

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

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

## I. INTRODUCTION

Several nitride insulators are known to exhibit high thermal conductivity, which is important for heat transfer materials at elevated temperatures. For example, Slack *et al.*<sup>1</sup> reported that wurtzite-type AlN has thermal conductivity that exceeds  $100 \text{ W m}^{-1} \text{ K}^{-1}$ .  $\text{Si}_3\text{N}_4$  has become another promising thermal conductive insulator because its thermal conductivity has been improved up to  $177 \text{ W m}^{-1} \text{ K}^{-1}$  through the use of advanced ceramic technologies related to densification and microstructure control.<sup>2–5</sup> The  $\text{Si}_3\text{N}_4$  ceramics also exhibit high mechanical strength at elevated temperatures; therefore, they are regarded as ideal materials for use in various applications, such as engine components, gas turbines, and heat sink substrates of power semiconductor devices.

At atmospheric pressure,  $\text{Si}_3\text{N}_4$  has two phases,  $\alpha$  and  $\beta$ , which are generally considered as low- and high-temperature phases, respectively.<sup>2,6,7</sup> Their crystal structures belong to the  $P31c$  and  $P6_3/m$  space groups, respectively.<sup>8,9</sup> These crystal structures are made of layers that stack along  $c$ -axis. Each layer is composed of  $\text{SiN}_4$  tetrahedron units, which is equivalent between these two phases. However, their manners of the stackings are different.<sup>10</sup> Fig. 1 depicts these layer structures from the principal axis direction. They are denoted as A, B, C, and D in the  $\alpha$  phase, and A and B in the  $\beta$  phase. The stacking manners are thus ABCDABCD... and ABAB..., respectively. The  $\alpha$  phase has additional two layer structures of C and D, which are related to A and B by the  $c$  glide operation.<sup>10</sup> Along  $c$ -axis, the lattice constant of the  $\alpha$  phase is approximately twice as long as that of the  $\beta$  phase.

The experimental thermal conductivities<sup>2–5,12</sup> of the  $\text{Si}_3\text{N}_4$  polymorphs were measured for bulk polycrystalline

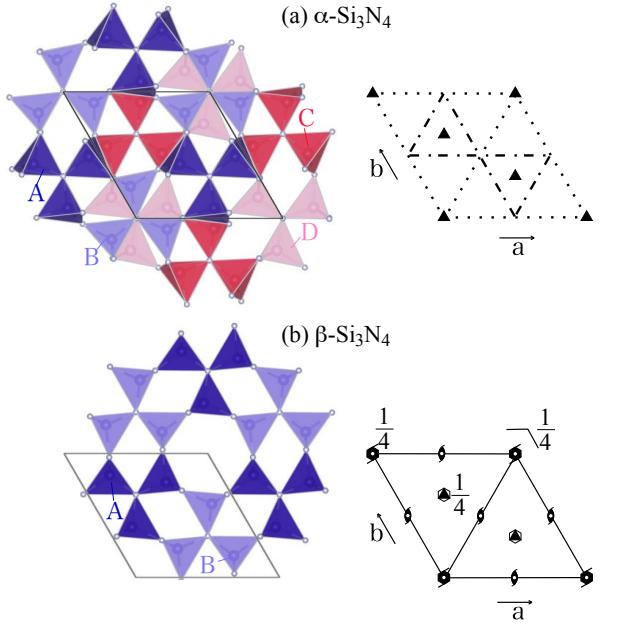


FIG. 1. (color online) Crystal structures of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ . Stackings of  $\text{SiN}_4$  tetrahedron layers are shown at the left. (a) ABCDABCD... for  $\alpha$ - $\text{Si}_3\text{N}_4$ . (b) ABAB... for  $\beta$ - $\text{Si}_3\text{N}_4$ . Space group diagrams<sup>11</sup> for  $P31c$  ( $\alpha$ - $\text{Si}_3\text{N}_4$ ) and  $P6_3/m$  ( $\beta$ - $\text{Si}_3\text{N}_4$ ) are shown on the right.

samples. These values were significantly affected by the lattice defects, impurities, shapes and orientations of the constituent crystal grains;<sup>6</sup> the intrinsic thermal conductivity of defect-free  $\text{Si}_3\text{N}_4$  has not been established. As an experimental approach to determine this, Li *et al.*<sup>13</sup> applied the high-resolution thermoreflectance mi-

croscopy to single  $\beta$ -Si<sub>3</sub>N<sub>4</sub> grains in a ceramic sample and they obtained the lattice thermal conductivities of  $\kappa_{xx} = 69$  and  $\kappa_{zz} = 180 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature. **How much tempareture?** showing large anisotropy of  $\kappa_{zz}/\kappa_{xx} \sim 2.6$ . For single-crystal grains of  $\alpha$  and  $\gamma$  phases, thermal conductivity values by experiments are not known. (correct?)

