -direction at 300 K. These values are quite low compared to those of some other penta-sheets, as listed in Table 1. For instance, the lattice thermal conductivities of the type-2 sheets, penta-SiC₂ and penta-SiN₂, are 101 and 185 W m^{−1} K^{−1}, respectively.⁴⁸ Moreover, the lattice thermal conductivity of penta-PbN₈ is anisotropic, which can be understood from the different group

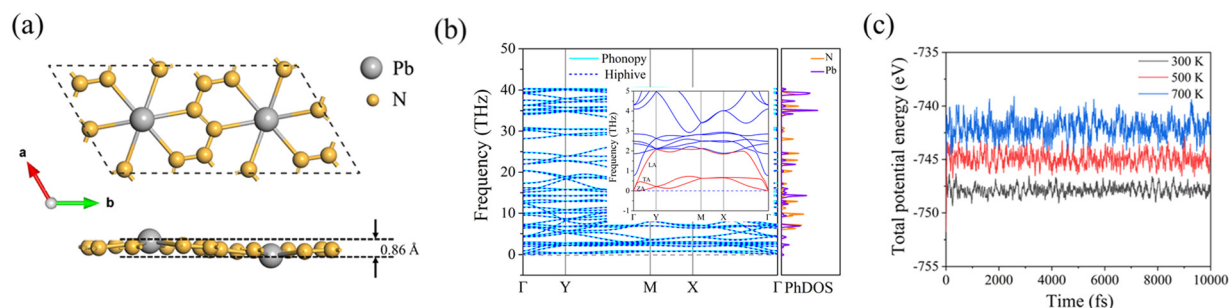


Fig. 1 (a) Top and side views of the optimized crystal structure, (b) phonon spectra, and (c) potential energy fluctuation during the AIMD simulations at 300, 500, and 700 K of the penta-PbN₈ sheet.

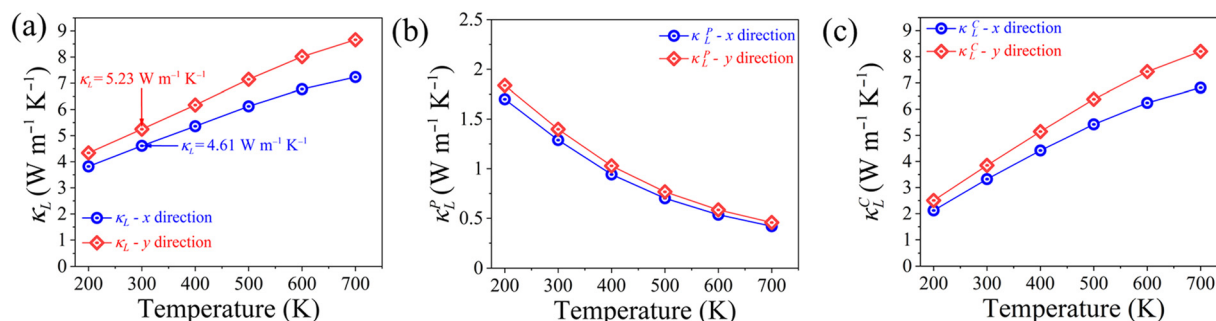


Fig. 2 (a) Total lattice thermal conductivity (κ_L), (b) particle-like contribution (κ_L^P), and (c) phonon coherence contribution (κ_L^C) of the penta-PbN₈ sheet.

