Anomalous thermal transport behavior in graphene-like carbon nitride (C$_3$N)

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The graphene’s success created a new era in materials science, especially for two-dimensional (2D) materials. New classes 2D carbon-based materials beyond graphene have been intensively studied for their promising applications in nano-/opto-/spin-electronics, catalysis, sensors, clean energy, etc. Very recently, the controllable large-scale synthesis of 2D single crystalline carbon nitride (C$_3$N) was reported, which is the first and the only crystalline, hole-free, single-layer carbon nitride. Due to the fascinating properties, monolayer C$_3$N attracts tremendous interest for the potential applications in various fields, where thermal transport property is severely concerned for developing high performance devices in terms of advanced thermal management, which, however, remain less investigated. Here, we perform a comparative study of thermal transport between monolayer C$_3$N and the parent graphene, by solving the phonon Boltzmann transport equation (BTE) based on first-principles calculations. The thermal conductivity ($\kappa$) of C$_3$N shows an anomalous temperature dependence, which is totally different from that for common crystalline materials and deviates largely from the well-known $\kappa \sim 1/T$ relationship. Consequently, the $\kappa$ of C$_3$N at high temperatures is larger than the expected value following the common trend of $\kappa \sim 1/T$. Moreover, the $\kappa$ of C$_3$N is found in surprise to be enlarged by applying bilateral tensile strain, despite its similar planar honeycomb structure as graphene, whose $\kappa$ is reduced upon stretching. Thus, it would benefit the applications of C$_3$N in nano- and opto-electronics in terms of efficient heat dissipation, considering the unexpectedly large $\kappa$ at high working temperature or under realistic conditions where residual strain usually exists after fabrication or synthesis. The underlying mechanism is revealed by providing direct evidence for the interaction between lone-pair N-e electrons and bonding electrons from C atoms in C$_3$N based on the analysis of orbital-projected electronic structures and electron localization function (ELF). Our study not only make a comprehensive investigation of the thermal transport in graphene-like C$_3$N, but also reveals the physical origins for its anomalous properties, which deepens the understanding of phonon transport in 2D materials and would also have great impact on future research in micro-/nanoscale thermal transport such as materials design with targeted thermal transport properties.

1. INTRODUCTION

Graphene, an atomically thin two-dimensional (2D) material with honeycomb lattice structure, exhibits numerous striking physical properties, and can, in principle, be considered as an elementary building block for various carbon allotropes. Ever since the recent developments in 2004, the field of graphene research took off rapidly. These developments in the science of graphene prompted an unprecedented surge of activity and demonstration of new physical phenomena with novel applications such as nanoelectronics, energy storage and conversion, medicine, catalysis, sensors, etc. Graphene has lots of excellent properties such as the surprisingly large room-temperature electron mobility, high strength and flexibility, and record high thermal conductivity. However, attempts to utilize graphene for practical applications are faced with some limitations, especially the poor on-off current ratio ($I_{ON}/I_{OFF} < 100$) in graphene-based devices due to the gapless nature of graphene. Thus, the substitutions of carbon (C) atom in graphene with heteroatoms were stimulated for the extension of graphene family to other 2D layered crystalline materials. Among these, monolayer hexagonal boron nitride (h-BN) with a wide band gap ($\sim$5.0-6.0 eV) offers an alternative solution beyond the gapless graphene, which establishes the key role of 2D nitrides in advancing the development of next generation nano-electronics. To benefit from carbon-based nanomaterials at the same time, partially substituting C atoms in graphene with N is a plausible approach to the formation of graphene-like 2D carbon nitrides. In the past years, different N/C ratios have been realized. For example, 2D crystalline layered C$_3$N$_4$ and C$_2$N-h2D are semiconductors with direct bandgaps of 2.76 and 1.96 eV, respectively, with potential applications in nanoelectronics, photo-catalysis, solar power generation, etc. However, large number of holes exist...
in the crystalline structures due to the large N/C ratios. Very recently, Yang et al.\textsuperscript{[23]} reported the controllable large-scale (up to hundreds of micrometer) synthesis of 2D single crystalline carbon nitride (C\textsubscript{3}N) sheet, which is the first and the only crystalline, hole-free, single-layer carbon nitride, showing graphene-like morphology (Fig. 1).

Monolayer C\textsubscript{3}N possesses the graphene-like planar honeycomb structure with a homogeneous distribution of C and N atoms, both of which show the D\textsubscript{6h}-symmetry\textsuperscript{[19]}. Despite various 2D carbon-based materials, C\textsubscript{3}N is the only one possessing indirect bandgap, which is 0.39 eV as verified both experimentally and theoretically and can be tuned to cover the entire visible range.\textsuperscript{[19]} Back-gated field-effect transistors (FET) made of monolayer C\textsubscript{3}N display an on-off current ratio reaching 5.5×10\textsuperscript{10}, which is much larger than those of graphene (< 10\textsuperscript{2}), C\textsubscript{2}N (10\textsuperscript{7}), and phosphorene (∼ 10\textsuperscript{3}).\textsuperscript{[22]} Moreover, C\textsubscript{3}N hydrogenated with a sufficient amount of hydrogen shows spontaneous magnetism (ferromagnetic, FM) at temperatures lower than 96 K. Considering almost all the novel applications of C\textsubscript{3}N in nanoelectronics are inevitably involved with heat dissipation, the thermal transport properties are of great interest for developing high performance C\textsubscript{3}N-based devices in terms of efficient thermal management.