Hirosaki *et al.*<sup>6</sup> theoretically estimated  $\kappa$  by application of the Green-Kubo formulation to the molecular dynamics (MD) method with the interatomic potentials proposed by Vashishta *et al.*<sup>14</sup>. They calculated  $\kappa_{xx}$  and  $\kappa_{zz}$  of  $\beta$ -Si<sub>3</sub>N<sub>4</sub> to be 170 and 450 W m<sup>-1</sup> K<sup>-1</sup> at 300 K, respectively. Although the calculation showed much larger  $\kappa_{xx}$  and  $\kappa_{zz}$  than the experimental values by Li *et al.*, the ratio,  $\kappa_{zz}/\kappa_{xx} \sim 2.6$ , was well reproduced. For  $\alpha$ -phase, they presented  $\kappa_{xx} = 105$  and  $\kappa_{zz} = 225$  at 300 K, for which the ratio  $\kappa_{zz}/\kappa_{xx} \sim 2.1$  is smaller than that of  $\alpha$ -phase. This indicates that the different stacking manners between the  $\alpha$  and  $\beta$  may result in different anisotropy of lattice thermal conductivites. (In this context, putting the reference is OK? NO.)

Based on first principles phonon calculations and linearized Boltzmann transport equation<sup>15</sup>, Togo *et al.* recently calculated lattice thermal conductivities of compounds with 33 different chemical compositions that are known to have either zincblende- or wurtzite-type structures. These crystal structures are only different in their stacking manners of the densest atomic planes: AB-CABC... for zincblende-type and ABAB... for wurtzite-type. Following this fact, in their calculations, lattice thermal conductivities of both zincblende- and wurtzite-type structures were calculated for each chemical composition and were compared. As a result, it was found that the different stacking manners differentiate little not only the lattice thermal conductivities, but the phonon lifetimes and the phonon densities of states (DOS).<sup>15</sup> Therefore, making crystal structures have different stacking manners does not always bring the different lattice thermal conductivities.

In this study, we have investigated the lattice thermal conductivities of  $\alpha$  and  $\beta$  phases of Si<sub>3</sub>N<sub>4</sub> by using the first principles phonon calculations and linearized Boltzmann transport equation. This calculation approach has recently become possible to apply to crystalline phases of compounds systematically due to increase computer power and efforts on methodological and software developments, and the calculated values are often more reliable than the other theoretical approach at this moment. In addition, using this approach, the microscopic analysis from the phonon picture is easily achieved, which is important in understanding the mechanism of thermal transport in crystals. By this, we achieved detailed analysis of lattice thermal conductivities of  $\alpha$  and  $\beta$  phases and discussed about the different anisotropies of  $\kappa_{zz}/\kappa_{xx}$  between them.

In addition to the  $\alpha$  and  $\beta$  phases, a cubic spinel phase ( $\gamma$ -Si<sub>3</sub>N<sub>4</sub>) is known to form upon compression and *in situ* heating.<sup>16,17</sup> The reported transition pressures are scat-

tered from 10 to 36 GPa, depending on the experimental conditions.<sup>18</sup> The  $\gamma$  phase is experimentally quenched to atmospheric pressure and room temperature. The thermal conductivity of the  $\gamma$  phase has not been experimentally reported, although it has been estimated by the Slack model.<sup>19</sup>

The present study aims to qualitatively elucidate the lattice thermal conductivity tensors among the three Si<sub>3</sub>N<sub>4</sub> phases by a first principles approach. We calculate lattice thermal conductivities of the  $\gamma$  phase as well, for systematic understanding. After the methodology is described, we examine the validity of the present results through comparison of the calculated thermal properties with the available experimental and theoretical references. The characteristic behaviors of the lattice thermal conductivities are then investigated in details.

## 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 approximation (single-mode RTA). The harmonic phonon states and lattice thermal conductivities were calculated with the phonopy<sup>20</sup> and phono3py<sup>15</sup> software packages, respectively. We also attempted the direct-solution of LBTE<sup>21</sup> and give the calculated  $\kappa$  values in the following section. The difference between  $\kappa$  calculated by the single-mode RTA and that by the direct solution was minor for our discussion, for which the detail is given in Sec. IIc. Therefore, this research was limited to use the single-mode RTA to take advantage of the closed form of  $\kappa$ , which can be intuitively understood in terms of mode-specific phonon properties.

