```
%#BIBTEX bibtex Si$_3$N$_4$
\documentclass[twocolumn,amsmath,amssymb,a4paper,prb,superscriptaddress,floatfix]{revtex4-1}
\usepackage[dvipdfmx]{graphicx}
\usepackage{natbib}
\usepackage{multirow}
\usepackage{amsmath}
\usepackage{bm}
\usepackage{mathrsfs}
\usepackage{url}
\usepackage{color}
\usepackage{ulem}
\begin{document}

\title{First-principles calculation of lattice thermal
conductivities of $\alpha$-, $\beta$-, and $\gamma$-Si$_3$N$_4$}

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\begin{abstract}

~~Lattice~~ The lattice thermal conductivities of α-, β- and γ-Si$_3$N$_4$ phases are investigated from {\it 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$_3$N$_4$ is calculated as $\kappa_{xx}=73$ and $\kappa_{zz}=199$ (in units of W m^{-1}K^{-1}), ~~that~~ which is consistent with the reported experimental values of 69 and 180, respectively. For α-Si$_3$N$_4$, $\kappa_{xx}=68$ and $\kappa_{zz}=100$ are obtained. The difference ~~of~~ in anisotropy between these phases ~~is originated~~ originates from the~~ir~~ characteristic differences in their phonon band structures, which is closely related to the crystal structures. In α-Si$_3$N$_4$, acoustic-mode phonons below 6 THz are the main heat carriers~~. I~~, while in β-Si$_3$N$_4$, the phonon modes up to 12 THz contribute to the lattice thermal conductivity. In γ-Si$_3$N$_4$, $\kappa=77$ is obtained. The distribution of phonon mode contributions to the lattice thermal conductivity with respect to phonon frequency ~~is found to~~ closely resembles that for κ_{xx} of β-Si$_3$N$_4$, although the phonon lifetimes ~~of~~ for γ-Si$_3$N$_4$ are twice as ~~shorter~~ short as~~than~~ those ~~of~~ for β-Si$_3$N$_4$.

\end{abstract}

\maketitle

\section{Introduction}

Several nitride insulators are known to exhibit high thermal ~~conductivities~~ conductivity, which is~~and are~~ important for heat transfer materials at elevated temperatures. For example, Slack {\it et al.}\cite{slack} reported that wurtzite-type AlN has thermal conductivity that ~~exceeding~~ exceeds 100 W m^{-1}K^{-1}. Si$_3$N$_4$ has become another promising thermal conductive insulator because its thermal conductivity has been improved up to 177 W m^{-1}K^{-1} ~~by using~~through the use of advanced ceramic technologies related to ~~the~~ densification and microstructure control.\cite{zhou,hirao-rev,watari,hirosaki} ~~Since t~~The Si$_3$N$_4$ ceramics also exhibit high mechanical strength at elevated temperatures; therefore, 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$_3$N$_4$ has two phases, α and β, which are generally considered as low- and high-temperature phases, respectively.\cite{zhou,hirosaki-md,riley} Their crystal structures belong to the ~~space groups of~~ P31c and P6$_3$/m space groups, respectively.\cite{yashima,boulay} These structures have different manners of stacking ~~manners of~~ equivalent basal layer structures composed of SiN$_4$ tetrahedra.\cite{hampshire} ~~In~~ Fig. \ref{fig:Fig1_cryst} depicts these layer structures ~~are depicted~~ from the principal axis direction. They are denoted as A, B, C, and D in the α phase, and A and B in the β phase~~, respectively~~. The stacking manners are thus ~~as~~ ABCDABCD~~..~~… and ABAB.., respectively. The α phase has additional two layer structures of C and D, which are related to A and B by the c glide operation.\cite{hampshire} Along this direction, the lattice constant of the α phase is approximately twice as ~~longer~~ long as ~~than~~ that of the β phase.

\begin{figure}[ht]
\begin{center}
\includegraphics[width=0.90\linewidth]{Fig1_crystal_str2.eps} \caption{(color online) Crystal structures of α- and β-Si$_3$N$_4$. Stacking of SiN$_4$ tetrahedron layers are shown ~~in~~ at the left. (a) ABCDABCD~~..~~… for α-Si$_3$N$_4$. (b) ABAB~~..~~… for β-Si$_3$N$_4$. Space group diagrams\cite{inttableA} ~~in~~ for P31c (α-Si$_3$N$_4$) and P6$_3$/m (β-Si$_3$N$_4$) are shown ~~in~~ at the right.}
\label{fig:Fig1_cryst}
\end{center}
\end{figure}

The experimental thermal conductivities \cite{zhou,hirao-rev,watari,hirosaki,hirai} of the Si$_3$N$_4$ polymorphs were measured ~~on the~~for bulk polycrystalline ~~bulk~~ samples. These values were significantly affected by the lattice defects, impurities, shapes and orientations of the constituent crystal grains;\cite{hirosaki-md} the intrinsic thermal conductivity ~~intrinsic to~~ of defect-free Si$_3$N$_4$ has not been established. As an experimental approach to determine this ~~for it~~, Li {\it et al.}\cite{li} applied the high-resolution thermoreflectance microscopy ~~on~~ to single β-Si$_3$N$_4$

grains in a ceramic sample. Thei~~r analyzed~~ thermal conductivity was analyzed as 69 and 180 W m$^{-1} $K^{-1} along the a and c axes, respectively. These values respectively correspond to the xx and zz elements of the lattice thermal conductivity tensor, $\boldsymbol{\kappa}$. We consider the anisotropy of $\kappa_{zz}/\kappa_{xx}\sim 3$ is relatively large. ~~Theoretically,~~ Hirosaki {\it et al.}\cite{hirosaki-md} theoretically estimated ~~the~~ $\boldsymbol{\kappa}$ by ~~applying~~application of the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta {\it et al.}\cite{vashishta}. They calculated $\kappa$$_{xx}$ and $\kappa$$_{zz}$ of α-Si$_3$N$_4$ ~~as~~to be 105 and 225 W m$^{-1} $K^{-1}, and those of β-Si$_3$N$_4$ as 170 and 450 W m$^{-1} $K^{-1}, respectively. The ratio κ_{zz}/κ_{xx} in β-Si$_3$N$_4$ agreed well with the experimental ratio; ~~the~~ κ_{xx} and κ_{zz} were overestimated by more than two times that of the experimental $\boldsymbol{\kappa}$ ~~more than twice~~.

Based on ~~a~~ first-principles calculations and the Boltzmann transport theory\cite{phono3py}, Togo {\it{et al.}} recently calculated $\boldsymbol{\kappa}$ ~~of~~ for many polymorphs of the zincblende- and wurtzite-type structures. Their crystal structures have stacking manners of the densest atom planes as ABCABC~~..~~… and ABAB~~..~~…, respectively. The different stacking manners merely altered ~~the~~ $\boldsymbol{\kappa}$, ~~as well as~~ the phonon linewidths and the phonon density of states (DOS).\cite{phono3py}
On the other hand, the previous MD results ~~presented~~ indicated that the different stacking manners between the α and β phases altered ~~the~~ $\boldsymbol{\kappa}$ ~~largely~~significantly. This has not been explained ~~through~~ with respect to their phonon properties. ~~It~~ Therefore, it is of interest~~ing~~ to investigate this based on the first-principles anharmonic phonon calculation.

In addition to the α and β phases, a cubic spinel phase (γ-Si$_3$N$_4$) is known to form upon compression and {\it{in situ}}~~in situ~~ heating.\cite{zerr,zhang} The reported transition pressures are scattered from 10 to 36 GPa, depending on the experimental conditions.\cite{xu} The γ phase is experimentally quenched to atmospheric pressure and room temperature.

~~Its~~ The thermal conductivity of the γ phase has not been experimentally reported~~;~~, although it has been
estimated by the Slack model.\cite{morelli}