Efficient regulation of heat transfer plays a key role in the high-performance thermal management of nanotechnologies. The heat conduction in semiconductors is mainly carried out by phonon transport\textsuperscript{[11]}. Therefore, the fundamental understanding of phonon transport is of great significance for the effective control of heat flow, and it is a thermophysical problem that has great practical significance related to energy technology, such as electrical cooling, thermoelectric technology, phase change storage\textsuperscript{[13]} thermal devices (diodes, transistors, logic gates)\textsuperscript{[15]}. In the past few decades, lots of studies have focused on the effective regulation of heat transport by nanostructuring\textsuperscript{[19]}. Besides, pores are introduced into the physicochemical treatment (hydrogenation, oxidation, etc.)\textsuperscript{[22]}. In addition, effective thermal modulation can also be achieved by external electric/magnetic field\textsuperscript{[23]} and strain engineering\textsuperscript{[24]}. Due to the robust reliability and strong flexibility, strain engineering has become one of the most promising and effective ways to achieve continuously adjustable heat transport. Moreover, the actual case of many systems and devices typically contain residual strain after fabrication\textsuperscript{[27]}. Therefore, the study of strain engineering on the regulation of thermal conductivity has a very important practical significance. However, previous studies have mainly focused on how to adjust thermal conductivity through mechanical strain, and there is still a lot of unclear understanding of the essential origin of its regulatory effect\textsuperscript{[21,22,24,31]}. These in-depth understanding benefits more effective and accurate thermal conductivity regulation, which would have a far-reaching guiding role. Thus, the modulation of the thermal transport properties of monolayer C\textsubscript{3}N by mechanical strain could be practically meaningful, and the origin of the underlying mechanism would deepen our understanding of phonon transport in 2D materials and have great impact on future research in materials design with targeted thermal transport properties.

In this paper, by solving the phonon Boltzmann transport equation (BTE) based on first-principles calculations, we perform a comparative study of phonon transport between monolayer C\textsubscript{3}N and graphene. Besides the anomalous temperature dependence of \(\kappa\) of C\textsubscript{3}N, it is very intriguing to find that the \(\kappa\) of C\textsubscript{3}N is more than one order of magnitude lower than graphene, considering the similar structures and the only difference of substituting 1/4 C with N atoms in C\textsubscript{3}N compared to graphene. By deeply analyzing the orbital projected electronic structure, we establish a microscopic picture of the lone-pair electrons driving strong phonon anharmonicity. We show that nonlinear restoring forces arise from the interactions between lone-pair electrons around N atoms and bonding electrons from adjacent atoms (C), leading to strong phonon anharmonicity and low \(\kappa\). Furthermore, the \(\kappa\) of C\textsubscript{3}N is unexpectedly enlarged by applying bilateral tensile strain despite the planar honeycomb structure of C\textsubscript{3}N (similar to graphene, with no buckling or puckering), which is in sharp contrast to the strain induced \(\kappa\) reduction in graphene. The opposite response of \(\kappa\) to mechanical strain between C\textsubscript{3}N and graphene further supports the established microscopic picture of the lone-pair electrons driving strong phonon anharmonicity.

2. METHODS

All the first-principles calculations are performed in the framework of density functional theory (DFT) using the projector augmented wave (PAW) method\textsuperscript{[32]} as implemented in the Vienna \textit{ab initio} simulation package (\textsc{VASP})\textsuperscript{[33]}. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) revised for solids (PBEsol)\textsuperscript{[34]} is chosen as the exchange-correlation
The kinetic energy cutoff of wave functions is set as 1000 eV and a Monkhorst-Pack $k$-mesh of $31 \times 31 \times 1$ is used to sample the Brillouin Zone (BZ) with the energy convergence threshold of $10^{-6}$ eV, where the $k$ is the electronic wavevector spanned by the reciprocal lattice vectors. A large enough vacuum spacing of 20 Å is used along the out-of-plane direction based on the convergence test. The applied biaxial strain is defined as $(l - l_0)/l_0$, where $l$ is the lattice constant under strains and $l_0$ corresponds to the original value with no strain applied. All geometries are fully optimized based on the primitive cell containing 8 atoms (6 C and 2 N) in which both C and N are calculated to be slightly different (1.40326 and 1.40288 Å, respectively). Based on the optimized structure, different from the buckled silicene and the puckered phosphorene, with the primitive cell containing 72 atoms is constructed and the Monkhorst-Pack $k$-mesh of $2 \times 2 \times 1$ is used to sample the BZ, which can accurately describe the system based on the convergence test. The space group symmetry properties are used to reduce the computational cost and the numerical noise of the forces. The translational and rotational invariance of IFCs are enforced using the Lagrange multiplier method. The Born effective charges ($Z^*$) and dielectric constants ($\epsilon$) are obtained based on the density functional perturbation theory (DFPT), which are added to the dynamical matrix as a correction to take long-range electrostatic interaction into account. Based on kinetic theory, $\kappa$ can be expressed as:

$$\kappa_\alpha = \sum_{\vec{q},p} C_V(\vec{q},p)\tilde{v}_\alpha(\vec{q},p)^2\tau(\vec{q},p),$$

where $C_V$ is the volumetric specific heat capacity of phonon following the Bose-Einstein statistics, $\tilde{v}_\alpha(\vec{q},p)$ is the $\alpha(=x,y,z)$ component of group velocity of phonon mode with wave vector $\vec{q}$ and polarization $p$, and $\tau$ is the relaxation time (phonon lifetime). The $\kappa$ is obtained by iteratively solving the phonon BTE with the ShengBTE package, which is equivalent to the solution of relaxation time approximation (RTA) if the iteration stops at the first step. The convergence test of $\kappa$ with respect to the cutoff distance and $Q$-grid are fully conducted based on which the cutoff distance is chosen as 7.36 Å (13th nearest neighbors) for the 3rd IFCs calculations and the $Q$-grid is chosen as $50 \times 50 \times 1$ for the $\kappa$ calculations. The $\kappa$ of graphene is calculated to be 3094.98 W/mK by using the iterative method. The good agreement with previous results confirms the reliability of our calculation.

### 3. STRUCTURE AND PHONON DISPERSION

Up to now, monolayer $\mathrm{C}_3\mathrm{N}$ is the only crystalline, hole-free, single-layer carbon nitride, which shows graphene-like morphology. $\mathrm{C}_3\mathrm{N}$ possesses a planar honeycomb structure, different from the buckled silicene and the puckered phosphorene, with the primitive cell containing 8 atoms (6 C and 2 N), in which both C and N atoms show a $D_{6h}$-symmetry. The optimized lattice constant of $\mathrm{C}_3\mathrm{N}$ is 4.86 Å. The C-C and C-N bond lengths in $\mathrm{C}_3\mathrm{N}$ are calculated to be slightly different (1.40326 and 1.40288 Å, respectively). Based on the optimized structure, we calculate the phonon dispersions and partial density of states (pDOS) of $\mathrm{C}_3\mathrm{N}$ [Fig. 2(a)]. No imaginary frequency is observed, indicating the thermodynamical stability of monolayer $\mathrm{C}_3\mathrm{N}$. The results of graphene are also plotted for comparison, which are calculated with the supercell of $2 \times 2 \times 1$ (i.e. 8 atoms, the same as $\mathrm{C}_3\mathrm{N}$)
used as the unit cell. We also plot the results of graphene with primitive cell (2 atoms) to give a hint. The flexural acoustic (FA) phonon branches ($z$-direction vibration) of both C$_3$N and graphene show the quadratic behavior, which is the typical feature of 2D materials\cite{43} and is also observed in silicene and phosphorene\cite{49,50}. The phonon dispersions of C$_3$N and graphene are highly consistent, especially for the longitudinal and transverse acoustic phonon branches. However, the FA phonon branch of C$_3$N is significantly softened (lower frequency and smaller group velocity) compared to graphene, which suggests possibly strong phonon anharmonicity.

Usually, the strength of the phonon anharmonicity can be quantified by the Grüneisen parameter, which characterizes the relationship between phonon frequency and crystal volume change. Thus, we further calculate the Grüneisen parameters of C$_3$N and graphene [Fig. 2(b)] to quantitatively assess the phonon anharmonicity. The magnitude of the Grüneisen parameters of C$_3$N are very large compared to graphene, especially for the FA phonon branch, confirming stronger phonon anharmonicity in C$_3$N. Considering the similar structures and the only difference of substituting 1/4 C with N atoms in C$_3$N compared to graphene, it is very intriguing to find the significantly softened FA phonon branch and strong phonon anharmonicity in C$_3$N. We will show later the electronic origin of the orbital driven strong phonon anharmonicity and the anomalous large magnitude of Grüneisen parameter in C$_3$N. As it is known that strong phonon anharmonicity can give rise to low $\kappa$ in ordered crystal structures, we would further study the thermal transport properties of C$_3$N.