Table 1 Comparison of the lattice thermal conductivity κ_L (W m⁻¹ K⁻¹) of penta-PbN₈ with that of some other pentagonal sheets

Tiling type	$\kappa_L = \kappa_L^P + \kappa_L^C$	Ref.
Type-5: penta-PbN ₈	4.61 (5.23)	This work
Type-2: penta-PtPSe	9.00	49
Type-2: penta-PdPTe	23.00	50

velocities in the x and y directions as indicated in Fig. S4 in the ESI† Fig. S5 (ESI†) shows the Grüneisen parameter as a function of frequency within the first Brillouin zone of penta-PbN₈. The mode Grüneisen parameter (γ) can be used to measure the strength of the scattering rates and qualitatively characterize the anharmonicity of lattice vibrations. A larger $|\gamma|$ implies a stronger anharmonicity and a lower lattice thermal conductivity. We calculated γ by using $\gamma = (A/\omega_\lambda)(\partial\omega_\lambda/\partial A)$, where A is the volume of the cell and ω_λ is the angular frequency. Large $|\gamma|$ is found in penta-PbN₈, showing strong anharmonicity. The significant mass difference between Pb and N atoms, together with the large atomic mass of Pb, may result in stronger lattice anharmonicity, which leads to enhanced phonon scattering, particularly at higher temperatures, and further facilitates phonon coherence, contributing to thermal conductivity behavior.

We then analyzed the lattice thermal conductivity contributed by phonon scattering (κ_L^P) and phonon coherence. Fig. 2b

and c show the coexistence of κ_L^P and κ_L^C , showing that the dominant transport mechanism depends on temperature. While κ_L^P significantly decreases with increasing temperature, κ_L^C shows an opposite trend. As shown in Fig. 2b, at 300 K, κ_L^P is 1.29 W m⁻¹ K⁻¹ along the x -direction and 1.39 W m⁻¹ K⁻¹ in the y -direction, which decreases with temperature due to the increased scattering rates.

We further studied the high-order phonon scattering processes and the phonon group velocities to understand the origin of the low contribution of particle-like phonon scattering to lattice thermal conductivity. The intrinsic three- and four-phonon scattering rates at 300 K are plotted in Fig. 3a, the blue points for three-phonon scattering only, while red points for including both three- and four-phonon scattering, resulting in higher scattering rates, especially in the mid-to-high frequency range (above ~20 THz) indicating the increased anharmonic interactions. When only three-phonon scattering is considered, the rates are noticeably lower, reflecting fewer anharmonic interactions and longer phonon lifetimes, which leads to enhanced propagation contributions to thermal transport and weaker phonon coherence. In contrast, the inclusion of four-phonon scattering further limits phonon lifetimes and reduces thermal transport efficiency. We further investigate the effect of different scattering mechanisms on the lattice thermal conductivity by comparing their results for three-phonon scattering. As shown in Fig. S6 (ESI†), the lattice thermal conductivity obtained from three-phonon scattering

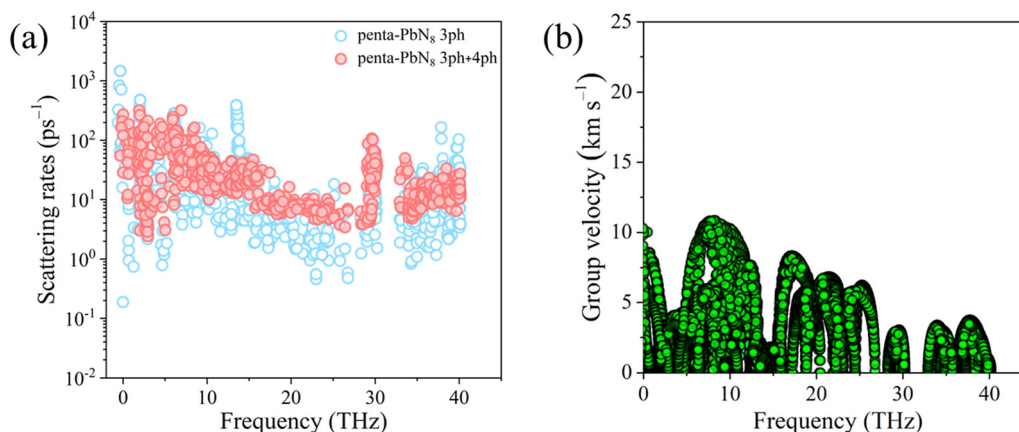


Fig. 3 (a) Phonon scattering rates of three- and four-phonon contributions, and (b) group velocity with frequency.