The present study aims to qualitatively ~~understand~~ elucidate the lattice thermal conductivity tensors among the three Si$_3$N$_4$ phases by ~~means of the~~a first principles approach. We calculate ~~the~~ $\boldsymbol{\kappa}$ of the γ phase as well, for systematic understanding. After the methodology section, we examine the validity of the present results ~~first~~. ~~Our~~ The calculated thermal properties are then compared with the available experimental and theoretical references. The~~n~~ ~~we investigate the~~ characteristic behaviors of ~~the~~ $\boldsymbol{\kappa}$ are then investigated in detail on the basis of the phonon band structures and phonon linewidths.

\section{Computational procedures}

\subsection{Lattice thermal conductivity calculation}

The lattice thermal conductivities were calculated by solving the linearized Boltzmann transport equation (LBTE) within the single-mode relaxation time approximation (single-mode RTA). The harmonic phonon states and lattice thermal conductivities were
calculated with the phonopy\cite{phonopy} and phono3py\cite{phono3py} software packages, respectively.
We also ~~tried~~ attempted the
direct-solution of LBTE\cite{chaput-direct} and ~~leave~~ give ~~its~~ the calculated $\boldsymbol{\kappa}$ values in the following section. The differences between ~~the~~ $\boldsymbol{\kappa}$ calculated by the single-mode RTA and that by the direct solution ~~were~~ was found to be minor for our discussion. Therefore, ~~we limited our~~ this research was limited
to use the single-mode RTA to take advantage of its intuitively closed form of $\boldsymbol{\kappa}$.

In the following sections, we denote ~~a~~ the 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 half the reciprocal of linewidth, $\tau_{\lambda,\text{ph-ph}}=(2\Gamma_\lambda)^{-1}$, where the linewidth that ~~we~~ was employed ~~in this study~~ is as follows:

\begin{align}
\label{eq:linewidth}
&\Gamma_\lambda = \frac{18\pi}{\hbar^2}
\sum_{\lambda' \lambda"}
\bigl|\Phi_{-\lambda\lambda'\lambda"}\bigr|^2 \times \nonumber \\
&\left\{ (n_{\lambda'} + n_{\lambda"}+1)
\delta(\omega_\lambda-\omega_{\lambda'}-\omega_{\lambda"}) \right.
+ \nonumber \\
&\;\;(n_{\lambda'}-n_{\lambda"})
\left[\delta(\omega_\lambda +\omega_{\lambda'}-\omega_{\lambda"})
\right.
\left. -\left. \delta(\omega_\lambda - \omega_{\lambda'}+\omega_{\lambda"})
\right]\right\}.
\end{align}

Here, ω_λ is the harmonic phonon frequency of the phonon mode λ, $n_\lambda=[\exp(\hbar\omega_\lambda/\mathrm{k_B}T)-1]^{-1}$ 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 the usual coordinate transformation of third-order force constants from direct space to phonon space.\cite{phono3py} The second- and third-order real-space force constants were obtained ~~from the~~by {\it ab- initio} calculation, ~~whose~~ of which the details are ~~written~~ given in the
next section.

~~In order t~~To more realistically compare the- calculated $\boldsymbol{\kappa}$ with the measured thermal conductivities, the isotopic scattering effect due to the natural isotope distribution was taken into account, according to the second-order perturbation theory.\cite{tamura} Using the relaxation times ~~of the~~for phonon-phonon scattering and isotopic scattering, $\tau_{\lambda,\text{ph-ph}}$ and $\tau_{\lambda,\text{iso}}$, respectively, the total relaxation time for a phonon mode, τ_{λ}, was calculated by assuming Matthiessen's rule, $1/\tau_{\lambda} = 1/\tau_{\lambda,\text{ph-ph}} +$

1/\tau_{\lambda,\text{iso}}$.

The experimental thermal conductivities in the Si$_3$N$_4$ system were measured ~~on the~~for polycrystalline samples and not ~~measured~~ from ~~any~~ single crystals. The conductivities measured ~~at~~ in a polycrystalline area were affected by various lattice defects within ~~it~~that area, such as grain boundaries, impurities, and vacancies. We crudely took them into account by ~~a~~ the relaxation time $\tau_{\lambda,\text{bs}}=L/|\mathbf{v}_\lambda|$ of a phonon boundary scattering model, where $\mathbf{v}_\lambda = \nabla_{\mathbf{q}}\omega_\lambda$ is the group velocity and L is a parameter related~~regarding~~ to the boundary mean free path. We consider $\tau_{\lambda,\text{bs}}$ as a variable parameter and partly include it ~~to~~ in the calculated $\boldsymbol{\kappa}$, according to Matthiessen's rule.

The closed form of $\boldsymbol{\kappa}$ within the RTA was obtained via

$$
\label{eq:kappa}
\boldsymbol{\kappa}(T) = \frac{1}{N_\mathbf{q}\Omega} \sum_\lambda
\tau_\lambda(T) \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda c_\lambda(T),
$$

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 $\boldsymbol{\kappa}$ in detail, ~~we calculate~~ the cumulative thermal conductivity:

$$
\label{eq:cum-kappa}
\boldsymbol{\kappa}^\text{c}(\omega) = \frac{1}{N_\mathbf{q}\Omega}
\int_0^\omega \sum_\lambda
\tau_\lambda(T) \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda
c_\lambda(T) \delta(\omega'-\omega)d\omega',
$$

and its derivative $\frac{\partial \boldsymbol{\kappa}^\text{c}(\omega)}{\partial \omega}$, were calculated to ~~see~~ determine the phonon mode contributions to $\boldsymbol{\kappa}$.

Computational details

The force constants required for the lattice dynamics were calculated using the first-principles projector augmented wave method\cite{paw} (VASP code\cite{vasp-1996,vasp-1995, vasp-1999}). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof\cite{pbe} was used for the exchange correlation potential. A plane wave energy cutoff of 500 eV was employed. The crystal structures were optimized for 0 K and 0 GPa until the residual forces acting on the constituent atoms were less than 10^{-6} eV~~/~~ AA^{-1}. ~~-~~Here, the temperature and pressure were considered only for the electronic system, and the zero point lattice vibration was not considered. The calculated lattice parameters were $a=7.808$ \AA~~~~ and $c=5.659$ \AA~~~~ for the α phase, $a=7.660$ \AA~~~~ and $c=2.925$ \AA~~~~ for the β phase, and $a=7.787$ \AA~~~~ for the γ phase, which are in agreement with the experimental data\cite{yashima,boulay,paszkowicz} within +0.7~~\~~% error~~s~~. The lattice volume optimized with the local density approximation (LDA)\cite{lda} for the exchange correlation potential was, for β-Si$_3$N$_4$, 3~~\~~% smaller than the volume optimized with GGA, which is a typical volume contraction of LDA. $\kappa_{xx}}$ and $\kappa_{zz}}$ calculated with LDA were larger by 0.3 and 2.6 ~~\~~% than those calculated with GGA. For our discussion, these differences are ~~enough~~sufficiently small~~,~~; therefore, the impact of the choice of exchange correlation potential is considered to be minor in ~~our~~ this study.

\begin{table}[ht]
\caption{\label{table:LTC} Calculated lattice thermal conductivities of α-, β-, and γ-Si$_3$N$_4$ (WK^{-1}m^{-1}) at 300 K with respect to several combinations of supercell sizes.}
\begin{ruledtabular}
\begin{tabular}{ccccc}
\multirow{2}{*}{Phase}
& \multicolumn{2}{c}{Supercell (\# of atoms)} &
\multicolumn{2}{c}{LTC} \\
\cline{2-5}
& 3^rd force constants & 2^nd force constants & xx & zz \\
\hline
\multirow{6}{*}{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 \\
  \hline
  \multirow{5}{*}{$\beta$}
  & $1\times 1\times 2$ (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 \\
  \hline
  \multirow{3}{*}{$\gamma$}
  & $1\times 1\times 1$ (56) & $1\times
  1\times 1$ (56) & \multicolumn{2}{c}{72} \\
  & $1\times 1\times 1$ (56) & $2\times
  2\times 2$ (448) & \multicolumn{2}{c}{77} \\
  & $1\times 1\times 1$ (56) & $3\times
  3\times 3$ (56) & \multicolumn{2}{c}{79} \\
 \end{tabular}
 \end{ruledtabular}
\end{table}
```