4. THERMAL TRANSPORT PROPERTIES

Fig. 3 shows the temperature dependent $\kappa$ of C$_3$N obtained by iteratively solving the phonon BTE together with the results from RTA method, in comparison with graphene. The room temperature $\kappa$ of C$_3$N is 103.02 W/mK, which is more than one order of magnitude lower than that of graphene (3094.98 W/mK). Note that Mortazavi\cite{49} reported a rather high $\kappa$ of C$_3$N (815 W/mK) based on the classical non-equilibrium molecular dynamics (MD) simulations, where the optimized Tersoff and original Tersoff potentials are used to describe the C-C and C-N interatomic interactions, respectively. Considering that classical MD simulation suffers from the accuracy of the empirical potential used\cite{52}, the discrepancy of the $\kappa$ between ours and Mortazavi et al.’s could be attributed to the different computational methods employed (first-principles vs. empirical potential).

For example, the C-C and C-N bond lengths in C$_3$N are calculated to be 1.44 and 1.43 Å in classical MD simulations, respectively\cite{49}, which also differ quite largely from the results by first-principles (1.40326 and 1.40288 Å, respectively). The $\kappa$ of C$_3$N obtained from the RTA method is very close to the accurate value obtained by iteratively solving the phonon BTE, suggesting small proportion of N-process and weak phonon hydrodynamics in C$_3$N. Previous studies showed that the phonon hydrodynamics due to momentum conserving processes is responsible for the ultra-high $\kappa$ of graphene\cite{50,51}. Thus, the weak effect of phonon hydrodynamics in C$_3$N would be responsible for the significantly lower $\kappa$ of C$_3$N compared to graphene. The FA contribution to the room temperature $\kappa$ of C$_3$N is 25.4%, which contributes the most compared to other phonon branches but is not large enough to dominate the phonon transport as the case for graphene (81.2%). More strikingly, as shown in Fig. 3 the $\kappa$ of C$_3$N shows an anomalous temperature dependence, which deviates largely from the well-known $\kappa \sim 1/T$ relation, being quite different from common cases of crystalline material\cite{23,47,48}. In fact, the $\kappa$ of C$_3$N has no considerable change over a large temperature range (200-800 K) due to the anomalous temperature dependence. Consequently, the $\kappa$ of C$_3$N at high temperature is larger than the expected value following the common $\kappa \sim 1/T$ trend, which would largely benefit its applications in nano- and opto-electronics in terms of efficient heat dissipation.

4.1. Anomalous temperature dependence

To understand the underlying mechanism of the anomalous temperature dependence of $\kappa$ of C$_3$N, we compare the frequency accumulated $\kappa$ of C$_3$N and graphene in Fig. 4. For graphene, the main contribution to $\kappa$ is from low-frequency acoustic phonon modes at both low and high temperatures. However, the situation in C$_3$N is quite different from that in graphene. High-frequency
optical phonon modes contribute largely to the $\kappa$ of C$_3$N, especially when the temperature becomes high. It is well-known that the lower the frequency, the lower the required temperature for thermal activation. The low frequency phonon modes can be much more easily thermally activated and already saturate at a lower temperature than the concerned temperatures. Whereas, high temperature is required for the thermal activation of high frequency phonon modes, which just begin to be thermally activated around the concerned temperatures. As revealed in Eq. (1), the temperature dependence of $\kappa$ is the competition between heat capacity and phonon mean free path (MFP) that follows the $\sim 1/T$ law. Thus, the temperature dependence of $\kappa$ contribution from low-frequency phonon modes is dominated by the phonon MFP and decreases with temperature increasing with the relation of $\sim 1/T$. Whereas for high-frequency phonon modes, the variation is dominated by the heat capacity due to its fast increase with the thermal activation and the $\kappa$ contribution increases quickly with temperature increasing, making the temperature dependence of $\kappa$ deviates largely from the well-known $\kappa \sim 1/T$ relation. Hence, the relatively large contribution of high-frequency phonon modes in C$_3$N (Fig. 4) is the direct reason for the anomalous temperature dependence of $\kappa$.

In addition to C$_3$N, the anomalous temperature dependence of $\kappa$ was also found in monolayer gallium nitride (GaN$^{37}$) and zinc oxide (ZnO$^{37}$), where the high-frequency phonon modes also contribute largely to the $\kappa$. It was analyzed that$^{37,38}$ in monolayer GaN and ZnO, the large contribution from high-frequency phonon modes is due to the enhanced phonon group velocity and the relatively large phonon lifetime, which are further traced back to the strongly polarized bond due to the electronegativity and the huge phonon bandgap in the phonon dispersion due to the difference in atom mass. Here, although the electronegativity and the difference in atom mass is not large for C$_3$N, the group velocity of LO phonon branch is still enhanced [Fig. 5(a)] due to the LO-TO splitting caused by the polarization in C-N bond [Inset of Fig. 7(c)]. Besides, the lifetime of high-frequency phonon modes in C$_3$N is relatively large due to the weakened phonon-phonon scattering [Fig. 5(b)] (the scattering rate is comparable to graphene while that of low-frequency phonon modes is much larger) caused by the phonon bunching and flattening [Fig. 2(a)]. Thus, the high-frequency phonon modes contribute largely to the $\kappa$ of C$_3$N (Fig. 4), which results in the anomalous temperature dependence of $\kappa$. It is worth pointing out that, a large difference in atom mass and consequently a huge bandgap in the phonon dispersion as analyzed in previous study$^{37}$ are not necessary for the anomalous temperature dependence of $\kappa$, while phonon bunching and flattening can also have the similar effect.