alone is higher than that obtained from including both three- and four-phonon scattering. As shown in Fig. 2a, incorporating both three- and four-phonon scattering significantly reduces the thermal conductivity. When only three-phonon scattering is considered, the lower phonon scattering rate restricts phonon coherence, resulting in lower coherent thermal conductivity. In contrast, when both three- and four-phonon scattering are considered, the enhanced scattering improves phonon coherence, as shown in Fig. 2c, leading to more efficient coherent thermal transport, particularly at higher temperatures. In addition, as shown in Fig. 3b, penta-PbN₈ exhibits low phonon group velocities with a maximum velocity of only 10.80 km s⁻¹, much less than that of penta-graphene (17.17 km s⁻¹).⁵¹ These results suggest that the relatively large size of Pb weakens the Pb–N bond as compared to the C–C and C–N bonds, which leads to low group velocity and high scattering rates, resulting in ultralow κ_L^p .

3.3 Lattice thermal conductivity from phonon coherence

To study the phonon coherence contribution to κ_L in penta-PbN₈, we calculated κ_L^C at different temperatures based on the phonon coherence equation⁴² coded by ourselves. Fig. 2c shows κ_L^C at different temperatures. The strong intrinsic phonon coherence leads to a large κ_L^C value of 3.32 W m⁻¹ K⁻¹ in the *x*-direction and 3.84 W m⁻¹ K⁻¹ in the *y*-direction at 300 K, making κ_L^C dominate the total lattice thermal conductivity. The intrinsic phonon coherence is particularly strong in penta-PbN₈, which results in a notable temperature dependence in the lattice thermal conductivity. As depicted in Fig. 2c, κ_L^C shows a clear increase with temperature, similar to the situation observed previously in systems like bilayer penta-NiN₂ with dominant phonon coherence.¹⁸ As temperature increases, phonon coherence can enhance thermal

conductivity by reducing phonon scattering, leading to a sharp increase in the phonon coherence. This effect is particularly noticeable for phonon modes with small frequency intervals, where the dephasing rate is reduced, and coherence time is prolonged and coherence is enhanced. The substantial difference between the *x*- and *y*-directions suggests the directional dependence of phonon coherence, which is influenced by the anisotropic nature of the material's phonon modes. Additionally, as shown in Fig. 1b, there is a high degree of overlap between the acoustic and optical branches, particularly in the frequency range below 4 THz. This results in a very narrow average frequency interval between phonons, which significantly influences phonon scattering processes. Due to the strong intrinsic anharmonicity and the reduced frequency intervals, the phonons in penta-PbN₈ experience less scattering and thus maintain phase coherence over longer distances. This enhanced phonon coherence across the entire temperature range substantially contributes to the material's overall thermal conductivity. Additionally, the phonon mean free path of penta-PbN₈ at 300 K is considerably low, as shown in Fig. S7 (ESI†). The mean free paths of many phonon modes are even shorter than the average bond length. To better illustrate the contributions to the lattice thermal conductivity, we present the relationship between the phonon lifetimes and the Ioffe–Regel limit ($1/\omega$). Several phonon modes in penta-PbN₈ fall below the Ioffe–Regel limit, indicating that these modes contribute significantly to phonon coherence.

To determine the precise contributions of coherent phonon modes across various frequency ranges, we analyse the two-mode-dependent contributions to the coherence thermal conductivity κ_L^C of the penta-PbN₈ sheet. Fig. 4a–d illustrate the involvement of degenerate and non-degenerate eigenstates across different temperature ranges, showing that the contributions from the

