

First-principles calculation of the lattice thermal conductivities of α -, β -, and γ - Si_3N_4

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Lattice thermal conductivities of α -, β - and γ - Si_3N_4 single crystals are investigated from *ab-initio* anharmonic lattice dynamics, within the single-mode relaxation-time approximation of the linearized phonon Boltzmann transport equation. At 300 K, the lattice thermal conductivity of β - Si_3N_4 is calculated as $\kappa_{xx} = 73$ and $\kappa_{zz} = 198$ (in units of $\text{Wm}^{-1}\text{K}^{-1}$), that is consistent with the reported experimental values of 69 and 180, respectively. For α - Si_3N_4 , $\kappa_{xx} = 69$ and $\kappa_{zz} = 99$ are obtained. The difference of anisotropy between α - Si_3N_4 and β - Si_3N_4 is originated from their characteristic difference in the phonon band structures, although their crystal structures are similar in their local atomic coordinates. In α - Si_3N_4 , acoustic-mode phonons below 6 THz are the main heat carriers. In β - Si_3N_4 , the phonon modes up to 12 THz contribute to the lattice thermal conductivity. In γ - Si_3N_4 , $\kappa = 81$ is obtained. The distribution of phonon mode contributions to lattice thermal conductivity with respect to phonon frequency is found to closely resemble κ_{xx} of β - Si_3N_4 although the phonon lifetimes of γ - Si_3N_4 are twice shorter than those of β - Si_3N_4 .

I. INTRODUCTION

Several nitride insulators are known to exhibit high thermal conductivities and are important for heat transfer materials at elevated temperatures. For example, Slack *et al.*¹ reported that wurtzite-type w-AlN has thermal conductivity of $\gg 100 \text{ Wm}^{-1}\text{K}^{-1}$. Si_3N_4 has become another promising thermal conductive insulator as its thermal conductivity has been improved up to $177 \text{ Wm}^{-1}\text{K}^{-1}$ by using the advanced ceramic technologies related to the densification and microstructure control.²⁻⁵ Since the Si_3N_4 ceramics also exhibit high mechanical strength at elevated temperatures, they are regarded as ideal materials for the use in various applications, such as engine components, gas turbines, and heat sink substrates of power semiconductor devices.

At atmospheric pressure, Si_3N_4 exists in one of two phases, α and β , which are generally considered as low- and high-temperature phases, respectively.^{2,5,6} Their crystal structures belong to the space groups of P31c and P6₃/m, respectively.^{7,8} These structures have different stacking orders of equivalent basal layer structures originated by SiN_4 tetrahedra.⁹ In Fig.1 these layer structures are depicted from the principal direction, as A, B, C, and D in the α phase and A and B in the β phase. The stacking manners in α - and β - Si_3N_4 are thus as ABCDABCD.. and ABAB.., respectively. The α phase has additional two layer structures of C and D, which are related to the A and B by the *c* glide operation.⁹ Along this direction the lattice constant of the α phase is approximately two times longer than that of the β phase.

The reported values^{2-5,11} of the thermal conductivity of the Si_3N_4 polymorphs were measured on polycrystalline bulk samples. These values were significantly af-

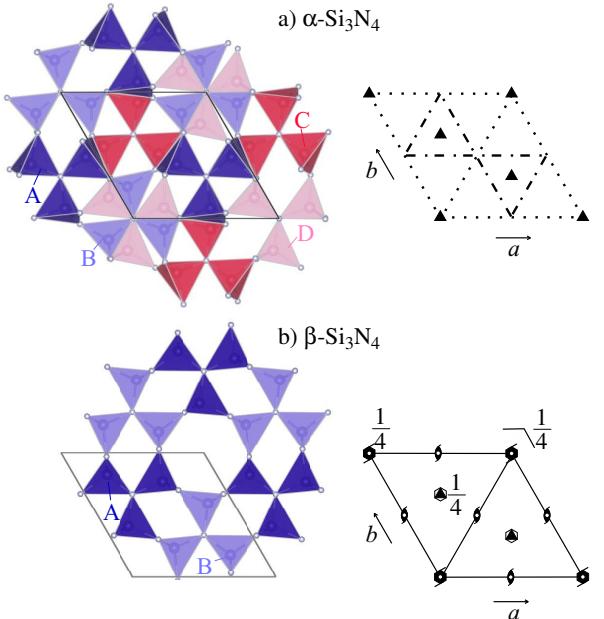


FIG. 1. (color online) Crystal structures of α - and β - Si_3N_4 . Stacking of SiN_4 tetrahedron layers are shown in left. (a) ABCDABCD.. for α - Si_3N_4 . (b) ABAB.. for β - Si_3N_4 . Space group diagrams¹⁰ in P31c (α - Si_3N_4) and P6₃/m (β - Si_3N_4) are shown in right.

fected by the contained lattice defects, impurities, shapes and orientations of the constituent crystal grains;¹² the thermal conductivity intrinsic to a defect-free single crystal has not been established. As an experimental access to the intrinsic thermal conductivity, Li *et al.*¹³ applied high-resolution thermoreflectance microscopy to a single β - Si_3N_4 grain in a ceramic sample. The analyzed

thermal conductivities were 69 and 180 Wm⁻¹K⁻¹ along the *a* and *c* axes, respectively. These thermal quantities correspond to the diagonal elements κ_{xx} and κ_{zz} of the lattice thermal conductivity tensor κ . We consider the anisotropy of $\kappa_{zz}/\kappa_{xx} \sim 3$ is relatively large. Theoretically, Hirosaki *et al.*¹² estimated κ by applying the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta *et al.*¹⁴. They calculated κ_{xx} and κ_{zz} of α -Si₃N₄ as 105 and 225 Wm⁻¹K⁻¹, and those of β -Si₃N₄ as 170 and 450 Wm⁻¹K⁻¹, respectively. The ratio κ_{zz}/κ_{xx} in β -Si₃N₄ agreed well with the experimental results obtained by Li *et al.*¹³: The κ_{ii} values overestimated the experimental by more than two times.