In the following sections, we denote 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 harmonic phonon frequency of the phonon mode  $\lambda$  is denoted by  $\omega_\lambda$ . The band index  $p$  is set as 1, 2, ... simply in ascending order of the harmonic phonon frequency at a  $\mathbf{q}$ -point. For the detailed analysis below, we refer to  $e_j(i, \lambda)$  as an eigenvector component for a phonon mode  $\lambda$ , with respect to a cartesian coordinate  $j$  ( $= x, y, z$ ) of an atom  $i$ . The relaxation time due to phonon-phonon scattering was obtained as,  $\tau_{\lambda, \text{ph-ph}} = [2\Gamma_\lambda(\omega_\lambda)]^{-1}$ , with

$$\Gamma_\lambda(\omega) = \frac{18\pi}{\hbar^2} \sum_{\lambda' \lambda''} |\Phi_{-\lambda \lambda' \lambda''}|^2 N_2(\mathbf{q}, \omega). \quad (1)$$

In this equation,  $\hbar$  is the reduced Planck constant and  $\Phi_{\lambda \lambda' \lambda''}$  denotes the three-phonon-scattering strength, obtained by the usual coordinate transformation of third-order force constants from direct space to phonon space.<sup>15</sup> The second- and third-order real-space force constants were obtained by *ab initio* calculation, of which

the details are given in the next section.  $N_2(\mathbf{q}, \omega)$  is a weighted joint DOS (WJDOS)<sup>15</sup>,

$$N_2(\mathbf{q}, \omega) = N_2^{(1)}(\mathbf{q}, \omega) + N_2^{(2)}(\mathbf{q}, \omega) \quad (2)$$

where

$$\begin{aligned} N_2^{(1)} &= \frac{1}{N_{\mathbf{q}}} \sum_{\lambda' \lambda''} (n_{\lambda'} - n_{\lambda''}) \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times [\delta(\omega + \omega_{\lambda'} - \omega_{\lambda''}) - \delta(\omega - \omega_{\lambda'} + \omega_{\lambda''})], \\ N_2^{(2)} &= \frac{1}{N_{\mathbf{q}}} \sum_{\lambda' \lambda''} (n_{\lambda'} + n_{\lambda''} + 1) \Delta(-\mathbf{q} + \mathbf{q}' + \mathbf{q}'') \\ &\times \delta(\omega - \omega_{\lambda'} - \omega_{\lambda''}), \end{aligned}$$

with  $\Delta(\mathbf{x})$  giving 1 if  $\mathbf{x}$  is a reciprocal lattice vector, and otherwise zero. This constraint comes from the lattice translational invariance that appears inside  $\Phi_{\lambda \lambda' \lambda''}$ ,<sup>15</sup> however, we let it appear in  $N_2$  in Eq. (1) in the same manner as in Ref. 22, for the analysis given below.  $N_{\mathbf{q}}$  is the number of  $\mathbf{q}$ -points.  $n_{\lambda} = [\exp(\hbar\omega_{\lambda}/k_B T) - 1]^{-1}$  is the Bose-Einstein distribution at temperature  $T$  with  $k_B$  of Boltzmann constant.

To more realistically compare the calculated  $\kappa$  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.<sup>23</sup> Using the relaxation times for the 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,  $\tau_{\lambda}$ , was calculated by assuming Matthiessen's rule,  $1/\tau_{\lambda} = 1/\tau_{\lambda, \text{ph-ph}} + 1/\tau_{\lambda, \text{iso}}$ .

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

$$\kappa = \frac{1}{N_{\mathbf{q}} \Omega} \sum_{\lambda} \tau_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda}, \quad (3)$$

where  $\Omega$  is the unit cell volume,  $\mathbf{v}_{\lambda} = \nabla_{\mathbf{q}} \omega_{\lambda}$  is the group velocity, and  $c_{\lambda} = \frac{\partial(n_{\lambda} \hbar \omega_{\lambda})}{\partial T}$  is the mode heat capacity. To analyze  $\kappa$  in detail, the cumulative thermal conductivity:

$$\kappa^c(\omega) = \frac{1}{N_{\mathbf{q}} \Omega} \int_0^{\omega} \sum_{\lambda} \tau_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda} \delta(\omega' - \omega_{\lambda}) d\omega', \quad (4)$$

and its derivative  $\frac{d\kappa^c(\omega)}{d\omega}$ :

$$\frac{d\kappa^c(\omega)}{d\omega} = \frac{1}{N_{\mathbf{q}} \Omega} \sum_{\lambda} \tau_{\lambda} \mathbf{v}_{\lambda} \otimes \mathbf{v}_{\lambda} c_{\lambda} \delta(\omega - \omega_{\lambda}), \quad (5)$$

were calculated to determine the phonon mode contributions to  $\kappa$ .