The force constants were calculated by the finite difference approach\cite{wei-supercell}. For this calculation, ~~we adopted~~ the following supercells were adopted: $1\times 1\times2$, $1\times 1\times3$, and $1\times 1\times1$ supercells of the conventional unit cells for the calculations of the third-order force constants of α, β, and γ-Si$_3$N$_4$, respectively, and $3\times 3\times4$, $3\times 3\times8$ and $2\times 2\times2$ for those of the second-order force constants. The length of the induced atomic displacements was set to 0.03 \AA. Table \ref{table:LTC} shows ~~the~~ $\boldsymbol{\kappa}$ calculated with several different sets of the supercells, which ~~indicating~~ indicates that ~~our~~ the calculated $\boldsymbol{\kappa}$ ~~is~~ has ~~reasonably~~reasonable ~~converging~~ convergence with respect to the size of the supercells.

Uniform $\mathbf{k}$-point sampling meshes of $4\times 4\times 2$, $4\times 4\times 3$, and $3\times 3\times 3$ were employed for ~~the~~ calculations of 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, a non-Γ center mesh was used. For the calculations of 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 employed to calculate $\boldsymbol{\kappa}$ in Eq.~(\ref{eq:kappa}) for the α, β, and γ phases, respectively.

Non-analytical term correction\cite{wang} was applied to the second-order force constants to take into account the long range ~~Coulomb~~ coulombic forces present in ionic crystals. For the correction, static dielectric constants and Born effective charges were calculated ~~by~~ using the density functional perturbation theory, as implemented in the VASP code\cite{vasp-lepsiron,lepsiron}.

~~We examined the~~ The effect of lattice thermal expansion on $\boldsymbol{\kappa}$ was examined. ~~For this, we~~by ~~calculated~~ the calculation of $\boldsymbol{\kappa}$ for several finite temperatures with the crystal structures optimized for the corresponding temperatures within the quasi-harmonic approximation

(QHA)\cite{dove-p76}. These $\boldsymbol{\kappa}$ were different from those calculated for the same temperatures with the structure optimized for 0 K. We consider these differences as the effect of lattice thermal expansion. ~~We found the~~Similar differences in $\boldsymbol{\kappa}$ ~~differences~~ for T=300, 600, 900, 1200, and, 1500 K within 1~~\~~%~~, similarly,~~ were determined in the case of Si and Ge\cite{ward-ltc}. For the present study, these differences are negligible and for finite temperatures ~~we adopted the~~ $\boldsymbol{\kappa}$ calculated with the structure optimized for 0 K was adopted.

~~In addition, we calculated t~~The volumetric thermal expansion coefficients were also calculated. ~~Their e~~Comparison with the experimental coefficients is useful to validate the present thermal conductivity calculation~~,~~ because the thermal expansion ~~is originated~~originates from both the anharmonicity of the interatomic potential ~~as well as~~and $\boldsymbol{\kappa}$. The calculated coefficients of the α and β phases were 4.31$\times 10^{-6}$ and 4.19$\times 10^{-6}$ K^{-1} for 300 K, while the experimental values\cite{minikayev-alpha} ~~are~~ were 3.75$\times 10^{-6}$ and 3.55$\times 10^{-6}$ K^{-1}. The calculation reproduced the experimental tendency that the α phase has a slightly larger thermal expansion coefficient than the β phase. This supports ~~that~~ the validity of the present calculation ~~enables us~~ to qualitatively compare the calculated $\boldsymbol{\kappa}$ among the Si$_3$N$_4$ phases.

~~In order t~~To compare the microscopic phonon properties among the three phases ~~at~~under the same conditions, ~~those~~ the 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 pressure~~s~~, ~~we calculated~~ $\boldsymbol{\kappa}$ of the γ phase was calculated at 10, 20, and 40 GPa, as shown in Fig.~\ref{fig:S1}. The phenomenological ~~behaviour~~behavior of the linear dependence of $\boldsymbol{\kappa}$ with respect to the pressure was reproduced, ~~as~~ similar to that in Ref.~\onlinecite{andersson-pressure}. The slope was 2.89 W m^{-1}K^{-1}GPa^{-1} for the γ phase. ~~By~~ From this dependence, we consider that the microscopic values are also varied smoothly with the pressure

and those at 0 GPa are valuable ~~to be~~for ~~compared~~ comparison with the corresponding values of the α and β phases.