On many polymorphs of the wurtzite and zincblende structures, the lattice thermal conductivities were recently calculated based on a first principles calculation and Boltzman transport theory.¹⁵ These polymorphs have different stacking orders of the densest atom planes as ABAB.. and ABCABC... The different stacking orders merely altered the lattice thermal conductivities.¹⁵ The phonon linewidth distribution and phonon density of states were similar between the structures as well.¹⁵ On the other hand, the previous MD results on α - and β -Si₃N₄ presented that the different stacking orders in these phases altered the κ values largely. The large difference has not been clarified based on the microscopic phonon properties. It is interesting to investigate it using the same approach as in Ref.15 for α - and β -Si₃N₄.

In addition to the α and β phases, a cubic spinel phase (γ -Si₃N₄) is known to form upon compression and in-situ heating.^{16,17} The reported transition pressures were scattered from 10 to 36 GPa depending on the experimental conditions.¹⁸ The γ phase is experimentally quenched to atmospheric pressure at room temperature. Its thermal conductivity has not been experimentally reported; it has been estimated only by the Slack model.¹⁹

The present study aims to qualitatively understand the lattice thermal conductivity tensors among the three Si₃N₄ phases by means of the first principles approach. We calculate κ of the γ phase as well, for systematic understanding of the lattice thermal conductivity in the Si₃N₄ system. After the methodology section, we examine the validity of the present results first. Our calculated thermal properties are compared with the available experimental and theoretical references. Then we investigate the characteristics in the calculated κ in detail on the basis of the phonon band structures and phonon linewidths.

II. COMPUTATIONAL PROCEDURES

A. Lattice thermal conductivity calculation

The lattice thermal conductivities were calculated by solving the linearized Boltzmann transport equation (LBTE) within the single-mode relaxation time approx-

imation (single-mode RTA). We also tried the direct solution of LBTE²⁰ and leave its calculated κ values in the following section. The difference in the calculated κ between by the single-mode RTA and by the direct solution was found minor for our discussion. Therefore we limited our research to use the single-mode RTA to take advantage of its intuitive closed form of κ .

In the following sections, we denote a phonon mode by $\lambda = (\mathbf{q}, p)$ with the set of the phonon wave vector \mathbf{q} and band index p and $-\lambda \equiv (-\mathbf{q}, p)$. The relaxation time due to phonon-phonon scattering was obtained as reciprocal of linewidth, $\tau_{\lambda,ph-ph} = (2\Gamma_{\lambda})^{-1}$, where the linewidth that we employed in this study is as follows:

$$\begin{aligned} \Gamma_{\lambda} = & \frac{18\pi}{\hbar^2} \sum_{\lambda'\lambda''} |\Phi_{-\lambda\lambda'\lambda''}|^2 \times \\ & \{(n_{\lambda'} + n_{\lambda''} + 1)\delta(\omega_{\lambda} - \omega_{\lambda'} - \omega_{\lambda''}) + \\ & (n_{\lambda'} - n_{\lambda''})[\delta(\omega_{\lambda} + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega_{\lambda} - \omega_{\lambda'} + \omega_{\lambda''})]\}. \end{aligned} \quad (1)$$

Here ω_{λ} is the harmonic phonon frequency of the phonon mode λ , $n_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_B T) - 1]^{-1}$ is the Bose-Einstein distribution at temperature T , and $\Phi_{\lambda\lambda'\lambda''}$ denotes the three-phonon-scattering strength. $\Phi_{\lambda\lambda'\lambda''}$ was obtained by usual coordinate transformation of third-order force constants from direct space to phonon space.¹⁵ The second- and third-order real-space force constants were obtained from the *ab-initio* calculation, whose details are written in the next section.

In order to compare the more realistic results of the calculated κ with the experimental data, the isotopic scattering effect due to the natural isotope distribution was taken into account according to the second-order perturbation theory.²¹ With the relaxation times of the phonon-phonon scattering and isotopic scattering, $\tau_{\lambda,ph-ph}$ and $\tau_{\lambda,iso}$, the total relaxation time for a phonon mode was assumed to be $1/\tau_{\lambda} = 1/\tau_{\lambda,ph-ph} + 1/\tau_{\lambda,iso}$, according to Matthiessen's rule.

The available experimental thermal conductivity data of the Si₃N₄ system have been measured on the polycrystalline samples and not measured from any single crystals. In order to consider the effect of various lattice defects in the polycrystalline samples, such as grain boundaries, impurities, and vacancies, we crudely took them into account by a relaxation time $\tau_{\lambda,bs} = L/|\mathbf{v}_{\lambda}|$ of a phonon boundary scattering model, where $\mathbf{v}_{\lambda} = \nabla_{\mathbf{q}}\omega_{\lambda}$ is the group velocity and L a parameter regarding to the boundary mean free path. We consider $\tau_{\lambda,bs}$ as a variable parameter and included it to κ according to Matthiessen's rule.

The closed form of κ within RTA was obtained via

$$\kappa(T) = \frac{1}{N_{\mathbf{q}}\Omega} \sum_{\lambda} \tau_{\lambda}(T) \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda}(T), \quad (2)$$

where $N_{\mathbf{q}}$ is the number of \mathbf{q} -points, Ω is the unit cell volume, and c_{λ} is the mode heat capacity. To analyze κ in

detail, we calculate the cumulative thermal conductivity:

$$\kappa^c(\omega) = \frac{1}{N_q\Omega} \int_0^\omega \sum_\lambda \tau_\lambda(T) \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda c_\lambda(T) \delta(\omega' - \omega) d\omega', \quad (3)$$

and its derivative $\frac{\partial \kappa^c(\omega)}{\partial \omega}$ to see the phonon mode contributions to κ .

The lattice thermal conductivities were calculated with the phonon-phonon interaction calculation code PHONO3PY¹⁵, while the harmonic phonon states were analyzed with the phonon calculation code PHONOPY²².

B. Computational details

The force constants were calculated using the first-principles projector augmented wave method²³ (VASP code^{24–26}). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof²⁷ was used for the exchange correlation potential. A plane wave energy cutoff of 500 eV was employed. The crystal structures were optimized until the residual forces acting on the constituent atoms was less than 10^{-6} eV/Å. The structural optimization was firstly performed for a temperature of 0 K and 0 GPa. Here the temperature and pressure were considered only for the electronic system and the zero point lattice vibration was not taken into account. The calculated lattice parameters were $a = 7.808$ Å and $c = 5.659$ Å for the α phase, $a = 7.660$ Å and $c = 2.925$ Å for the β phase, and $a = 7.787$ Å for the γ phase, which agree with the experimental data^{7,8,28} within +0.7 % errors. The lattice volume optimized within the local density approximation (LDA)²⁹ for the exchange correlation potential was, for $\beta\text{-Si}_3\text{N}_4$, 3 % smaller than within GGA, which is a typical volume contraction of LDA. The κ calculated within LDA was larger by 2.6 % than within GGA. For our discussion, this difference is enough small, therefore the impact of choice of exchange correlation potential is considered to be minor in our study.