## B. Computational details

The force constants required were calculated using the first-principles projector augmented wave method<sup>24</sup> (VASP code<sup>25–27</sup>). The generalized gradient approximation (GGA) parameterized by Perdew, Burke, and

Ernzerhof<sup>28</sup> 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 Å<sup>-1</sup>. 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  $a = 7.808$  Å and  $c = 5.659$  Å for the  $\alpha$  phase,  $a = 7.660$  Å and  $c = 2.925$  Å for the  $\beta$  phase, and  $a = 7.787$  Å for the  $\gamma$  phase, which are in agreement with the experimental data<sup>8,9,29</sup> within  $+0.7$  % error. The lattice volume optimized with the local density approximation (LDA)<sup>30</sup> for the exchange correlation potential was, for  $\beta\text{-Si}_3\text{N}_4$ , 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 sufficiently small; therefore, the impact of the choice of exchange correlation potential is considered to be minor in this study.

TABLE I. Calculated lattice thermal conductivities of  $\alpha$ -,  $\beta$ -, and  $\gamma\text{-Si}_3\text{N}_4$  (W K<sup>-1</sup> m<sup>-1</sup>) at 300 K with respect to several combinations of supercell sizes.

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

The force constants were calculated by the finite difference approach<sup>31</sup>. For this calculation, the following supercells were adopted: 1 × 1 × 2, 1 × 1 × 3, and 1 × 1 × 1 supercells of the conventional unit cells for the calculations of the third-order force constants of  $\alpha$ ,  $\beta$ , and  $\gamma\text{-Si}_3\text{N}_4$ , respectively, and 3 × 3 × 4, 3 × 3 × 8 and 2 × 2 × 2 for those of the second-order force constants. The length of the induced atomic displacements was set to 0.03 Å. Table I shows  $\kappa$  calculated with several different sets of the supercells, which indicates that the calculated  $\kappa$  has reasonable convergence with respect to the size of the supercells.

Uniform  $\mathbf{k}$ -point sampling meshes of 4 × 4 × 2, 4 × 4 × 3,

and  $3 \times 3 \times 3$  were employed for calculations of the third-order force constants of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases. For the  $\alpha$  and  $\beta$  phases, the center of the  $a^*b^*$  plane was sampled, while the center on the  $c^*$ -axis was not. For the  $\gamma$  phase, a non- $\Gamma$  center mesh was used. For the calculations of the second-order force constants, the  $\Gamma$ -point was only sampled for the  $\alpha$  and  $\beta$  phases, and the only one  $\mathbf{k} = (0.5, 0.5, 0.5)$  point was sampled for the  $\gamma$  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  $\kappa$  in Eq. (3) for the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, respectively.

Non-analytical term correction<sup>32</sup> was applied to the second-order force constants to take into account the long range coulombic forces present in ionic crystals. For the correction, static dielectric constants and Born effective charges were calculated using the density functional perturbation theory as implemented in the VASP code<sup>33,34</sup>.

The effect of lattice thermal expansion on  $\kappa$  was examined by the calculation of  $\kappa$  for several finite temperatures with the crystal structures optimized for the corresponding temperatures within the quasi-harmonic approximation (QHA)<sup>35</sup>. These  $\kappa$  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. The differences in  $\kappa$  for  $T=300, 600, 900, 1200$ , and,  $1500$  K, for the  $\beta$  phase, were within 1 %. They were similar to those for Si and Ge calculated by Ward *et al.*<sup>36</sup>. For the present study, these differences are negligible and  $\kappa$  calculated with the structure optimized for 0 K was adopted.

The volumetric thermal expansion coefficients were also calculated. Comparison with the experimental coefficient is useful to validate the present thermal conductivity calculation because both the thermal expansion and  $\kappa$  originate from the anharmonicity of the interatomic potential. The calculated coefficients of the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases were  $4.31 \times 10^{-6}$ ,  $4.19 \times 10^{-6}$ , and  $1.13 \times 10^{-5}$  K<sup>-1</sup> for 300 K, while the experimental values<sup>37,38</sup> were  $3.75 \times 10^{-6}$ ,  $3.55 \times 10^{-6}$ , and  $9.48 \times 10^{-6}$  K<sup>-1</sup>. The calculation systematically overestimated the experimental values, but reproduced the experimental tendencies, including that the  $\alpha$  phase has a slightly larger coefficient than the  $\beta$  phase. This supports the validity of the present calculation to qualitatively compare the calculated  $\kappa$  among the Si<sub>3</sub>N<sub>4</sub> phases.

To compare the microscopic phonon properties among the three phases under the same conditions, the results calculated at 0 GPa are shown and discussed. For the  $\gamma$  phase, this means that we assume the condition of a virtually quenched  $\gamma$  phase at 0 GPa from the high pressure. To examine the analytical continuity of the properties with respect to pressure,  $\kappa$  of the  $\gamma$  phase was calculated at 10, 20, and 40 GPa, as shown in Fig. 7. The phenomenological behavior of the linear dependence of  $\kappa$  with respect to the pressure was reproduced, similar to that in Ref. 39. The slope was  $2.89 \text{ W m}^{-1} \text{ K}^{-1} \text{ GPa}^{-1}$  for the  $\gamma$  phase. From this dependence, we consider that the microscopic values are also varied smoothly with the

pressure and those at 0 GPa are valuable for comparison with the corresponding values of the  $\alpha$  and  $\beta$  phases.