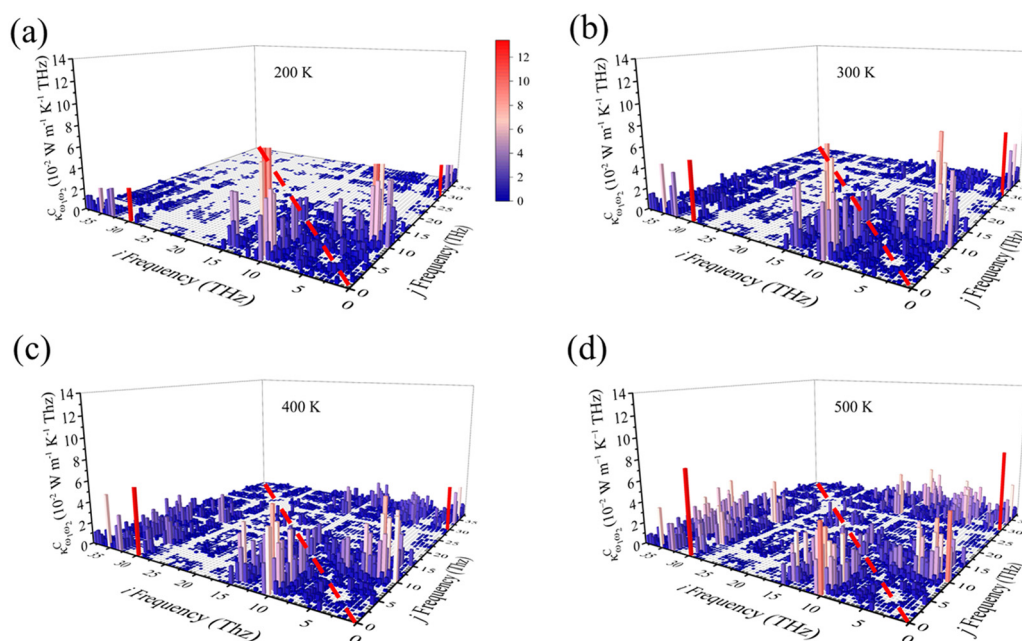


Fig. 4 (a)–(d) Two-mode-dependent contributions to κ_L^C versus the coupling phonon frequencies ω_1 and ω_2 at temperatures from 200 to 500 K, respectively, in the penta-PbN₈ sheet.

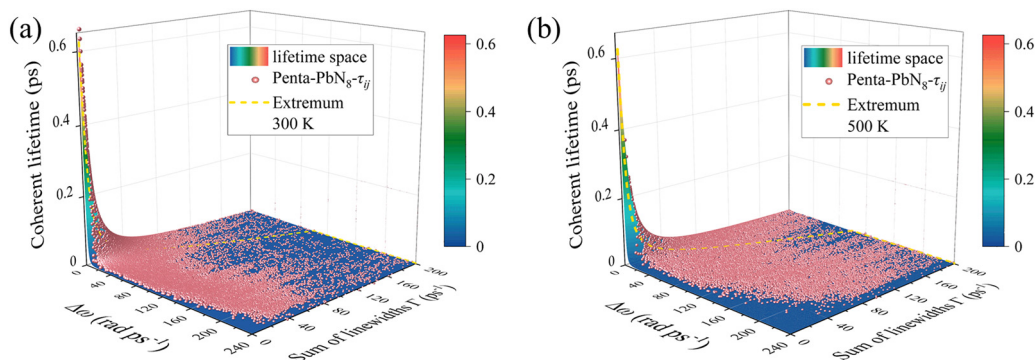


Fig. 5 (a) and (b) Generalized coherent lifetime τ_{ij} distribution at 300 and 500 K. The dashed yellow lines represent the extremum value of τ_{ij} at the same $\Delta\omega$.