Supercell and finite difference approaches were used to calculate the force constants.³⁰ The supercells were $1 \times 1 \times 2$, $1 \times 1 \times 3$, and $1 \times 1 \times 1$ supercells of the conventional unit cells for the calculation of the third-order force constants in α , β , and $\gamma\text{-Si}_3\text{N}_4$, respectively; they were $3 \times 3 \times 4$, $3 \times 3 \times 8$ and $2 \times 2 \times 2$ for the second-order force constants. The length of the induced atomic displacement was set to 0.03 Å. Table I shows the κ calculated with several different sets of the supercells, indicating that our calculated κ is reasonably converging with respect to the size of the supercells.

Non-analytical term correction³¹ was applied to the second-order force constants to take into account the long range Coulomb forces present in ionic crystals. For the correction, static dielectric constants and Born effective charges were calculated by using the density func-

TABLE I. Calculated lattice thermal conductivities of α -, β -, and $\gamma\text{-Si}_3\text{N}_4$ ($\text{WK}^{-1}\text{m}^{-1}$) at 300 K with respect to several combinations of supercell sizes.

| Phase | Supercell (# of atoms) | | LTC | |
|----------|---------------------------------|---------------------------------|-----------|-----------|
| | 3 rd force constants | 2 nd force constants | <i>xx</i> | <i>zz</i> |
| α | 1 \times 1 \times 1 (28) | 1 \times 1 \times 1 (28) | 37 | 57 |
| | 1 \times 1 \times 2 (56) | 1 \times 1 \times 2 (56) | 41 | 79 |
| | 1 \times 1 \times 1 (28) | 2 \times 2 \times 2 (224) | 55 | 81 |
| | 1 \times 1 \times 2 (56) | 2 \times 2 \times 2 (224) | 67 | 95 |
| | 1 \times 1 \times 2 (56) | 2 \times 2 \times 3 (336) | 68 | 97 |
| | 1 \times 1 \times 2 (56) | 3 \times 3 \times 4 (1008) | 68 | 100 |
| β | 1 \times 1 \times 2 (28) | 1 \times 1 \times 2 (28) | 44 | 173 |
| | 1 \times 1 \times 2 (28) | 2 \times 2 \times 4 (224) | 76 | 208 |
| | 1 \times 1 \times 3 (42) | 2 \times 2 \times 4 (224) | 71 | 194 |
| | 1 \times 1 \times 3 (42) | 2 \times 2 \times 5 (280) | 72 | 196 |
| | 1 \times 1 \times 3 (42) | 3 \times 3 \times 8 (1008) | 73 | 199 |
| γ | 1 \times 1 \times 1 (56) | 1 \times 1 \times 1 (56) | 72 | |
| | 1 \times 1 \times 1 (56) | 2 \times 2 \times 2 (448) | 77 | |
| | 1 \times 1 \times 1 (56) | 3 \times 3 \times 3 (56) | 79 | |

tional perturbation theory (DFPT) as implemented in the VASP code^{32,33}.

Uniform \mathbf{k} -point sampling meshes of $4 \times 4 \times 2$, $4 \times 4 \times 3$, and $3 \times 3 \times 3$ were used for the third-order force constants of the α , β , and γ phases. For the α and β phases the center of the a^*b^* plane was sampled while the center on the c^* -axis was not. For the γ phase, non- Γ center mesh was used. For the second-order force constants, the Γ -point was only sampled for the α and β phase and the only one $\mathbf{k} = (0.5, 0.5, 0.5)$ point was sampled for the γ phase. The \mathbf{q} -point sampling meshes of $10 \times 10 \times 14$, $10 \times 10 \times 26$, and $12 \times 12 \times 12$ were used to calculate κ in Eq. (2) for the α , β , and γ phases.

We examined the effect of thermal expansion on κ by calculating them with the crystal structures optimized for several finite temperatures within the quasi-harmonic approximation (QHA)³⁴. The structure was optimized for a temperature and 0 GPa so as to show a minimum Helmholtz free energy. κ for the temperature was calculated with the optimized structure. This κ was differed from the one for the temperature, calculated with the structure optimized for 0 K and 0 GPa. We consider that this difference is caused by the thermal expansion of the lattice. For $\beta\text{-Si}_3\text{N}_4$ and the temperatures of 300, 600, 900, 1200, and 1500 K, the differences in κ between the two structures were found less than 1 %, similar to the case of Si and Ge³⁵. For the present study, these differences are negligible and we adopt the κ calculated with the structure optimized for 0 K and 0 GPa.

We calculated the volumetric thermal expansion coefficients and compared them with the reported experimental values so as to check the validity of the present thermal conductivity calculation, because the thermal expansion is originated from the anharmonicity of the

interatomic potential as well as κ . The calculated values of the α and β phases are 4.31×10^{-6} and $4.19 \times 10^{-6} \text{ K}^{-1}$ for 300 K, while the experimental values³⁶ were 3.75×10^{-6} and $3.55 \times 10^{-6} \text{ K}^{-1}$. The present calculation reproduced the experimental tendency where the α phase has a slightly larger thermal expansion coefficient than the β phase, supporting that the present calculations enable us to qualitatively compare the calculated κ of the Si_3N_4 phases.

In order to compare the microscopic phonon properties among the three phases at the same conditions, those results calculated at 0 GPa are shown and discussed. For the γ phase, this means that we assume the condition of a virtually quenched γ phase at 0 GPa from the high pressure. To examine the analytical continuity of the properties with respect to pressures, we calculated κ of the γ phase at 10, 20, and 40 GPa as shown in Fig. 8. The phenomenological behaviour of linear dependence of κ with respect to pressure was reproduced as similar to Ref. 37. The slope was $2.89 \text{ Wm}^{-1}\text{K}^{-1}\text{GPa}^{-1}$ for the γ phase. By this dependence, we consider that the microscopic values are also varied smoothly with the pressure and those at 0 GPa are valuable to compare with the α and β phases.