### C. Direct solution of LBTE

The advantage of employing the single-mode RTA for thermal conductivity calculations is the closed form in Eq. (3), by which the qualitative character of  $\kappa$  can be intuitively understood in terms of the phonon-mode specific properties. The microscopic understanding of the full solution of LBTE is still under development,<sup>40</sup> and the microscopic picture based on collective phonons<sup>41</sup> will require more complicated investigation.

Single-mode RTA solutions of LBTE often underestimate the full solution.<sup>36,42</sup> To check this underestimation,  $\kappa$  for the  $\alpha$  and  $\beta$  phases were calculated by the direct solution of LBTE<sup>21</sup>, which is one of the methods of LBTE full solutions.  $\kappa_{xx}$  and  $\kappa_{zz}$  without the isotope effect were 69 and  $102 \text{ W m}^{-1} \text{ K}^{-1}$  for the  $\alpha$  phase, and 76 and  $238 \text{ W m}^{-1} \text{ K}^{-1}$  for the  $\beta$  phase, respectively, while the corresponding single-mode RTA values were 70 and  $102 \text{ W m}^{-1} \text{ K}^{-1}$  for the  $\alpha$  phase, and 76 and  $210 \text{ W m}^{-1} \text{ K}^{-1}$  for the  $\beta$  phase.  $\kappa_{zz}$  for the  $\beta$  phase from the direct solution was 13 % larger than that of the single-mode RTA solution. The differences in  $\kappa$  between the LBTE solutions are not significant; therefore, we expect that the physics of these lattice thermal conductivities is well understood within the single-mode RTA at the current level of our interest. Therefore, we discuss the lattice thermal conductivities calculated by the single-mode RTA solution.

## III. RESULTS AND DISCUSSION

### A. Lattice thermal conductivities

TABLE II. Calculated thermal conductivities of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub> (trigonal),  $\beta$ -Si<sub>3</sub>N<sub>4</sub> (trigonal), and  $\gamma$ -Si<sub>3</sub>N<sub>4</sub> (cubic) at 300 K in units of  $\text{W m}^{-1} \text{ K}^{-1}$ , compared with the experimental and theoretical reference data, and bulk moduli  $B$  (in units of GPa), calculated from the elastic constant calculation routine<sup>43</sup> in the VASP code.

|  | This work     |               | $B$ | $\kappa$         | Ref. Theo.       |                  | Ref. Expt.      |                  |
|--|---------------|---------------|-----|------------------|------------------|------------------|-----------------|------------------|
|  | $\kappa_{xx}$ | $\kappa_{zz}$ |     |                  | $\kappa_{xx}$    | $\kappa_{zz}$    | $\kappa_{xx}$   | $\kappa_{zz}$    |
| $\alpha$ -Si <sub>3</sub> N <sub>4</sub> | 68            | 100           | 224 | 70 <sup>a</sup>  | 105 <sup>b</sup> | 225 <sup>b</sup> | -               | -                |
| $\beta$ -Si <sub>3</sub> N <sub>4</sub>  | 73            | 199           | 237 | 250 <sup>a</sup> | 170 <sup>b</sup> | 450 <sup>b</sup> | 69 <sup>c</sup> | 180 <sup>c</sup> |
| $\gamma$ -Si <sub>3</sub> N <sub>4</sub> | 77            | -             | 296 | 80 <sup>a</sup>  | -                | -                | -               | -                |

<sup>a</sup> Ref. 19, Slack model.

<sup>b</sup> Ref. 6, molecular dynamics (Green-Kubo).

<sup>c</sup> Ref. 13, single crystalline grains of poly-crystals.

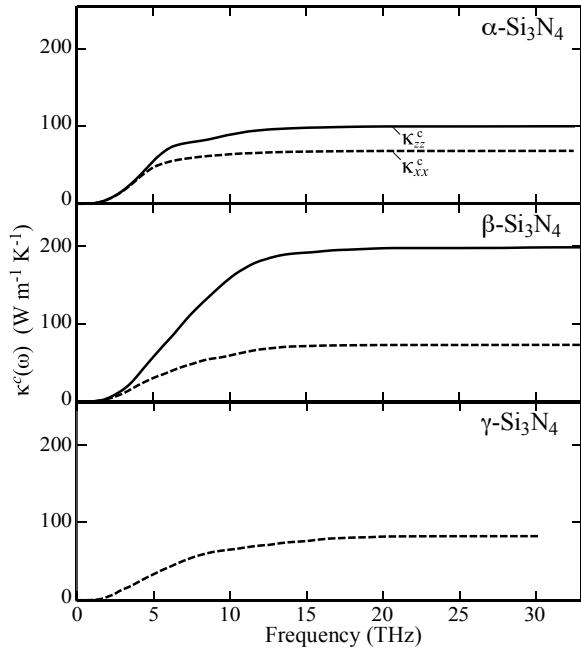


FIG. 2. Cumulative thermal conductivity of the three phases.