\subsection{Direct solution of LBTE}

The ~~merit to~~advantage of employing the single-mode RTA for thermal conductivity calculations is the closed form, by which ~~we can intuitively understand~~ the qualitative character of $\boldsymbol{\kappa}$ can be intuitively understood in terms of the phonon-mode specific properties. The microscopic understanding of the full solution of LBTE is still under ~~the~~ development,\cite{cepellotti-relaxons} and the microscopic picture based on collective phonons\cite{hardy-collective} will require more complicated investigation.

~~It is known that the s~~Single-mode RTA solutions of LBTE often underestimate~~s~~ the full solution.\cite{mukhopadhyay-ltc,ward-ltc} To check ~~the~~ this underestimation, ~~we calculated~~ $\boldsymbol{\kappa}$ ~~of~~ for the α and β phases were calculated by ~~a~~ the direct solution of LBTE\cite{chaput-direct}, which is one of the methods of LBTE full solutions. ~~Their~~ κ_{xx} and κ_{zz} without the isotope effect were 69 and 102 W m$^{-1} $K^{-1} for~~-~~ the α phase, and 76 and 238 W m$^{-1} $K^{-1} for the β phase, respectively, while the corresponding single-mode RTA values were 70 and 102 W m$^{-1} $K^{-1} for the α phase, and 76 and 210 W m$^{-1} $K^{-1} for the β phase. ~~The~~ κ_{zz} for the β phase ~~of~~ from the direct solution ~~in the β phase~~ was 13~~\~~% larger than that of the single-mode RTA solution. ~~Since t~~The differences in $\boldsymbol{\kappa}$ between the LBTE solutions are not significant; therefore, we expect that the physics ~~on~~ of ~~those~~ these lattice thermal conductivities ~~is~~ can be well understood within the single-mode RTA ~~in~~ at the current level of our interest. Therefore, we discuss the lattice thermal conductivities calculated by the single-mode RTA solution.

\section{Results and discussion}

\subsection{Lattice thermal conductivities}

\begin{table}[ht]
\caption{\label{table:LTC-exp} Calculated thermal conductivities of α-Si$_3$N$_4$ (trigonal), β-Si$_3$N$_4$ (trigonal), and γ-Si$_3$N$_4$ (cubic) at 300 K in units of W m^{-1} $K^{-1}, compared with the experimental and theoretical reference 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.}

\begin{ruledtabular}
\begin{tabular}{ccccccccc}
& \multicolumn{3}{c}{This work} & \multicolumn{3}{c}{Ref. Theor.}
& \multicolumn{2}{c}{Ref. Expt.} \\
\cline{2-9}
& κ_{xx} & κ_{zz} & B & κ & κ_{xx} & κ_{zz} & κ_{xx} & κ_{zz} \\
\hline
α-Si$_3$N$_4$ & 68 & 100 & 224 & 70\footnotemark[1] & 105\footnotemark[2] & 225\footnotemark[2] & - & - \\
β-Si$_3$N$_4$ & 73 & 199 & 237 & 250\footnotemark[1] & 170\footnotemark[2] & 450\footnotemark[2] & 69\footnotemark[3] & 180\footnotemark[3] \\
γ-Si$_3$N$_4$ & 77 & - & 296 & 80\footnotemark[1] & - & - & - & -
\footnotetext[1]{Ref.~\onlinecite{morelli}, Slack model.}
\footnotetext[2]{Ref.~\onlinecite{hirosaki-md}, molecular dynamics (Green-Kubo).}
\footnotetext[3]{Ref.~\onlinecite{li}, single crystalline grains of poly-crystals.}
\end{tabular}
\end{ruledtabular}
\end{table}

Table \ref{table:LTC-exp} shows the calculated $\boldsymbol{\kappa}$ for 300 K. β-Si$_3$N$_4$ has a markedly more anisotropic $\boldsymbol{\kappa}$ than α-Si$_3$N$_4$. The directional averages $\sum_i \kappa_{ii}/3$, are 79, 115, and 77 W m^{-1} $K^{-1} for the α, β, and γ phases, respectively. The value of for the γ phase is similar to that of for the α phase, in despite ofthe comparatively large difference among the bulk moduli (B) that are also shown

in Table \ref{table:LTC-exp}.

Table \ref{table:LTC-exp} also lists the previously reported experimental\cite{li} and theoretical\cite{hirosaki-md} $\boldsymbol{\kappa}$ for ~~the~~ reference~~s~~.~~-~~ The theoretical results\cite{morelli} of the Slack model, which do not include the anisotropy in $\boldsymbol{\kappa}$, are shown as κ in Table \ref{table:LTC-exp}.~~-~~ ~~For the β phase, compared~~ Compared to ~~the~~ $\boldsymbol{\kappa}$ ~~of the~~from ~~molecular dynamics~~MD\cite{hirosaki-md}, our $\boldsymbol{\kappa}$ for the β phase has ~~agrees~~ better agreement with the experimental $\boldsymbol{\kappa}$.
~~Also, c~~Compared to ~~the~~ κ ~~of~~ from the Slack model, our directional average $\sum_i \kappa_{ii}/3$ is also much closer to the experimental average.

Fig.~\ref{fig:Fig1_338} shows the theoretical $\boldsymbol{\kappa}$ ~~of~~ for the α and β phases as a function of T, together with the reference experimental data\cite{hirosaki,hirai}. The experimental thermal conductivities for a series of temperatures were measured on polycrystalline areas by the laser flash method. These thermal conductivities (denoted as $\kappa_\mathrm{polycrystal}$) cannot be directly compared with the calculated intrinsic $\boldsymbol{\kappa}$, because they are largely ~~depended~~ dependent on the microstructure of the samples~~: T~~; they ~~were~~ deviate~~d~~ 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~~ the parameter $0\le{w}\le{1}$ and fitting the quantity $w\kappa_{xx} + (1-w) \kappa_{zz}$ to the experimental $\kappa_\mathrm{polycrystal}$ by the least squares method. We regard ~~it as~~this as theoretical $\kappa_\mathrm{polycrystal}$.

\begin{figure}[ht]
 \begin{center}
  \includegraphics[width=0.90\linewidth]{Fig1_m1010.eps} \caption{(color online) ~~Temperature d~~Dependence~~s~~ of thermal ~~conductivities~~ conductivity on the temperature for α- and
  β-Si$_3$N$_4$. For β-Si$_3$N$_4$, theoretical conductivities with the boundary scattering effect are shown by broken lines. Theoretical $\kappa_\mathrm{polycrystal}$
  (see ~~in~~ text) for the β-Si$_3$N$_4$ sample are

also shown ~~to be compared~~for comparison with the experimental conductivities.}
\label{fig:Fig1_338}
\end{center}
\end{figure}**[Fig. edit: Capitalize only first letter of first word in axis captions (e.g., Lattice thermal conductivity). Space units correctly (W m^{-1} K^{-1}). Change "theo." to "Theor.".]**