C. Direct solution of LBTE

The merit to employ the single-mode RTA for thermal conductivity calculation is the closed form, by which we can intuitively understand the qualitative character of κ in terms of the relaxation time and group velocity. The microscopic understanding of the full solution of LBTE is still under the development³⁸ and the microscopic picture based on collective phonons³⁹ will require more complicated investigation although it is known that the single-mode RTA solution of LBTE often underestimates the full solution.^{35,40}

On the κ of the α and β phases, we adopted a direct solution of LBTE²⁰, which is one of the methods of LBTE full solutions. Their κ_{xx} and κ_{zz} without the isotope effect were 69 and $102 \text{ Wm}^{-1}\text{K}^{-1}$ for the α phase and 76 and $238 \text{ Wm}^{-1}\text{K}^{-1}$ for the β phase, respectively, while the corresponding single-mode RTA values were 70 and $102 \text{ Wm}^{-1}\text{K}^{-1}$ for the α phase and 76 and $210 \text{ Wm}^{-1}\text{K}^{-1}$ for the β phase. The κ_{zz} of the direct solution in the β phase was 13 % larger than that of the single-mode RTA solution. Since the differences in κ between the LBTE solutions are not significant, we expect the physics on those lattice thermal conductivities is well understood within RTA in the current level of our interest. Therefore, we discuss the lattice thermal conductivities using the results of the single-mode RTA solution.

III. RESULTS AND DISCUSSION

A. Lattice thermal conductivities

TABLE II. Calculated thermal conductivities of $\alpha\text{-Si}_3\text{N}_4$ (trigonal), $\beta\text{-Si}_3\text{N}_4$ (trigonal), and $\gamma\text{-Si}_3\text{N}_4$ (cubic) at 300 K, compared with the experimental data. Theoretical bulk moduli B in units of GPa, calculated by the authors by using the present band method, are presented in the fourth column.

| | This work | | κ | Ref. Theo. | | Ref. Expt. | |
|--------------------------------|---------------|---------------|----------|------------------|------------------|------------------|----------------------------------|
| | κ_{xx} | κ_{zz} | | κ_{xx} | κ_{zz} | κ_{xx} | κ_{zz} |
| $\alpha\text{-Si}_3\text{N}_4$ | 68 | 100 | 224 | 70 ^a | 105 ^b | 225 ^b | - |
| $\beta\text{-Si}_3\text{N}_4$ | 73 | 199 | 237 | 250 ^a | 170 ^b | 450 ^b | 69 ^c 180 ^c |
| $\gamma\text{-Si}_3\text{N}_4$ | 77 | - | 296 | 80 ^a | - | - | - |

^a Ref. 19, Slack model.

^b Ref. 12, molecular dynamics (Green-Kubo).

^c Ref. 13, single crystalline grains of poly-crystals.

Table II shows the present results of the κ for 300 K. $\beta\text{-Si}_3\text{N}_4$ has markedly more anisotropic κ than $\alpha\text{-Si}_3\text{N}_4$. The directional averages $\sum_i \kappa_{ii}/3$ are 79, 115, and 77 $\text{Wm}^{-1}\text{K}^{-1}$ for the α , β , and γ phases, respectively. The value of the γ phase is similar to that of the α phase, in spite of comparatively large difference among the bulk moduli (B) that are also shown in Table II.

Table II also shows the previously reported experimental¹³ and theoretical¹² thermal conductivities for the references. Previously Morelli *et al.*¹⁹ employed the Slack model for estimating the lattice thermal conductivities of the three phases. They are shown as κ in Table II. For the β phase, our κ agrees better with the experimental, than that of the molecular calculation¹² does. Also, our directional average $\sum_i \kappa_{ii}/3$ agrees better with the experimental average, than the Slack model does.

Fig. 2 shows the theoretical κ of the α and β phases as a function of T , together with the reference experimental data^{5,11}. The thermal conductivities for a series of temperatures were only reported on the polycrystalline bulk samples and measured by the laser flash method. These thermal conductivities (denoted as $\kappa_{\text{polycrystal}}$) cannot be directly compared with the calculated intrinsic κ because they largely depended on the microstructure of the samples: They were deviated from the simple directional averages of the intrinsic κ_{ii} , depending on the shapes of the crystal grains. We treated this effect by using a parameter $0 \leq w \leq 1$ and fitting the quantities of $w\kappa_{xx} + (1-w)\kappa_{zz}$ to the experimental $\kappa_{\text{polycrystal}}$ by the least squares method. We consider these as theoretical $\kappa_{\text{polycrystal}}$.

In Fig. 2, the κ_{ii} calculated without $\tau_{\lambda,\text{bs}}$ are nearly proportional to T^{-1} because n_λ in Eq. (1) can be reduced to $\exp(-\hbar\omega_\lambda/k_B T)$. In Fig. 2-a, the experimental $\kappa_{\text{polycrystal}}$ of a chemically vapor-deposited $\alpha\text{-Si}_3\text{N}_4$ sample¹¹ is not proportional to T^{-1} and intersects the theoretical κ_{ii} . Thus no value of w adjusts the theoretical

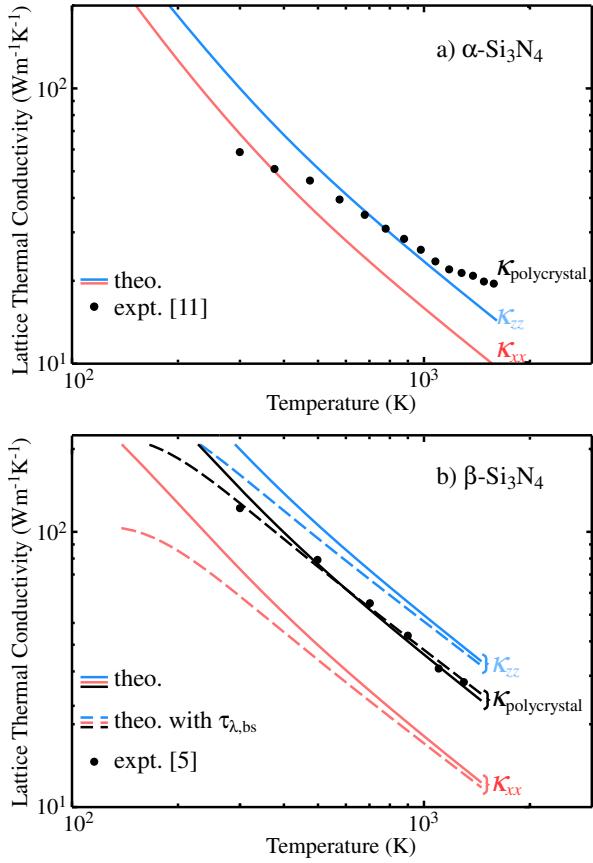


FIG. 2. (color online) Temperature dependence of thermal conductivities for α - and β - Si_3N_4 . For β - Si_3N_4 , theoretical results with the boundary scattering effect are shown by broken lines. Theoretical $\kappa_{\text{polycrystal}}$ (see in text) for the β - Si_3N_4 sample are also shown to be compared with the experimental conductivities.