4.2. Strong phonon anharmonicity and low thermal conductivity

The room temperature $\kappa$ of C$_3$N (103.02 W/mK) is more than one order of magnitude lower than that of graphene (3094.98 W/mK). To gain insight into the mechanisms underlying the significantly lower $\kappa$ of C$_3$N than graphene, we perform detailed mode level phonon analysis. Due to the highly consistent phonon dispersions of C$_3$N and graphene [Fig. 2(a)], their phonon group velocities differ from each other a little, except the FA phonon branch. The phonon group velocity of FA for C$_3$N is much lower compared to other phonon branches and those in graphene [Fig. 2(a)], which is due to the significant softness of FA. The relatively small phonon group velocity of FA in C$_3$N is partially responsible for its relatively smaller contribution to $\kappa$ in C$_3$N (25.4%) than graphene (81.2%). Considering the similar phonon group velocity and the larger specific heat capacity of C$_3$N (18.94×10$^5$ Jm$^{-3}$K$^{-1}$) than graphene (16.19×10$^5$ Jm$^{-3}$K$^{-1}$), the significantly lower $\kappa$ of C$_3$N than graphene must stem from the smaller phonon lifetime (larger scattering rate) based on Eq. (1), which is evidently shown in Fig. 5(b).

It is well-known that the scattering rate is governed by two factors: the scattering phase space and the scattering strength, which quantify how often and how strongly the phonon mode would be scattered, respectively. The scattering phase space is determined based on phonon dispersion only with the criteria of energy and momentum conservation$^{23}$. As shown in Fig. 5(c), the scattering phase space of C$_3$N and graphene are consistent with each other for both the absorption and emission processes. This is understandable in terms of the consistent phonon dispersions of C$_3$N and graphene as shown in Fig. 2(a). Furthermore, we study the mode level Grüneneisen parameter that quantifies the phonon anharmonicity and the
FIG. 5. (Color online) Comparison of mode level (a) phonon group velocity, (b) scattering rate, (c) scattering phase space (absorption and emission process), and (d) Grüneisen parameter between C$_3$N and graphene. The significantly lower $\kappa$ of C$_3$N than that of graphene lies in the larger scattering rate, which is caused by the larger phonon anharmonicity instead of the scattering phase space.

scattering strength. Fig. 5(d) shows consistent results with Fig. 2(b), revealing much stronger phonon anharmonicity in C$_3$N than graphene. The strong phonon anharmonicity in C$_3$N is consistent with the softened FA phonon branch [Fig. 2(a)] as analyzed above. Thus, the significantly lower $\kappa$ of C$_3$N than graphene originates from the large scattering rate [Fig. 5(b)], which is due to the strong phonon anharmonicity [Fig. 2(b) and Fig. 5(d)] rather than the scattering phase space [Fig. 5(c)].

As for the relatively smaller contribution from FA to $\kappa$ for C$_3$N (25.4%) than graphene (81.2%), there are more underlying mechanisms despite the relatively small phonon group velocity of FA in C$_3$N caused by the significant softness of FA. The phonon scattering channels quantifying the specific scattering process among different phonon branches can provide fundamental insight into the phonon scattering process, which are ruled by the conservation of energy and momentum. The scattering rates for emission process are multiplied by 1/2 to avoid counting twice for the same process. As shown in Fig. 6(a), the scattering channels of FA phonon branch for graphene is FA+FA→TA/LA, which is governed by the so-called symmetry-based selection rule of phonon-phonon scattering. Due to the inversion symmetry of the planar structure of graphene, only the scattering channels with participation of even numbers of FA are allowed, leading to limited scattering rate of FA and its dominating role in phonon transport. However, it is totally different in C$_3$N where there exist also narrow scattering channels involving odd number of FA such as FA+O→O and FA+TA/LA→O/TA/LA in addition to the primary scattering channels of FA+FA→TA/LA [Fig. 6(b)]. The extra scattering channels involving odd number of FA reveal the slightly broken inversion symmetry in C$_3$N. The different diameter and mass of C and
FIG. 6. (Color online) Scattering channels of FA phonon modes along the Γ-M direction for (a) graphene and (b) C$_3$N. There exist extra narrow scattering channels involving odd number of FA in C$_3$N.

N atoms reduce the symmetry in C$_3$N by changing the bond lengths or force constants, despite its similar planar structure as graphene. Same situation is also found in monolayer GaN(18). The extra scattering channels for FA [Fig. 6(b)] in C$_3$N together with the relatively small phonon group velocity [Fig. 5(a)] lead to the lower contribution to $\kappa$ from FA (25.4%) compared with that in graphene (81.2%).