In Fig.~\ref{fig:Fig1_338}, ~~the~~ κ_{ii} calculated without $\tau_{\lambda,\text{bs}}$ are ~~nearly~~ almost proportional to T^{-1} because n_λ in Eq.~(\ref{eq:linewidth}) can be reduced to $\frac{\mathrm{k_B}T}{\hbar\omega_\lambda}-\frac{1}{2}$. In Fig.~\ref{fig:Fig1_338}~~-~~(a), the experimental $\kappa_\mathrm{polycrystal}$ of a chemically vapor-deposited α-Si$_3$N$_4$ sample\cite{hirai} is not proportional to T^{-1} and intersects the theoretical κ_{ii}. ~~-~~Thus, w does not adjust the theoretical $\kappa_\rm{polycrystal}$ to the experimental $\kappa_\rm{polycrystal}$. ~~-~~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 could not explain the discrepancy ~~as well~~either. A L value of 0.6 μm, which was much smaller than the experimental grain size\cite{hirai} of 10 μm, decreased the theoretical $\kappa$$_{ii}$ ~~in~~ at the low temperature side toward the experimental values; however, ~~but the~~ $\kappa$$_{ii}$ ~~in~~ at the high temperature side continued to be ~~severely~~significantly smaller than the experimental values. At present, the reason for the discrepancy between the theoretical and experimental behavior~~s~~ is unclear. ~~-~~Although the crystal structure of the experimental sample was characterized as α-Si$_3$N$_4$, significant lattice defects ~~existed~~ were present in the sample, as pointed out by Hirosaki {\it et al.}\cite{hirosaki-md}, ~~and~~ so that the simple phonon boundary scattering model may fail to describe their effects on the $\kappa_\mathrm{polycrystal}$.

For the β phase, the experimental $\kappa_\mathrm{polycrystal}$ is located in-between the theoretical $\kappa$$_{xx}$ and~~-~~ $\kappa$$_{zz}$ curves, being ~~nearly~~almost proportional to T^{-1}. Simple directional averages of the theoretical κ_{ii} slightly underestimate these experimental values.~~-~~ This is understood from the ~~fact that~~control of the microstructure ~~was controlled~~ to increase ~~the~~

$\kappa_\mathrm{polycrystal}$, and the crystalline grains were selectively grown along the c axis of the most conductive direction.\cite{hirosaki} The theoretical $\kappa_\mathrm{polycrystal}$ was fit well with $w=0.44$ ~~-~~to the experimental data. ~~-~~For the effects of lattice defects, most of which were grain boundaries, ~~we included~~ $\tau_{\lambda,\text{bs}}$ was included with $L=0.6$ μm to further fit the theoretical curve ($w=0.33$) to the experimental data.~~ -~~ ~~The~~ L ~~value~~ is slightly smaller than the average grain size\cite{hirosaki} of 2 μm in the experiment; therefore, the discrepancy can presumably be explained by the presence of other ~~existing~~ lattice defects than by the grain boundaries.

\subsection{Dispersion curves}

~~Figure~~ Fig. \ref{fig:Fig4_ver5_338} shows ~~the~~ phonon band diagrams ~~of~~ for the three Si$_3$N$_4$ phases. The branches are classified according to their symmetry group~~, s by~~ using different colors and line styles. The ~~full~~ solid and ~~broken~~ dashed lines are used ~~for~~ to represent degenerate and non-degenerate modes, respectively. ~~The entire~~All of the band diagrams are almost identical to those reported earlier\cite{kuwabara,xu} and thus are not shown.~~ -~~ Here we investigate the frequency gradients, the group velocities projected on the paths~~. We especially~~, with particular focus on their anisotropy in the α and β phases. This was not investigated ~~by~~ in the previous works.

\begin{figure}[ht]
 \begin{center}
  \includegraphics[width=0.90\linewidth]{Fig4_ver5_338_resize2_woDOS_color_simplified.eps}
   \caption{(color online) Calculated phonon band
                diagrams (top) for three Si$_3$N$_4$ phases and Brillouin-zones (bottom).
  \label{fig:Fig4_ver5_338} }
 \end{center}
\end{figure}

~~Because t~~The α phase unit cell contains two times more basal layer structures than the β phase unit cell; therefore, the edge of the α phase Brillouin zone in ~~the~~ stacking direction A is half as far as that of the β phase. The number of phonon branches in the α phase are twice ~~more than~~

that in the β phase. ~~In general, p~~Phonon branches ~~being~~ that are adjacent in frequency and belong~~ing~~ to the same symmetry group generally show a band gap, and an anticrossing occurs when they are close to each other. If we regard the α phase lattice as a superlattice of the β phase lattice, then the phonon branches of the α phase in Fig.~\ref{fig:Fig4_ver5_338~~}~~}(a) are produced by folding the phonon branches of the β phase at the perpendicular bisector plane of ΓA. Taking for example the folding of the acoustic phonon branch, in Fig.~\ref{fig:Fig4_ver5_338~~}~~}(a), an upper branch that ~~belonging~~ belongs to the same symmetry group is located very close in frequency, which inevitably ~~entailing~~ entails an anticrossing and a band gap between them. This explains why the folded branch, which is degenerate at A with the acoustic branch due to the non-symmorphic symmetry, can not increase its frequency as it goes back on ΓA in Fig.~\ref{fig:Fig4_ver5_338~~}~~}(a).~~-~~ The band gap and anticrossings ~~creations~~ are reported in the theoretical study on the lattice thermal conductivities of GaAs/AlAs superlattices.\cite{GaAs/AlAs} It is interesting that these effects occur~~,~~ in the present system, due to the stacking manners of the unit structures composed of the same elements.

As a result, in Fig.~\ref{fig:Fig4_ver5_338~~}~~}(a), the acoustic phonon branches increase their frequencies similarly between these paths. In contrast, the corresponding frequencies in Fig.~\ref{fig:Fig4_ver5_338~~}~~}(b) increase much more from Γ to A than from Γ to K. ~~-~~The anisotropic frequency increments indicate ~~the~~ an anisotropic $\mathbf{v}_\lambda$. Compared with the α and γ phases, the β phase shows significantly steep slopes for the low frequency optical phonon branches on ΓA~~. This~~, which indicates that $\rm{v}_{\lambda,z}$ of these phonon modes are large. The anisotropic $\mathbf{v}_\lambda$ of the acoustic and low~~-~~frequency optical phonons will be investigated further in the following sections.