conductivities to the experimental data. The full solution of LBTE would negligibly cure the disagreement. Including the simple phonon lifetime of boundary scattering, $\tau_{\lambda,\text{bs}} = L/|\mathbf{v}_{\lambda}|$, into the total phonon lifetime according to Matthiessen's rule, could not explain the discrepancy as well. A L value of $0.6 \mu\text{m}$, which was much smaller than the experimental grain size¹¹ of $10 \mu\text{m}$, decreased the theoretical κ_{ii} in the low temperature side toward the experimental values, but severely underestimated in the high temperature side. At present, the reason for the discrepancy between the theoretical and experimental behaviors is unclear. Although the crystal structure of the experimental sample was characterized as α - Si_3N_4 , significant lattice defects existed in the as-deposited sample as pointed out by Hirosaki *et al.*¹² and the simple phonon boundary scattering model may fail to describe their effects on the $\kappa_{\text{polycrystal}}$.

The experimental $\kappa_{\text{polycrystal}}$ of the β phase are located in-between the theoretical κ_{xx} and κ_{zz} , being nearly proportional to T^{-1} . Simple directional averages of the theoretical κ_{ii} slightly underestimate these experimen-

tal values. This is understood from the fact that the microstructure was controlled to improve the $\kappa_{\text{polycrystal}}$, and the crystalline grains were selectively grown along the c axis of the most conductive direction.⁵ The theoretical $\kappa_{\text{polycrystal}}$ were fit well with $w = 0.44$ to the experimental. For the effects of lattice defects most of which were grain boundaries, we included $\tau_{\lambda,\text{bs}}$ with $L = 0.6 \mu\text{m}$ to further fit the theoretical curve ($w = 0.33$) to the experimental data. The L value is slightly smaller than the average grain size⁵ of $2 \mu\text{m}$ in the experiment.

B. Dispersion curves

Figure 3 shows the phonon band diagrams of the three Si_3N_4 phases. The entire band diagrams are almost identical to those reported earlier^{18,41}. However, here we investigate the gradients of the band dispersions, that is, the group velocities projected on the high-symmetry paths. We especially focus on their anisotropy in the α and β phases. This was not investigated by the previous works.

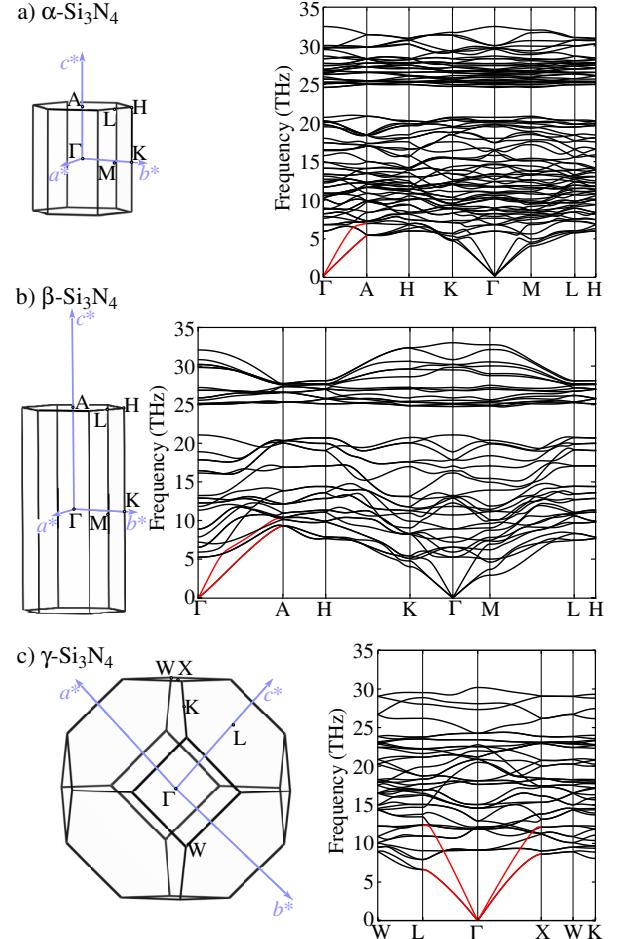


FIG. 3. (color online) Brillouin-zones (left) and calculated phonon band diagrams (right) for three Si_3N_4 phases.

The ω_λ on the acoustic branches in the β phase increase much more from Γ to A than from Γ to K or M. In the α phase, the corresponding ω_λ increase more equally among the paths. This difference is due to the different Γ -A path lengths. The β phase has an approximately twice longer path than the α phase; the lattice constant c of the β phase is nearly half that of the α phase, owing to the difference in the stacking manner of the basal layer structures. The anisotropic dispersions indicate large anisotropy in \mathbf{v}_λ . This will be investigated further in the following sections. Normally, optical branches are flat; however, the β phase has significantly large gradients in its low frequency optical phonon branches. This indicates that the phonons on these branches have large v_λ .

In the γ phase, the acoustic phonon branches show significant linear dispersions on the Γ -L and Γ -X paths. Their roughly constant gradients are large, reflecting the large bulk modulus of the γ phase as shown in Table II.