5. LONE-PAIR ELECTRONS

Based on the above analysis, there exists strong phonon anharmonicity [Fig. 2(b) and Fig. 5(d)] in C$_3$N, corresponding to the softened FA phonon branch [Fig. 2(a)], which is responsible for the significantly lower $\kappa$ of C$_3$N than graphene (Fig. 3). Considering the similar structures and the only difference of substituting 1/4 C atoms with N in C$_3$N compared to graphene, it is very intriguing to find the significantly softened FA phonon branch, strong phonon anharmonicity, and low $\kappa$ of C$_3$N. To have a bottom-up understanding on the mechanisms underlying the low $\kappa$ of C$_3$N, we further study the strong phonon anharmonicity in C$_3$N based on the fundamental analysis of orbital projected electronic structures. We will show that the stereochemically active lone-pair electrons drive the remarkable phonon anharmonicity in C$_3$N.

In graphene, the C-$s/p_x/p_y$ orbitals hybridize and contribute to the C-C $\sigma$ bonds, while the C-$p_z$ orbital comes into being the $\pi$ bonds and the electronic Dirac cone(17), which are evidently shown in Fig. 7(a). In contrast, the bonding states in C$_3$N are totally different with an intrinsic electronic bandgap. The electronic bandgap is calculated to be 0.39 eV in this study, which agrees perfectly with previous studies and experimental measurements(13,14). As shown in Fig. 7(b), the bonding states of C atom in C$_3$N are similar to graphene that the hybridized C-$s/p_x/p_y$ orbitals contribute to the $\sigma$ bonds and C-$p_z$ orbital contributes to the weakened $\pi$ bonds despite the intrinsic electronic bandgap. The situation for the orbitals is different for the N atom where the $s$ orbital is largely (∼20 eV) confined below the valence band, forming an isolated band [Fig. 7(c)]. As a result, the $\sigma$ bonds linking C and N atoms are jointly contributed by the valence configuration of C-$s/p_x/p_y$ and N-$p_x/p_y/p_z$, where the $s^2$ electrons in the N-$s^2p^3$ do not participate in the bonding. Note that the doping of $s^2$ electrons from N atoms leads to the up-shift of Fermi level in C$_3$N compared to graphene [Fig. 7(b)], which opens the intrinsic bandgap above the maintained Dirac cone(63).

It was proposed by Petrov and Shtrum that lone-pair electrons could lead to low $\kappa$(64). The principle under-
The unusual strain enhanced $\kappa$ of C$_3$N, in sharp contrast to graphene. All the $\kappa$ are normalized to their respective intrinsic $\kappa$ without strain. Inset: The absolute $\kappa$ of C$_3$N from iterative and RTA methods, together with contributions from FA phonon branch and all other branches. Lines are for eye guiding.

The concept is that the overlapping wave functions of lone-pair electrons with valence electrons from adjacent atoms induce nonlinear electrostatic forces upon thermal agitation, leading to increased phonon anharmonicity in the lattice and thus reducing the $\kappa$. However, this is only a qualitative description. So far, no direct evidence is available for the interactions from a fundamental point of view. Here, based on Figs. 7(b), (c), and (e), it is clearly shown that the non-bonding lone-pair $s$ electrons arise around N atoms in C$_3$N due to the special orbital hybridization. The N-$s$ electrons interact with the covalently bonding electrons of adjacent atoms (C) due to the orbital distribution in the same energy range [Figs. 7(b,c)] and wave functions overlap [Fig. 7(e)]. Additional nonlinear electrostatic force among atoms is induced by the interactions when they thermally vibrate around the equilibrium positions. Consequently, a more asymmetric potential energy well would be induced, which reveals the strong phonon anharmonicity in C$_3$N [Fig. 7(b) and Fig. 7(d)] and significantly reduces the $\kappa$ (Fig. 8).

Thus, based on the fundamental orbital hybridizations analysis of the electronic structures, direct evidence is provided in Figs. 7(b,c,e) for the interactions between lone-pair electrons around N atoms and bonding electrons from adjacent atoms (C). Moreover, the microscopic picture is established to explain how the phonon anharmonicity arises from a underlying level of electronic structure and leads to the low $\kappa$.

Furthermore, it should be noted that there exists slight difference in the electronegativity of C and N atoms. Polarization of the C-N bonds is generated by the different electronegativity as evidently revealed by the electron localization function (ELF), in contrast to the nonpolarized C-C bonds [Figs. 7(d) and (e)]. Consequently, the bonding electrons for the C-N bonds is relatively closer to N atom, which contributes positively to the stronger interaction with the non-bonding N-$s$ electrons and thus leads to a stronger phonon anharmonicity. Furthermore, it could be expected that the phonon anharmonicity and $\kappa$ can be effectively manipulated by altering the interaction strength. For example, with a tensile mechanical strain applied, the interaction strength would be weakened due to the increased distance, which is inferred to reduce the phonon anharmonicity and thus enlarge the $\kappa$ of C$_3$N.