In the γ phase, the longitudinal acoustic branches ~~keep~~ maintain linear dispersion at higher frequencies than in the other phases. ~~-~~The gradients of ω_λ for the γ phase are the largest among the three phases, as expected by the largest B. **[Is this your intended meaning?]**

\subsection{ω_λ contour map on the reciprocal plane}

\begin{figure}[ht]
\centerins
\includegraphics[width=\linewidth]{Fig2_small.eps} \caption{(color
online) Contour maps of phonon frequency (THz) on the b^*c^*
planes of Brillouin -zones. The ~~coordination~~ coordinates in the reciprocal plane
are in units of 10^{-2} \AA^{-1}. The maps for the four lowest- frequency
phonon modes are shown. The frequency landscapes are formed by simply
connecting the frequencies of the same band indices, assigned ~~by~~in
ascending order of frequency at the respective $\mathbf {q}$
points. \label{fig:Fig3_338} }
\centering
\end{figure}**[Fig. edit: Change "band" to "Band".]**

We investigate the anisotropy in ~~the~~ $\mathbf{v}_{\lambda}$ of the α- and
β-Si$_3$N$_4$ ~~by~~ phases using another geometry, ~~that is~~i.e., a cross-section of the
Brillouin-zone. -Fig.~\ref{fig:Fig3_338} shows contour maps of
ω_{λ}- on the b^*c^* plane. We show the maps for the four
lowest-frequency bands~~,~~ because they contribute significantly to ~~the~~
$\boldsymbol{\kappa}$, which will be confirmed in the next section. There were
negligible differences between the distributions on the b^*c^* plane and the
other planes containing the c^* axis.- ~~Thus~~ Therefore, ~~we select~~ the b^*c^* plane was selected
as a
representative plane.- In the α phase, the ω_{λ} distributions and
thus $\mathbf{v}_{\lambda}$ are ~~nearly~~ almost isotropic. In the β phase, the
contours are rather parallel to the b^* axis, and thus the
$\mathbf{v}_{\lambda}$ tends to orient toward the c^* axis direction. This
confirms the large anisotropy of ~~the~~ $\mathbf{v}_{\lambda}$ ~~of the β phase~~
~~for~~ of the acoustic and low-frequency optical phonon branches for the β phase.

\subsection{Frequency -distributions of phonon properties}

\begin{figure*}[ht]
\begin{center}

\includegraphics[width=0.9\linewidth]{figure_dos_jdos_kc_m1010_dos_wo_arrows_bw.eps}

\caption{(color online) Microscopic phonon properties of three Si$_3$N$_4$ phases. (a) Cumulative thermal conductivity $\boldsymbol{\kappa}^\text{c}$ and its frequency derivative ~~(a)~~, (b) DOS as $g(\omega)$ ~~(b)~~, (c) DOS weighted with $\mathbf{v}_\lambda \otimes \mathbf{v}_\lambda$ as $\boldsymbol{h}(\omega)$ ~~(c)~~, and (d) scatter plots of linewidths and phonon frequencies, $(\Gamma_\lambda,\omega_\lambda)$, (d).
\label{fig:Fig5_338_rev} }
\end{center}
\end{figure*}**[Fig. edit: Space units correctly (W m^{-1} K^{-1}, etc.).]**

~~We have investigated in~~ In the previous two sections, we have investigated the anisotropy in ~~the~~ $\mathbf{v}_\lambda$, which may explain the anisotropy in ~~the~~ $\boldsymbol{\kappa}$. Here we examine which phonon frequencies and which terms in the RTA closed form characterize the behavior~~s~~ of the present $\boldsymbol{\kappa}$. In the following, we disregard the term of mode heat capacity ~~since~~ because it is approximately constant for 300 K.
For simplicity, ~~T~~the effects of ~~the~~ isotope scattering and boundary scattering are not considered ~~for simplicity~~.
For the investigation, the cumulative thermal conductivity, $\boldsymbol{k}^c(\omega)$ in Eq.(\ref{eq:cum-kappa}), ~~as well as~~and its derivative~~,~~ $d\boldsymbol{\kappa}^c/d\omega$, are shown at the top of Fig.~\ref{fig:Fig5_338_rev}.~~-~~ From this figure, ~~we clearly find~~it is evident that~~,~~ in the α, β, and γ phases, the phonon modes with their frequencies up to ~~$\sim$~~ca. 6, ~~$\sim$~~12 and ~~$\sim$~~10 THz largely contribute to ~~the~~ each respective $\boldsymbol{\kappa}$. The frequencies shown in the contour maps in Fig.~\ref{fig:Fig3_338} are within these frequency ranges, and thus ~~we~~ it is confirmed that ~~those~~ these bands make a significant~~ly~~ ~~contribute~~ contribution to ~~the~~ $\boldsymbol{\kappa}$.

Assuming that τ_λ and $\mathbf{v}_\lambda$ are constant, then $d\kappa_{ii}^c/d\omega$ (ii=xx,zz) are proportional to the phonon ~~density of states (~~DOS~~)~~:

\begin{align}
\label{eq:dos}
g(\omega) = \frac{1}{N_\mathbf{q}\Omega}
\sum_\lambda

\delta(\omega-\omega_{\lambda}).
\end{align}

In this context, we view $g(\omega)$ as frequency distributions of heat carrier density. Alternatively, assuming that only τ_λ is constant, then $d\boldsymbol{\kappa}^c/d\omega$ is proportional to:

\begin{align}
\label{eq:wdos}
\boldsymbol{h}(\omega) = \frac{1}{N_\mathbf{q}\Omega}
\sum_\lambda
\mathbf{v}_\lambda \otimes \mathbf{v}_\lambda
\delta(\omega-\omega_{\lambda}),
\end{align}

from which we examine the impacts of both of ~~the~~ $\mathbf{v}_\lambda$ and the heat carrier density. ~~-~~$g(\omega)$ and~~-~~ $\boldsymbol{h}(\omega)$ are shown in Figs.~\ref{fig:Fig5_338_rev~~)~~}(b) and (c).~~-~~ As for the frequency variation of $\tau_{\lambda,ph-ph}$, the phonon linewidths are shown as scatter plots of $(\Gamma_\lambda,\omega_\lambda)$ in Fig.~\ref{fig:Fig5_338_rev~~)~~}(d).

~~Comparing~~ Comparison of~~between~~ the α and β phases~~,~~ indicates their linewidth distributions are qualitatively similar, except for a striking difference below ~~$\sim$~~ca. 5 THz, which will be examined later. The markedly different $d\kappa_{ii}^c/d\omega$ between the two phases are therefore ascribed to the corresponding h_{ii}. ~~Moreover, because t~~The overall spectral shapes of $g(\omega)$ are also similar between the two phases~~,~~; therefore, $\mathbf{v}_\lambda$ alone accounts for the different behavior~~s~~ of ~~the~~ $d\kappa_{ii}^c/d\omega$. ~~Thus~~It is thus ~~we~~ concluded that the different anisotropy in $\boldsymbol{\kappa}$ ~~is~~can be qualitatively explained by the different $\mathbf{v}_\lambda$~~,~~ due to the folding effects of the band gaps and anticrossings. In contrast ~~to this~~, ~~in the case of~~for the zincblende and wurtzite structures, the group velocities are suggested to be similar from their band structures\cite{phono3py}~~,~~ because the anticrossings are not created by ~~the~~ folding, as the optical branches are located at much higher frequencies than in the present system. This must result in ~~the~~ similar $\boldsymbol{\kappa}$ between these structures, irrespective of the stacking manner~~s~~.