Table II shows the calculated  $\kappa$  for 300 K with the isotope effect.  $\beta\text{-Si}_3\text{N}_4$  has a markedly more anisotropic  $\kappa$  than  $\alpha\text{-Si}_3\text{N}_4$ . The directional averages  $\sum_i \kappa_{ii}/3$  are 79, 115, and 77 W m<sup>-1</sup> K<sup>-1</sup> for the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, respectively. The value for the  $\gamma$  phase is similar to that for the  $\alpha$  phase, despite the comparatively large difference among the bulk moduli ( $B$ ) that are also shown in Table II.

Table II also lists the previously reported experimental<sup>13</sup> and theoretical<sup>6</sup>  $\kappa$  for reference. The theoretical results<sup>19</sup> of the Slack model, which do not include the anisotropy in  $\kappa$ , are shown as  $\kappa$  in Table II. Compared to the  $\kappa$  from MD<sup>6</sup>, our  $\kappa$  for the  $\beta$  phase has better agreement with the experimental  $\kappa$ . Compared to  $\kappa$  from the Slack model, our directional average  $\sum_i \kappa_{ii}/3$  is also much closer to the experimental average.

Fig. 2 shows the cumulative thermal conductivity,  $\kappa^c(\omega)$ , with the isotope effect. From this figure, it is evident that in the  $\alpha$ ,  $\beta$ , and  $\gamma$  phases, the phonon modes with their frequencies up to  $\sim 6$ ,  $12$  and  $10$  THz largely contribute to each respective  $\kappa$ . Thus we investigate the phonon modes in these frequency ranges.

### B. Distribution of group velocity in Brillouin zone

The Brillouin zones and phonon band diagrams of the three phases are shown in Fig. 3 (a). In this figure, we investigate the gradient of  $\omega_\lambda$ , the group velocity projected on the paths along the nonequivalent axes of the reciprocal lattice. We particularly focus on the anisotropy of the group velocity in the  $\alpha$  and  $\beta$  phases. This was

not investigated in the previous works<sup>18,44</sup>. The band diagrams on the other high-symmetry paths are almost identical to those reported<sup>18,44</sup> and thus are not shown. For the  $\alpha$  and  $\beta$  phases, in order to investigate the distribution of the group velocities all over the Brillouin zone, the cross-sections of the phonon frequency distributions for the band indices  $p=1$ ,  $2$ ,  $3$  and  $4$  are shown in Fig. 3 (b). As seen in Fig. 2, the frequencies for these band indices cover a large part of the frequency ranges where  $\kappa^c$  increase significantly. The cross-sections are on the  $b^*c^*$  plane. There were negligible differences among the cross-sections on the planes containing  $c^*$  axis, we focus on the  $b^*c^*$  plane as a representative of all such planes. The A-Γ and Γ-K paths of the band diagram respectively correspond to the left and bottom end lines in the cross-section area. Thus, the distribution profiles on the end lines appear in the dispersion curves in the band diagrams. Just for clarification purposes, the dispersion curves corresponding to the profiles for  $p=4$  are highlighted by gray color.

In the band diagram of the  $\alpha$  phase, the dispersion relation on the A-Γ path for a band index is similar to that on the K-Γ path. This suggests nearly isotropic group velocities, which is more clearly seen in the cross-sections for  $p=1$ ,  $2$  and  $3$ , where the most of the contour lines are nearly parallel to the circular dash lines inserted as a guide. In contrast, in the band diagram of the  $\beta$  phase, the dispersion relation is much more different between the two paths. For example, the frequencies of the acoustic-mode phonons at the A point are much higher than those at the K point. Consistently, the gradients of frequencies