6. UNUSUALLY STRAIN ENHANCED THERMAL CONDUCTIVITY

To verify the inference based on the above established microscopic picture of the lone-pair electrons driving strong phonon anharmonicity, we further study the effect of bilateral tensile strain on the $\kappa$ of C$_3$N, in comparison with graphene. Note that the C$_3$N has a much weaker stiffness (6.656 GPa with 7% strain applied) compared to graphene, which means that it is very easy for the strain to be applied to C$_3$N in experiments. As shown in Fig. 8, the $\kappa$ of graphene decreases with tensile strain, which agrees very well with previous reports. In contrast, the $\kappa$ of C$_3$N is tremendously enhanced. It was reported in previous studies of silicene that such an enhancement by strain engineering should be attributed to the flattening of the buckled structure upon stretching. Similar analysis is applied to the phosphorene which possesses puckered structure. Therefore, it is very unusual for the anomalous positive response of $\kappa$ to tensile strains in C$_3$N, since it has a planar honeycomb structure that is similar to graphene but different from silicene and phosphorene.

We first study the contribution to $\kappa$ of C$_3$N from different phonon branches with strain applied. As shown in the inset of Fig. 8, the absolute contribution to $\kappa$ from FA phonon branch and all the others keep consistent with the variation trend of the total $\kappa$, and the relative contribution keeps almost the same. Detailed mode level analysis based on Fig. 9 reveals that the phonon group velocity and scattering phase space almost keep unchanged with strain applied, except the little decrease of group velocity. Note that due to phonon bunching of high-frequency phonon modes caused by the softened phonon dispersions, the scattering phase space of absorption process for high-frequency phonon modes decreases [Fig. 9(c)]. However, the scattering phase space of the dominating emission process for high-frequency phonon modes keeps unchanged. Thus, the largely strain enhanced $\kappa$ of C$_3$N is primarily due to the overall weakened phonon-phonon scattering [Fig. 9(b)], which is governed by the strain weakened phonon anharmonicity as quanti-
The phonon anharmonicity can be further qualitatively characterized by the deviation of energy potential well from the harmonic (quadratic) profile [26,29]. By displacing the N atom in C$_3$N along the bonding direction as shown in the inset of Fig. 10, we calculate the energy potential well. The energy deviation is calculated by subtracting the energy with the harmonic profile which is obtained by fitting the first 5 points with a quadratic function. As shown in Fig. 10, the energy deviation from the harmonic profile increases with atomic displacement increasing. Considering the increased maximal displacement of atom with temperature increasing, the enhanced phonon anharmonicity as revealed by the increased energy deviation is consistent with the decreased $\kappa$ at increased temperatures (Fig. 3). Moreover, the deviation of energy potential well from the harmonic profile decreases with the increased strain until the strain reaches 4%, and then increases with 6% strain applied. The strain modulated phonon anharmonicity as revealed by the energy deviation is consistent with the strain modulated $\kappa$ (Fig. 8), which provides coherent understanding together with above mode level analysis (Fig. 9).

The underlying mechanism for the anomalous strain enhanced $\kappa$ of C$_3$N can be well understood based on the microscopic picture of the lone-pair electrons driving phonon anharmonicity as established in this work. With tensile strain applied, the separation distance between atoms becomes larger. Thus, the interaction between the lone-pair $s$ electrons around N atoms and the bonding electrons of adjacent atoms (C) are weakened. Consequently, the phonon anharmonicity is attenuated, reducing phonon-phonon scattering [78]. Based on the microscopic picture, the strain enhanced $\kappa$ of C$_3$N is well understood. In fact, the opposite response of $\kappa$ to stretching between C$_3$N and graphene further supports the established microscopic picture of the lone-pair electrons driving strong phonon anharmonicity. Furthermore, it is anticipated that other systems possessing lone-pair electrons should also have a low $\kappa$ and their $\kappa$ can be gener-
1. **FIG. 10.** (Color online) Energy deviation from the harmonic profile of C$_3$N with different typical strains applied, revealing the strain modulated phonon anharmonicity. Inset: The displacement direction of N atom in the primitive cell.

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ally enhanced by weakening the interaction strength between the lone-pair electrons and the bonding electrons of adjacent atoms, such as by increasing the bonding length with tensile strain. The possible systems possessing lone-pair electrons might be group V compounds, just name a few, h-BC$_2$N, h-BN, h-AlN, h-GaN, and h-BAs.