The γ phase has much different ~~-~~$g(\omega)$, $\boldsymbol{h}(\omega)$, and, Γ_λ from the other phases, as expected from the large differences in their crystal structures. The most significant difference is in ~~its~~ the phonon linewidths. Below ~~$\sim$~~ca. 10 THz, ~~they~~ the phonon linewidths are approximately twice as ~~larger~~ large as~~than~~ those of the other phases. We will examine this in detail~~s~~ later. ~~-~~As a result, ~~the~~ $d\kappa_{xx}^c/d\omega$ ~~shows~~ has relatively low intensities. ~~Since t~~The longitudinal acoustic phonon branch increases its frequencies ~~much~~significantly, as we have examined in the band diagram; therefore, $d\kappa_{xx}^c/d\omega$ rather gradually attenuates as the frequency increases, occasionally resembling ~~to~~ $d\kappa_{xx}^c/d\omega$ of the β phase.

~~It is left curious that t~~The similar linewidths ~~are similar~~ between the α and β phases remains a curiosity, although their group velocities ~~show~~ have marked differences ~~between them~~.~~-~~ ~~In a~~Analog~~y~~ous to the report by Lindsay {\it et al.}\cite{Lindsay}, we can say that Γ_λ in the present form is ~~depends~~ dependent on the phase space for the available two phonons, $\{\lambda', \lambda"\}$, and is also ~~depends~~ dependent on $|\Phi_{\lambda\lambda'\lambda"}|^2$. We examine these terms one-by-one. A distribution of two-phonon configurations is represented as a joint ~~density of states~~DOS (JDOS), ${D_2(\mathbf{q},\omega~~)}$~~,)}~~$:

\begin{align}
\label{eq:jdos}
&D_2(\mathbf{q},\omega) = D_2^{(1)}(\mathbf{q},\omega) + D_2^{(2)}(\mathbf{q},\omega),
\end{align}

where

\begin{eqnarray*}
D_2^{(1)} &=& \frac{1}{N_\mathbf{q}Z^2} \sum_{\lambda'\lambda"}\Delta(-\mathbf{q} + \mathbf{q'} + \mathbf{q"}) \nonumber \\
&\times& [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda"}) + \delta(\omega - \omega_{\lambda'} + \omega_{\lambda"})],\\
D_2^{(2)} &=& \frac{1}{N_\mathbf{q}Z^2} \sum_{\lambda'\lambda"}\Delta(-\mathbf{q} + \mathbf{q'} + \mathbf{q"}) \nonumber \\
&\times&

\delta(\omega - \omega_{\lambda'} - \omega_{\lambda"}),
\end{eqnarray*}
with Δ($\mathbf{x}$) giving 1 if $\mathbf{x}$ is a reciprocal lattice vector, and otherwise zero. Z is the number of formula units in the primitive unit cell and is included as a scaling factor to compare JDOS for ~~the~~ structures with different Z.~~-~~ The equation of the linewidth in Eq.~(\ref{eq:linewidth}) contains terms of $(n_{\lambda'}+n_{\lambda"}+1)$ and $(n_{\lambda'}-n_{\lambda"})$. Thus, in more rigorous study, instead of $D_2^{(1)}$ and $D_2^{(2)}$,~~-~~ we should employ weighted JDOS with these terms.~~-~~ We firstly employ the JDOS in Eq.~(\ref{eq:jdos}) to intuitively examine the similarity between the linewidths of the α and β phases. The weighted JDOS (WJDOS) will be briefly shown later, including that of the γ phase.

Fig.~\ref{fig:Fig6_338} shows frequency-functions of JDOS at several different $\mathbf{q}$-points. They have very weak $\mathbf{q}$-point dependences. ~~At~~ In the low~~-~~frequency region up to $\simeq$ 10 THz, $D_2^{(1)}$ is dominant between the two terms. ~~The~~ $D_2^{(1)}$ are similar between the phases.~~-~~ In the present Si$_3$N$_4$ system, the phonon modes of the acoustic and low-frequency optical branches, which largely contribute to ~~the~~ $\boldsymbol{\kappa}$, are ~~much~~ significantly fewer than the other phonon modes.~~-~~ The JDOS are mainly determined by the latter majorities.
As in the band diagrams, the branches of the majorities are rather flat. ~~Thus~~ Therefore, ~~we can approximately disregard~~ in Eq.~(\ref{eq:jdos}) the dependences of the $\omega_{\lambda'}$ and $\omega_{\lambda"}$ on the $\mathbf{q}'$ and $\mathbf{q}"$~~.~~ can be approximately disregarded. **[This means something like "partially disregarded". Is that your intended meaning? Or do you mean you obtain an approximation by (fully) disregarding the dependences? If so, just "disregarded" (and it is clear that you are obtaining an approximation).]** In this case, $D_2^{(1)}$ is simplified to the half part ($\omega \geq 0$) of the auto-correlation function of DOS. The DOSs for both ~~of~~ the α and β phases in Fig.~\ref{fig:Fig5_338_rev~~)~~}(a) have a frequency gap. The $D_2^{(1)}$ reflect this DOS feature, dropping suddenly around 0 THz ~~and showing~~with a small shoulder around 5 THz, which ~~corresponding~~ corresponds to the
width of the gap. ~~Because t~~The gap originates~~is originated~~ from the local modes of the ~~planer~~ planar NSi$_3$ that ~~composing~~ compose each of the α and β crystal structures~~,~~;\cite{kuwabara} therefore, the ~~the~~ $D_2^{(1)}$ are similar in these phases.

\begin{figure}[ht]
\centering
\includegraphics[width=0.9\linewidth]{figure_jdoss.eps} \caption{(color online) JDOS of α- and β-Si$_3$N$_4$ at different $\mathbf q$ points. The first and fourth rows are JDOS at the same Γ-point but calculated with the polarization for the non-analytic term correction set along c^* and b^*, respectively. \label{fig:Fig6_338} }
\centering
\end{figure}**[Fig. edit: Space units correctly (THz^{-1} f.u.$^{-2}$).]**

~~The WJDOS are shown in~~ Fig.~\ref{fig:Fig_wjdos} shows the WJDOS.~~—~~ The terms that correspond~~ing~~ to $D_2^{(1)}$ and $D_2^{(2)}$ are denoted as $N_2^{(1)}$ and $N_2^{(2)}$, respectively. They are weighted $D_2^{(1)}$ and~~-~~ $D_2^{(2)}$ with $(n_{\lambda'}-n_{\lambda"})$ and $(n_{\lambda'}+n_{\lambda"}+1)$, respectively. For the comparison among the three phases, we only show the frequency distributions at $\mathbf{q}=(0,0,0)$ because the $\mathbf{q}$ dependence~~s~~ of the WJDOS ~~were~~ was as weak as that for the JDOS.~~-~~ The weighting factors reduce ~~the~~ $N_2^{(1)}$ near 0 THz and enhance ~~the~~ $N_2^{(2)}$ in the high frequency range. The latter reduces ~~the~~ $d\boldsymbol{\kappa}^c/d\omega$ in the high frequency range~~,~~ for all the phases. The total WJDOSs are similar between the α and β phases. The γ phase has slightly small intensities of the total WJDOS below ~~$\sim$~~ca. 10 THz.