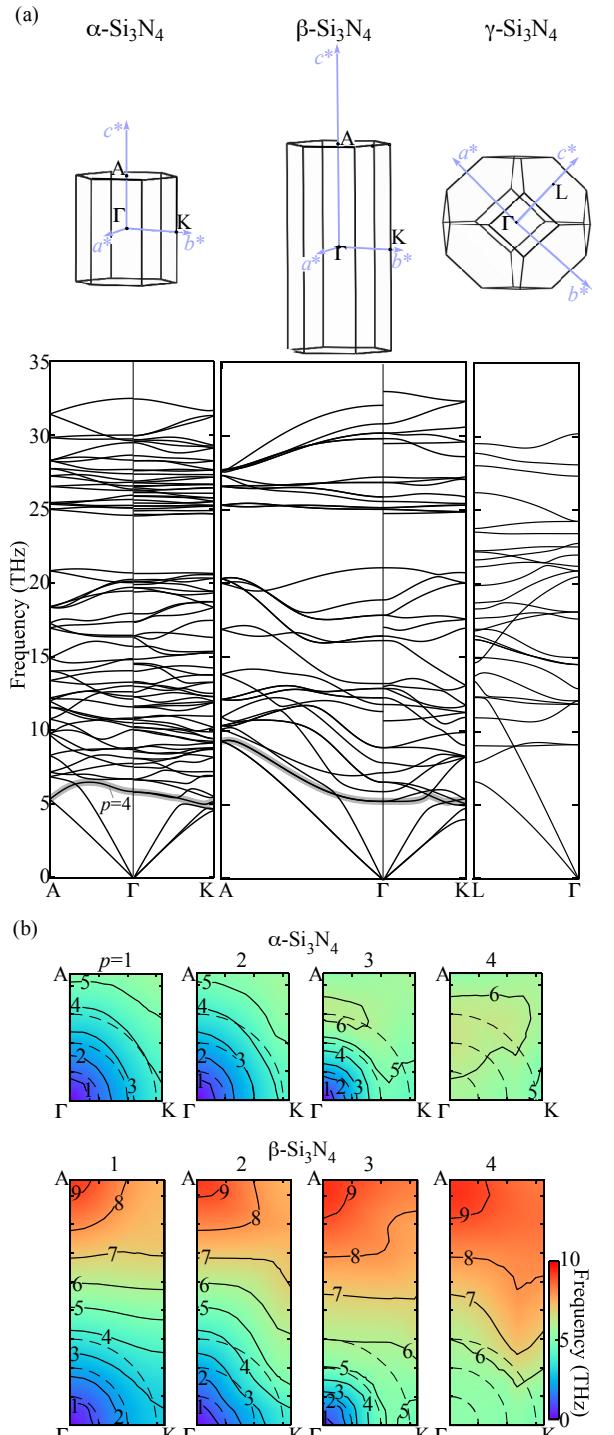


FIG. 3. (color online) (a) Brillouin-zones and band diagrams of the three phases. (b) Contour maps of phonon frequencies for the  $\alpha$  and  $\beta$  phases, on the  $b^*c^*$  planes of Brillouin-zones. The maps for the four lowest-frequency phonon modes ( $p=1, 2, 3$ , and 4) are shown. In the band diagrams for the  $\alpha$  and  $\beta$  phases, the dispersion curve for  $p=4$  is denoted by a thick gray line.

in the cross-sections are, in the most part, parallel to the vertical edges; the group velocities orient closely to the  $c^*$  axis direction. This difference in group velocities between the  $\alpha$  and  $\beta$  phases is due to the  $A-\Gamma$  path lengths. The  $\beta$  phase has an approximately twice longer path than the  $\alpha$  phase; the lattice constant  $c$  of the  $\beta$  phase is nearly half that of the  $\alpha$  phase, owing to the different stacking manners of the basal layer structures (Fig. 1). Comparing the cross-sections for  $p=4$  between the  $\alpha$  and  $\beta$  phases, the  $\beta$  phase has larger gradients of frequencies than the  $\alpha$  phase. Comparing the band diagrams of the  $\alpha$  and  $\beta$  phases, the same tendency is also seen for the most of