7. **CONCLUSIONS**

In summary, we have performed a comparative study of phonon thermal transport between monolayer C$_3$N and graphene. The $\kappa$ of C$_3$N shows an anomalous temperature dependence, which is totally different from that for common crystalline materials and deviates largely from the well-known $\kappa \sim 1/T$ relationship. Consequently, the $\kappa$ of C$_3$N at high temperatures is larger than the expected value that follows the general trend of $\kappa \sim 1/T$, which would be much beneficial for the applications in nano- and opto-electronics in terms of efficient heat dissipation. Moreover, it is very intriguing to find that the $\kappa$ of C$_3$N is substantially lower than graphene, considering the similar structures and the only difference of substituting 1/4 C with N atoms in C$_3$N compared to graphene. The large scattering rate is responsible for the significantly low $\kappa$ of C$_3$N, which is due to the strong phonon anharmonicity. By deeply analyzing the orbital projected electronic structure, we establish a microscopic picture of the lone-pair electrons driving strong phonon anharmonicity. Direct evidence is provided for the interactions between lone-pair electrons (N-s) and bonding electrons from adjacent atoms (C), which induce nonlinear electrostatic force among atoms when they thermally vibrate around the equilibrium positions, leading to the strong phonon anharmonicity and significantly low $\kappa$ of C$_3$N. Furthermore, the $\kappa$ of C$_3$N is unexpectedly enlarged by applying bilateral tensile strain despite the planar honeycomb structure of C$_3$N (similar to graphene, with no buckling or puckering), which is in sharp contrast to the strain induced $\kappa$ reduction in graphene. The anomalous positive response of $\kappa$ to tensile strain is attributed to the attenuated interaction between the lone-pair s electrons around N atoms and the bonding electrons of neighboring C atoms, which reduces phonon anharmonicity. The opposite response of $\kappa$ to mechanical strain between C$_3$N and graphene further supports the established microscopic picture of the lone-pair electrons driving strong phonon anharmonicity. We propose that other systems possessing lone-pair electrons would also have low $\kappa$ and the $\kappa$ can be generally enhanced by weakening the interaction strength between the lone-pair electrons and the bonding electrons of adjacent atoms, such as by increasing the bonding length with tensile mechanical strain. The microscopic picture for the lone-pair electrons driving phonon anharmonicity established from the fundamental level of electronic structure deepens our understanding of phonon transport in 2D materials and would also have great impact on future research in micro-/nanoscale thermal transport such as materials design with targeted thermal transport properties.

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58. J. Carrete, N. Mingo, and S. Curtarolo, Appl. Phys. Lett. 105, 101907 (2014).

59. L.-C. Zhang, G. Qin, W.-Z. Fang, H.-J. Cui, Q.-R. Zheng, Q.-B. Yan, and G. Su, Sci. Rep. 6, 19830 (2016).

60. L. Lindsay, D. A. Broido, and T. L. Reinecke, Phys. Rev. B 87, 165201 (2013).

61. H. Wang, G. Qin, G. Li, Q. Wang, and M. Hu, Phys. Chem. Chem. Phys. 19, 12882 (2017).

62. L. Lindsay, D. A. Broido, and N. Mingo, Phys. Rev. B 82, 115427 (2010).

63. X. Zhou, W. Feng, S. Guan, B. Fu, W. Su, and Y. Yao, Journal of Materials Research 32, 2993 (2017).

64. A. V. Petrov and E. L. Shtrum, Sov. Phys. Solid State 4, 1061 (1962).

65. D. T. Morelli, V. Jovovic, and J. P. Heremans, Phys. Rev. Lett. 101, 035901 (2008).

66. E. J. Skoug and D. T. Morelli, Phys. Rev. Lett. 107, 235901 (2011).

67. M. D. Nielsen, V. Ozolins, and J. P. Heremans, Energy Environ. Sci. 6, 570 (2013).

68. J. P. Heremans, Nat. Phys. 11, 990 (2015).

69. M. K. Jana, K. Pal, U. V. Waghmare, and K. Biswas, Angew. Chem. Int. Ed. 55, 7792 (2016).

70. Y. Xiao, C. Chang, Y. Pei, D. Wu, K. Peng, X. Zhou, S. Gong, J. He, Y. Zhang, Z. Zeng, and L.-D. Zhao, Phys. Rev. B 94, 125203 (2016).

71. Z. Qin, G. Qin, and M. Hu, Nanoscale 10, 10365 (2018).

72. N. Bonini, J. Garg, and N. Marzari, Nano Lett. 12, 2673 (2012).

73. L. Lindsay, W. Li, J. Carrete, N. Mingo, D. A. Broido, and T. L. Reinecke, Phys. Rev. B 89, 155426 (2014).

74. Q.-X. Pei, Y.-W. Zhang, Z.-D. Sha, and V. B. Shenoy, J. Appl. Phys. 114, 033526 (2013).

75. Y.-Y. Zhang, Q.-X. Pei, J.-W. Jiang, N. Wei, and Y.-W. Zhang, Nanoscale 8, 483 (2016).

76. Z.-Y. Ong, Y. Cai, G. Zhang, and Y.-W. Zhang, J. Phys. Chem. C 118, 25272 (2014).

77. G. Qin and M. Hu, Small 14, 1702465, https://onlinelibrary.wiley.com/doi/pdf/10.1002/smll.201702465.

78. G. Qin, Z. Qin, H. Wang, and M. Hu, Nano Energy 50, 425 (2018).