non-degenerate modes ($\omega_1 \neq \omega_2$) are dominant, while the degenerate modes ($\omega_1 = \omega_2$) seldom contribute to κ_L^P , as marked by the red dashed lines in Fig. 4a–d. The eigenstates with non-degenerate energy levels exhibit sufficient scattering rates, leading to the dominance in κ_L^C . It is worth mentioning that phonons coupled with frequencies below 14.50 THz significantly contribute to the overall coherent thermal transport at 300 K, while the coherent contributions in the high-frequency range show a monotonic temperature dependence and become dominant at 500 K. According to eqn (5), the lifetimes of the coherent phonon modes are determined by the scattering rates and frequency intervals. The scattering rates increase rapidly with temperature, as shown in Fig. S8 in the ESI,[†] which would result in contributions from the high optical modes coupled with the low-frequency phonons to exhibit dominance at high temperatures, leading to the monotonic changes with temperature in the coherent thermal transport. To illustrate the mechanism of this temperature dependence of κ_L^C , we then discussed the coherent lifetime τ_{ij} at different temperatures.

3.4 Coherent lifetime and the frequency interval of coherent phonon modes

To present the significant impact of generalized coherent lifetime (τ_{ij}) on the coherent lattice thermal conductivity, we depicted the distribution of τ_{ij} in the coherent lifetime space in Fig. 5a and b. At both 300 and 500 K, τ_{ij} is higher in the region with low-frequency intervals ($\Delta\omega = 0$ to 40 rad ps^{−1}), which suggests that the long lifetime of coherent phonon modes with smaller $\Delta\omega$ is crucial for coherent thermal conductivity. This alignment is influenced by the small $\Delta\omega$ values (close to 0 rad ps^{−1}) in this sheet, which are associated with low-frequency phonons that tend to maintain coherence for longer periods. Meanwhile, τ_{ij} of the coherent modes with lower $\Delta\omega$ decreases with increasing temperature, which leads to the decrease in the contributions from low-frequency modes. In Fig. 5a, the distribution of τ_{ij} at 300 K shows higher values of τ_{ij} (up to 0.6 ps) that are less concentrated around the extremum values marked by the yellow dashed line, especially in the region with large $\Delta\omega$. This more extensive distribution implies that different phonon states, both degenerate and non-degenerate, contribute significantly to the coherent thermal

conductivity at lower temperature. Conversely, in Fig. 5b, τ_{ij} at 500 K is more concentrated around the extremum, displaying higher absolute values. This comparison highlights that higher temperature can enhance the phonon scattering, particularly for coupling phonons with higher $\Delta\omega$ resulting in larger coherent lifetimes, thus enhancing κ_L^C . The overall enhancement in τ_{ij} increases the contribution of coherent phonons to thermal conductivity as shown in Fig. S9 (ESI[†]).

4. Conclusions

In summary, our study focuses on the thermal transport properties of the penta-PbN₈ sheet that has the largest atomic mass difference in the recently reported type-5 pentagonal tiling pattern family. It is due to the large atomic mass difference and the unique geometric structure that penta-PbN₈ possesses strong anharmonicity. This not only enhances the 3-phonon and 4-phonon scattering to suppress the particle-like contributions, resulting in the low κ_L^P values of 1.29 W m^{−1} K^{−1} in the x-direction and 1.39 W m^{−1} K^{−1} in the y-direction but also significantly boosts the phonon coherence with the long coherent lifetime, leading to the much larger κ_L^C value of 3.32 (3.84) W m^{−1} K^{−1} in the x(y)-direction at 300 K. The total lattice thermal conductivity of penta-PbN₈ is found to be 4.61 (5.23) W m^{−1} K^{−1} in the x(y)-direction, which is indeed very low as compared to that of other penta-sheets. Our work clearly demonstrates a principle in the design of materials with low lattice thermal conductivity, namely, reducing the atomic mass differences between constituent atoms to suppress the phonon coherence.

Data availability

Data generated or analyzed during this study are available from the corresponding author upon reasonable request.

Conflicts of interest

The authors declare no conflict of interest.