C. ω_λ counter map on reciprocal plane

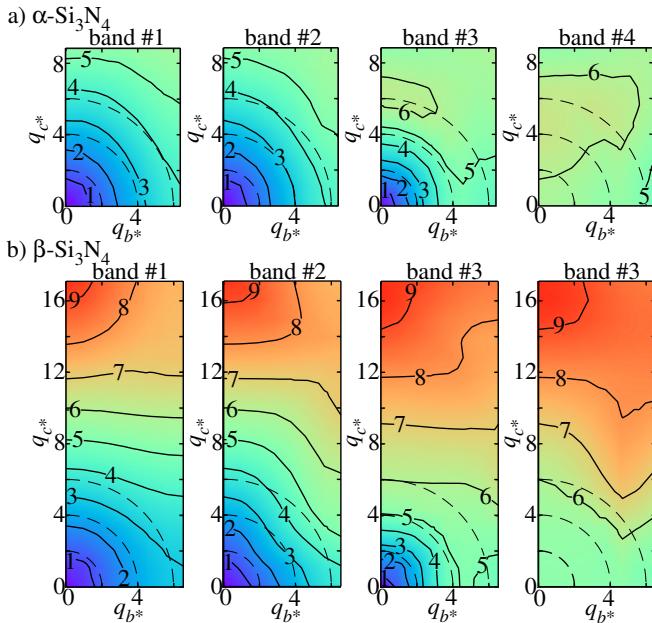


FIG. 4. (color online) Contour maps of phonon frequency (THz) on the b^*c^* planes of Brillouin-zones. The coordination in the reciprocal plane are in units of 10^{-2} \AA^{-1} . The maps for the four lowest-frequency phonon states are shown. The frequency landscapes are formed by simply connecting the frequencies of the same band indices, assigned by ascending order of frequency at the respective \mathbf{q} points.

We investigate the anisotropy in \mathbf{v}_λ by using another geometry, that is, a cross-section of the Brillouin-zone. Fig. 4 shows counter maps of ω_λ on the b^*c^* plane. We show the counter maps for the four lowest-frequency bands, because these bands contribute significantly to

the κ . There were no significant differences in the distributions between the b^*c^* plane and the other planes containing the c^* axis. Thus we select the b^*c^* plane as a representative. In the α phase, the ω_λ distributions are nearly isotropic. Their gradients, the group velocities projected onto the plane, are thus nearly isotropic. In the β phase, the iso-frequency lines in $0.06 \leq q_{c^*} \leq 0.12 \text{ \AA}^{-1}$ are rather parallel to the q_{b^*} axis. The \mathbf{v}_λ in the β phase orient closely to the c axis direction. This confirms the large anisotropy in \mathbf{v}_λ for the β phase.

D. Frequency-dependences of κ^c , \mathbf{v}_λ and Γ_λ

We have investigated in the previous two sections the anisotropy in \mathbf{v}_λ , which gives an insight on the anisotropy in the κ . Here we completely investigate the characteristic points in the κ by using the important phonon properties existing in the closed form of RTA in Eq. (2). These properties are taken over the Brillouin zone because κ is a quantity integrated there. In order to investigate these properties with respect to the phonon branches, we plot in Fig. 5 the frequency distribution of these properties: Phonon densities of states (DOS) in Fig. 5-a show distributions of heat carriers. Distinct first peaks in the DOS are denoted by arrows. They roughly correspond to the flattening of the acoustic branches near the Brillouin zone boundaries. Cumulative thermal conductivities κ^c in show frequencies where phonons largely contribute to κ . In Fig. 5-c, κ^c and their first derivatives are also shown in order to show the contributions clearly. We weighted the DOS with $v_{\lambda,i}^2$ and they are shown in Fig. 5-c. These profiles show both of the impacts of $v_{\lambda,i}$ and number of heat carriers. We abbreviate these weighted DOS as WDOS. Phonon linewidths are a remaining important property. They are shown as scatter plots ($\Gamma_\lambda, \omega_\lambda$) in Fig. 5-d.

Among the panels in Fig. 5, the γ phase has DOS, WDOS and Γ_λ distribution much different from those of the other phases, consistently with the large differences in the crystal structure. Some of the remarkable differences are explained by its characteristic chemical bonding: (1) In the DOS, the first peak is located at a higher frequency than that of the other phases. This is consistent with the finding in the band diagram; the linear dispersions of the acoustic phonon branches with the large gradients. This reflects the strong chemical bonding as indicated by the large bulk modulus. (2) In most of the frequencies with phonons largely contributing to κ , the γ phase has WDOS the next largest to the WDOS for $v_{\lambda,z}$ of the β phase. This is also explained by the large gradients in the acoustic phonon branches. (3) In the same frequencies as mentioned in (2), the linewidths are larger than those in the other phases. For this point, we investigate the three-phonon-scattering strength $\Phi_{\lambda\lambda'\lambda''}$. In Table. III, the magnitudes of $\Phi_{-\lambda\lambda'\lambda''}$ are compared as their averages over two different frequency ranges of ω_λ and all indices in λ' and λ'' . Its average over ω_λ in 0–15 THz is much larger