\begin{figure}[ht]
\centering
\includegraphics[width=0.9\linewidth]{Fig_wjdos.eps} \caption{(color online) Comparison of WJDOS among the three phases at $\mathbf{q}=(0,0,0)$ ~~for~~ and 300 K~~ among the three phases~~.
} \label{fig:Fig_wjdos}
\centering
\end{figure}**[Fig. edit: Space units correctly (THz^{-1} f.u.$^{-2}$).]**

\begin{table}[ht]
\caption{\label{table:aveavepp} Averages of

```
$|\Phi_{\lambda\lambda'\lambda"}|^2$ over frequency ranges of
$\omega_\lambda$ (0--15 and 0--35 THz) and all ($\lambda'$,$\lambda'$). The
values are in units of 10$^{-9}$ eV$^2 $f.u.$^{2}$.}
\begin{ruledtabular}
\begin{tabular}{cccc}
\multirow{2}{*}{Frequency ~~Range~~ range (THz)}
& \multicolumn{3}{c}{Phase} \\
\cline{2-4}
& $\alpha$ & $\beta$ & $\gamma$ \\
\hline
\multirow{1}{*}{0--15}
& 1.1 & 1.1 & 2.3 &
\multirow{1}{*}{0--35}
& 5.2 & 5.2 & 4.6 &
\end{tabular}
\end{ruledtabular}
\end{table}

As for $|\Phi_{\lambda\lambda'\lambda"}|^2$, in Table.~\ref{table:aveavepp},
they are averaged over two ~~kinds of~~ frequency ranges of 0--15 or 0--35 THz for
$\omega_\lambda$ and all indices in $\lambda'$ and $\lambda"$.~~-~~ The averages
are very similar ~~values between~~for the $\alpha$ and $\beta$ phases. With the
similar impact~~s~~ of the (W)JDOS and $|\Phi_{\lambda\lambda'\lambda"}|^2$, the
linewidths in these phases are also similar.~~-~~ For the $\gamma$ phase, the large
$|\Phi_{\lambda\lambda'\lambda"}|^2$ is attributed to the large linewidths. ~~We set~~
~~t~~The frequency ranges for $\omega_\lambda$ were set so that the narrower frequency range
approximately corresponds to the range where the phonon modes largely contribute
to ~~the~~ $\boldsymbol{\kappa}$. A small change in the frequency range~~s~~ by a few
~~THz~~ terahertz did not change the qualitative characteristics of the averages.

\begin{figure}[ht]
\centering
\includegraphics[width=\linewidth]{figure_analyze_gamma3_m1010_print.eps} \caption{(color
online) Distribution of linewidths $\omega_\lambda$ $\leq$ 5 THz
shown ~~with~~ in color~~s~~ with respect to the strengths of the eigenvector
components along (a) $\mathbf q$ ~~(a)~~
```

and (b) on the ab plane (b).} \label{fig:Fig7_338}

\centering

\end{figure}**[Fig. edit: "Fraction of eigenvector components".]**

Finally, we examine the exceptional, but striking difference in the linewidth distributions between the α and β phases:. In the α phase, Γ_λ below $\sim$ca. 5 THz are aligned on a single smooth line, while in the β phase, they are scattered roughly on two branches. This difference is was investigated by trying an attempt to relate the linewidths with to the directions of the atomic vibrations of the phonon modes. Fig.~\ref{fig:Fig7_338} enlarges the $(\Gamma_\lambda,\omega_\lambda)$ plots in this frequency range. In Fig.~\ref{fig:Fig7_338}) }(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 show no clear contrast between the two branches in the β phase. Fig.~\ref{fig:Fig7_338}) }(b) shows the same plot as Fig.~\ref{fig:Fig7_338}) }(a), but with colors according to the sums of the squares of the eigenvector components along the ab plane, which is 1 when the eigenvector lays lies onin the ab plane. There is a tendency in the β phase that Γ_λ are large for atomic vibrations along the ab plane. This means that; therefore, the vibration modes along the ab plane, that belonging to the acoustic phonon branches, are more easily scattered in the β phase, no matter whetherregardless of whether they are longitudinal or transverse. For the panel of β-Si$_3$N$_4$ in Fig.~\ref{fig:Fig7_338}) }(b), a straight line splits the phonon modes into two groups. The numbers of the phonon modes assigned to the larger and smaller Γ_λ groups are 157 and 58, whose of which the ratio is confirmed to be close to the population ratio of the vibration modes along and out of the ab plane.

\section{Summary}

In the present study, we investigate the lattice thermal conductivities of the three Si$_3$N$_4$ phases, were investigated by using the lattice dynamics based on the first-principles interatomic force constants. The main remarks are as follows:

1) In the α- and β-Si$_3$N$_4$, whose of which the crystal structures are

characterized by the stacking manners of the basal layer structures, which largely alter $\boldsymbol{\kappa}$, is largely altered due to the folding effects of the band gaps and anticrossings. This is in contrasts with the case of the zincblende and wurtzite structures in the previous study\cite{phono3py}. The $\boldsymbol{\kappa}$ of for α-Si$_3$N$_4$ is rather isotropic, while the $\kappa$$_{zz}$ of for the β phase is twice or more larger than the other κ_{ii} of 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 $\boldsymbol{\kappa}$. Their group velocities are confirmed to characterize the behaviourbehaviors of $\boldsymbol{\kappa}$.

3) In the γ phase, the frequency distribution of the phonon mode contributions to $\boldsymbol{\kappa}$ is similar to that for κ_{xx} of β-Si$_3$N$_4$. Its , which is attributed to its large phonon-phonon scattering strength and steep longitudinal acoustic branches attribute to this.

\section*{ACKNOWLEDGMENTS}

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\appendix

\section{Pressure dDependence of the lattice thermal conductivity of γ-phase on pressure }

\begin{figure}[ht]

\begin{center}

\includegraphics[width=0.80\linewidth]{S1.eps} \caption{(color online) Pressure dependence of lLattice thermal conductivity of γ-Si$_3$N$_4$ as a function of pressure. \label{fig:S1} }

\end{center}

\end{figure}**[Fig. edit: Change axis captions from all capitals to on the first letter of the first word as uppercase capital. Change “FIG. 9.” to “FIG. S1.” or “FIG. A1.”]**

\bibliography{Si3N4}

\end{document}