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References

- 1 S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe and P. Jena, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 2372–2377.
- 2 M. A. Nazir, A. Hassan, Y. Shen and Q. Wang, *Nano Today*, 2022, **44**, 101501.
- 3 Y. Shen and Q. Wang, *Phys. Rep.*, 2022, **964**, 1–42.
- 4 A. D. Oyedele, S. Yang, L. Liang, A. A. Poretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A. W. Ghosh and Z. Liu, *J. Am. Chem. Soc.*, 2017, **139**, 14090–14097.
- 5 W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. H. Hsu, C. Zhu, J. Zhou and X. Wang, *Adv. Mater.*, 2017, **29**, 1602969.
- 6 X. Zhang, G. Su, J. Lu, W. Yang, W. Zhuang, K. Han, X. Wang, Y. Wan, X. Yu and P. Yang, *ACS Appl. Mater. Interfaces*, 2021, **13**, 43063–43074.
- 7 M. Bykov, E. Bykova, A. V. Ponomareva, F. Tasnadi, S. Chariton, V. B. Prakapenka, K. Glazyrin, J. S. Smith, M. F. Mahmood and I. A. Abrikosov, *ACS Nano*, 2021, **15**, 13539–13546.
- 8 Y. Wang, Y. Li and Z. Chen, *J. Mater. Chem. C*, 2015, **3**, 9603–9608.
- 9 J.-H. Yuan, Y.-Q. Song, Q. Chen, K.-H. Xue and X.-S. Miao, *Appl. Surf. Sci.*, 2019, **469**, 456–462.
- 10 Z. Cheng, X. Zhang, H. Zhang, H. Liu, X. Yu, X. Dai, G. Liu and G. Chen, *Nanoscale*, 2022, **14**, 2041–2051.
- 11 Y. Shen, Y. Guo and Q. Wang, *Adv. Theory Simul.*, 2020, **3**, 2000027.
- 12 C. Hou, Y. Shen, Q. Wang, Y. Kawazoe and P. Jena, *J. Mater. Chem. A*, 2023, **11**, 167–177.
- 13 W. Sun, Y. Shen, Y. Guo, Y. Chen and Q. Wang, *Appl. Surf. Sci.*, 2021, **554**, 149499.
- 14 C. Hou, Y. Shen, W. Sun, Y. Chen, D. Ni and Q. Wang, *J. Mater. Chem. C*, 2022, **10**, 10302–10309.
- 15 K. Zhao, Y. Guo, Y. Shen, Q. Wang, Y. Kawazoe and P. Jena, *J. Phys. Chem. Lett.*, 2020, **11**, 3501–3506.
- 16 C. Zhang, J. Sun, Y. Shen, W. Kang and Q. Wang, *J. Phys. Chem. Lett.*, 2022, **13**, 5734–5741.
- 17 Y. Chen, C. Zhang, J. Sun, D. Ni, C. Zhang and Q. Wang, *Appl. Surf. Sci.*, 2023, **635**, 157718.
- 18 C. Zhang, J. Sun, Y. Shen, C. Zhang, Q. Wang, A. Yoshikawa, Y. Kawazoe and P. Jena, *Small*, 2023, **19**, 2303295.
- 19 Y.-S. Lan, X.-R. Chen, C.-E. Hu, Y. Cheng and Q.-F. Chen, *J. Mater. Chem. A*, 2019, **7**, 11134–11142.
- 20 Y. Shen, J. Sun, Y. Chen, D. Ni, T. Li, A. Yoshikawa, Y. Kawazoe and Q. Wang, *J. Mater. Chem. A*, 2022, **10**, 21356–21367.
- 21 M. Long, Y. Wang, P. Wang, X. Zhou, H. Xia, C. Luo, S. Huang, G. Zhang, H. Yan and Z. Fan, *ACS Nano*, 2019, **13**, 2511–2519.
- 22 A. M. Afzal, G. Dastgeer, M. Z. Iqbal, P. Gautam and M. M. Faisal, *ACS Appl. Mater. Interfaces*, 2020, **12**, 19625–19634.
- 23 J.-L. Fan, X.-F. Hu, W.-W. Qin, Z.-Y. Liu, Y.-S. Liu, S.-J. Gao, L.-P. Tan, J.-L. Yang, L.-B. Luo and W. Zhang, *Nanoscale*, 2022, **14**, 13204–13213.