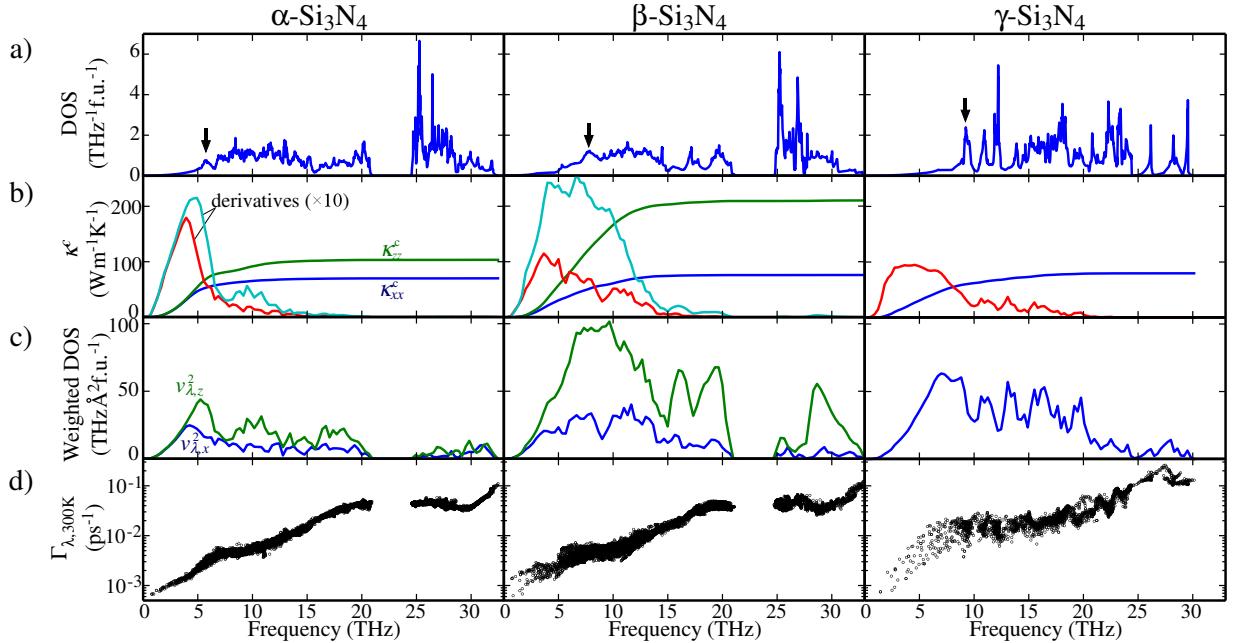


FIG. 5. (color online) Microscopic phonon properties of three Si_3N_4 phases. Cumulative thermal conductivity κ^c and its derivative (a), DOS (b), weighted DOS with $v_{\lambda,i}^2$ (c) and linewidth Γ_λ (d).

than that of the other phases. This is consistent with the larger linewidths. Because of the opposite impacts of the linewidths and WDOS, the κ_{xx}^c is relatively small. It qualitatively resembles to the κ_{xx}^c of the β phase.

TABLE III. Averages of $\Phi_{-\lambda\lambda'\lambda''}$ over frequency ranges of ω_λ (0–15 and 0–35 THz) and all (λ', λ'') . The values are in units of $10^{-10} \text{ eV}^2 \text{f.u.}^{-1}$.

| Frequency Range (THz) | Phase | | |
|-----------------------|----------|---------|----------|
| | α | β | γ |
| 0–15 | 2.66 | 2.63 | 5.76 |
| 0–30 | 13.1 | 13.0 | 11.4 |

We hereafter focus on the comparison between the α and β phases. It is interesting that κ^c in the β phase still increase significantly in the higher frequency range than the DOS first peak position. In this frequency range, WDOS of the β phase show still large intensities. The linewidths are distributed in a similar way for both of the phases. The DOS are similar as well. Thus the significant increase in κ^c across the DOS first peak position is ascribed only to the large \mathbf{v}_λ . The large \mathbf{v}_λ in this frequency range reflect the characteristic points in the band diagram as investigated in the previous section; the anisotropic dispersions in the acoustic phonon branches and the large gradients in the low frequency optical phonon branches. In Figs. 5-b and c, the profiles of $\frac{d\kappa_{ii}^c}{d\omega_\lambda}$ are characterized by those of WDOS with $v_{\lambda,i}^2$, for the same directional indicies. Because DOS and Γ_λ are similar between the phases, the anisotropy in \mathbf{v}_λ simply

accounts for the different anisotropy in κ between the two phases.

It is still curious that Γ_λ are similar between these phases although \mathbf{v}_λ have marked differences. We investigate this further. As for not Γ_λ but κ , previously, Lindsay *et al.*⁴² found a significant positive correlation between the κ and the number of the configurations for the three phonons, $\{\lambda, \lambda', \lambda''\}$ (the phase space available for the three-phonon scattering), among many crystals of the zincblende structure. Closely relateing to this, as for Γ_λ , Γ_λ strongly depends on the number of configurations for the two phonons, $\{\lambda', \lambda''\}$, available in the three-phonon scatering. This is because the formula of Γ_λ contains delta functions corresponding to the selection rule of the three-phonon scattering¹⁵. The distribution of these configurations is represented as a joint density of states (JDOS), $D_2(\mathbf{q}, \omega)$,

$$D_2(\mathbf{q}, \omega) = D_2^{(1)}(\mathbf{q}, \omega) + D_2^{(2)}(\mathbf{q}, \omega) \quad (4)$$

where

$$\begin{aligned} D_2^{(1)} &= \frac{1}{N} \sum_{\lambda' \lambda''} \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) + \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})], \\ D_2^{(2)} &= \frac{1}{N} \sum_{\lambda' \lambda''} \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}), \end{aligned}$$

with $\Delta(\mathbf{x})$ giving 1 if \mathbf{x} is a reciprocal lattice vector and otherwise zero. JDOS were employed to analyze the linewidths Γ_λ of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ⁴⁰ and the imaginary parts

of the self energy $\Gamma_\lambda(\omega)$ of many zincblende and wurtzite polymorphs¹⁵. Following to these studies, we employ the JDOS to examine the similarity between Γ_λ of the α and β phases.

Fig. 6 shows the frequency-functions of JDOS at different \mathbf{q} -points on the Γ -A and Γ -K paths. There are very weak \mathbf{q} -point dependences among the functions. At the low frequency region with phonons largely contributing to the κ , among the two terms of $D_2^{(1)}$ and $D_2^{(2)}$ in Eq. (4), dominant is $D_2^{(2)}$. The $D_2^{(2)}$ basically corresponds to the half part ($\omega \geq 0$) of the auto-correlation function of the DOS. The DOS for both of the α and β phases show the frequency gap (Fig. 5-a). The $D_2^{(2)}$ reflect this DOS feature, dropping suddenly around 0 THz and showing a small shoulder around 5 THz, which corresponds to the width of the gap. Moreover the $D_2^{(2)}$ shows a broad peak around 18 THz, which corresponds to the frequency shift to make the largest correlation between the higher and lower portions of DOS across the gap. Because the gap is originated from the differences in the vibrations of the planer NSi₃ contained in both of the α and β crystal structures,⁴¹ the major shapes of the $D_2^{(2)}$, reflecting this gap feature, are similar in these phases. With the same origin, the $D_2^{(1)}$ are also similar in these phases. As indicated in Table. III, the $\Phi_{-\lambda\lambda'\lambda''}$ have similar impacts on the linewidths. With these similar impacts of the JDOS and $\Phi_{-\lambda\lambda'\lambda''}$, Γ_λ in Fig. 5-d are similar.