- 24 F. Shojaei, J. R. Hahn and H. S. Kang, *J. Mater. Chem. A*, 2017, **5**, 22146–22155.
- 25 Y. Shen, C. Zhang and Q. Wang, *J. Phys. Chem. Lett.*, 2023, **14**, 8734–8740.
- 26 P.-H. Du, D. Ni, Y. Shen, J. Cheng, C. Hou and Q. Sun, *Mater. Today Phys.*, 2023, **38**, 101259.
- 27 P. Tangpakonsab, P. Moontragoon, T. Hussain and T. Kaewmaraya, *ACS Appl. Energy Mater.*, 2022, **5**, 14522–14530.
- 28 M. Simoncelli, N. Marzari and F. Mauri, *Nat. Phys.*, 2019, **15**, 809–813.
- 29 G. Kresse and J. Furthmüller, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, **54**, 11169.
- 30 P. E. Blöchl, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953.
- 31 G. Kresse and D. Joubert, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1999, **59**, 1758.
- 32 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 33 L. Isaeva, G. Barbalinardo, D. Donadio and S. Baroni, *Nat. Commun.*, 2019, **10**, 3853.
- 34 A. Jain, *Phys. Rev. B*, 2020, **102**, 201201.
- 35 M. Simoncelli, N. Marzari and F. Mauri, *Phys. Rev. X*, 2022, **12**, 041011.
- 36 M. Omini and A. Sparavigna, *Phys. B*, 1995, **212**, 101–112.
- 37 Z. Han, X. Yang, W. Li, T. Feng and X. Ruan, *Comput. Phys. Commun.*, 2022, **270**, 108179.
- 38 A. Togo and I. Tanaka, *Scr. Mater.*, 2015, **108**, 1–5.
- 39 F. Eriksson, E. Fransson and P. Erhart, *Adv. Theory Simul.*, 2019, **2**, 1800184.
- 40 X. Wu, V. Varshney, J. Lee, Y. Pang, A. K. Roy and T. Luo, *Chem. Phys. Lett.*, 2017, **669**, 233–237.
- 41 Z. Sun, K. Yuan, X. Zhang, G. Qin, X. Gong and D. Tang, *Phys. Chem. Chem. Phys.*, 2019, **21**, 15647–15655.
- 42 R. Hanus, J. George, M. Wood, A. Bonkowski, Y. Cheng, D. L. Abernathy, M. E. Manley, G. Hautier, G. J. Snyder and R. P. Hermann, *Mater. Today Phys.*, 2021, **18**, 100344.
- 43 P. Gray and T. C. Waddington, *Nature*, 1955, **176**, 653.
- 44 L. D. Whalley, J. M. Skelton, J. M. Frost and A. Walsh, *Phys. Rev. B*, 2016, **94**, 220301.
- 45 H. Şahin, S. Cahangirov, M. Topsakal, E. Bekaroglu, E. Akturk, R. T. Senger and S. Ciraci, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2009, **80**, 155453.
- 46 Y. Le Page and P. Saxe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 104104.
- 47 N. Ouyang, D. Shen, C. Wang, R. Cheng, Q. Wang and Y. Chen, *Phys. Rev. B*, 2025, **111**, 064307.
- 48 H. Liu, G. Qin, Y. Lin and M. Hu, *Nano Lett.*, 2016, **16**, 3831–3842.
- 49 H. Huang, W. Li, C. Hu and X. Fan, *J. Mater. Chem. C*, 2023, **11**, 9449–9464.
- 50 B. Mortazavi, M. Shahrokhi, X. Zhuang, T. Rabczuk and A. V. Shapeev, *J. Mater. Chem. C*, 2022, **10**, 329–336.
- 51 F. Q. Wang, J. Yu, Q. Wang, Y. Kawazoe and P. Jena, *Carbon*, 2016, **105**, 424–429.