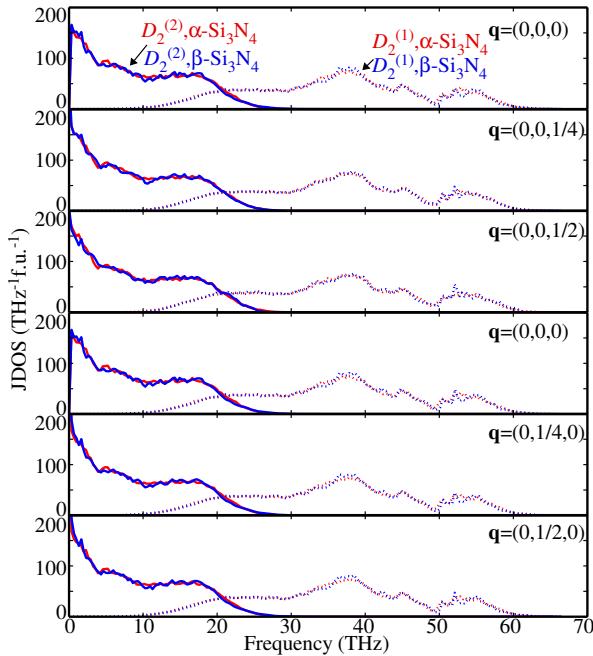


FIG. 6. (color online) JDOS of α - and γ -Si₃N₄ at different \mathbf{q} points. The first and forth rows are JDOS at the same Γ -point but calculated with the polarization for non-analytic term correction set along c^* and b^* , respectively.

As a small but interesting difference in linewidths distributions, Γ_λ below 5 THz are aligned on a single smooth

line in the α phase, while those in the β phase are scattered roughly on two lines. This difference can be explained by the vibration directions. In Fig. 7-a, the Γ_λ are classified using colors according to the sums of the squares of the eigenvector components along the \mathbf{q} ; the sum is 1 for a perfectly longitudinal wave. However, these sums have no clear contrast to distinguish the two branches in the β phase. Fig. 7-b shows the same plot as Fig. 7-a, but with colors according to the sums of the squares of the eigenvector components along the ab plane, which has 1 when the eigenvectors lie on the ab plane. There is a tendency in the β phase that Γ_λ are large for vibrations along the ab plane. Therefore, within the single-mode RTA, for the phonon modes below 5 THz, all of which belong to the acoustic phonon branches, vibration modes along the ab plane are more easily scattered in the β phase, no matter whether they are longitudinal or transverse. For the panel of β -Si₃N₄ in Fig. 7-b, a straight line can divide the phonon modes into the two groups. The numbers of the phonon modes in the upper and lower parts are 157 and 58, whose ratio is consistent to the population ratio of the vibration modes along and out of the ab plane.

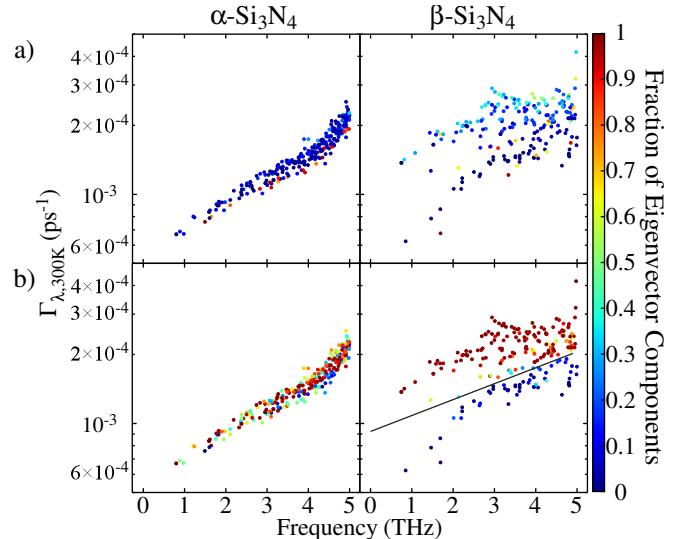


FIG. 7. (color online) Distribution of linewidths $\omega_\lambda \leq 5$ THz with colormaps with respect to strengths of eigenvector components along \mathbf{q} (a) and on a - b plane (b).

IV. SUMMARY

In the present study, we investigate the lattice thermal conductivities of the three Si₃N₄ phases, by using the lattice dynamics based on the *ab-initio* interatomic force constants. The main remarks are as follows:

1) In the α - and β -Si₃N₄, whose crystal structures are characterized by the stacking manners of the basal layer structures, which largely alter κ . In α -Si₃N₄, the κ are rather isotropic, while the κ_{zz} in the β phase is much

larger than the κ_{xx} , showing remarkable anisotropy in the κ . The κ_{xx} in the β phase is 2 times or more larger than the others κ_{ii} in the three phases.

2) In the α phase, the acoustic mode phonons below 6 THz are the main heat carriers, while in the β phase, the phonons below 12 THz contribute to the κ . The group velocities alone qualitatively explains this and the different anisotropy in κ between the α and β phases.

3) In the γ phase, the κ_{xx} is relatively small. The κ_{xx}^c is similar to that of $\beta\text{-Si}_3\text{N}_4$. Its number of heat carriers, group velocities and linewidths are much different from those of the other phases. They are not configured toward high κ_{xx} .

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Appendix A: Pressure dependence of LTC of γ -phase

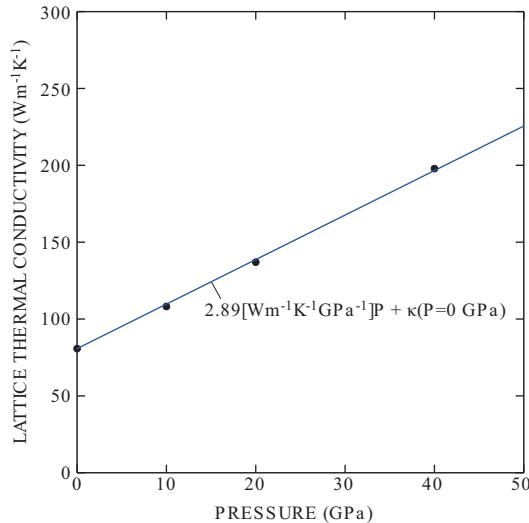


FIG. 8. (color online) Pressure dependence of LTC of $\gamma\text{-Si}_3\text{N}_4$.

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