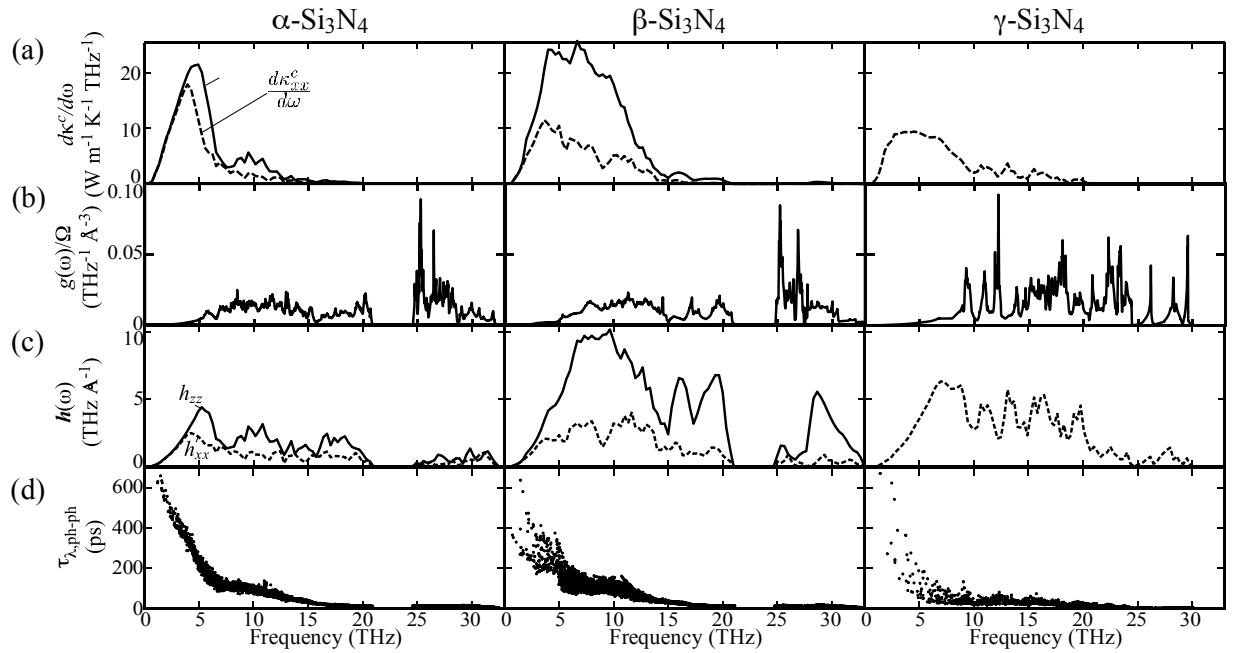


FIG. 4. Microscopic phonon properties of three  $\text{Si}_3\text{N}_4$  phases. (a) Cumulative thermal conductivity  $\kappa^c$  and its frequency derivative, (b) DOS as  $g(\omega)$ , (c) DOS weighted with  $\mathbf{v}_\lambda \otimes \mathbf{v}_\lambda$  as  $\mathbf{h}(\omega)$ , and (d) scatter plots of phonon lifetimes and phonon frequencies, ( $\tau_\lambda, \omega_\lambda$ ).

### C. Microscopic analysis on $\kappa$ behavior

In the previous section, we have investigated the anisotropy in  $\mathbf{v}_\lambda$ , which may explain the anisotropy in  $\kappa$ . Here we examine which terms in Eq.(3) characterize the behavior of the calculated  $\kappa$ . In the following, we omit the term of mode heat capacity because it is approximately constant for the phonon modes that mainly carry heat at 300 K. For simplicity, the effect of isotope scattering is not considered in this section. For the investigation, the derivative of cumulative thermal conductivity,  $d\kappa^c/d\omega$  in Eq.(5), is shown at the top of Fig. 4.

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

$$g(\omega) = \frac{1}{N_q} \sum_\lambda \delta(\omega - \omega_\lambda). \quad (6)$$

We refer to  $g(\omega)/\Omega$  as a frequency distribution of a heat carrier density. Alternatively, assuming that only  $\tau_\lambda$  is constant, then  $d\kappa^c/d\omega$  is proportional to:

$$\mathbf{h}(\omega) = \frac{1}{N_q \Omega} \sum_\lambda \mathbf{v}_\lambda \otimes \mathbf{v}_\lambda \delta(\omega - \omega_\lambda), \quad (7)$$

from which we examine the impacts of both of  $\mathbf{v}_\lambda$  and the heat carrier density.  $g(\omega)/\Omega$  and  $\mathbf{h}(\omega)$  are shown in Figs. 4 (b) and (c). As for the frequency variation of  $\tau_{\lambda,\text{ph-ph}}$ , scatter plots of  $(\tau_{\lambda,\text{ph-ph}}, \omega_\lambda)$  are shown in Fig. 4 (d).

Comparison of the  $\alpha$  and  $\beta$  phases indicates their phonon lifetimes distributions are qualitatively similar,

except for a striking difference below  $\sim 5$  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  $h_{ii}$ . The overall spectral shapes of  $g(\omega)/\Omega$  are also similar between the two phases; therefore,  $\mathbf{v}_\lambda$  alone accounts for the different behavior of  $d\kappa_{ii}^c/d\omega$ . It is thus concluded that the different anisotropy in  $\kappa$  can be qualitatively explained by the different  $\mathbf{v}_\lambda$ . In contrast, for the zincblende and wurtzite structures, the group velocities of these structures are suggested to be similar from their band structures<sup>15</sup>. This must result in similar  $\kappa$  between these structures, irrespective of the stacking manner.

The  $\gamma$  phase has much different  $g(\omega)/\Omega$ ,  $\mathbf{h}(\omega)$ , and,  $\tau_{\lambda,\text{ph-ph}}$  from the other phases, as expected from the large differences in their crystal structures. The most significant difference is in the phonon lifetimes. For  $4 \text{ THz} \lesssim \omega_\lambda \lesssim 10 \text{ THz}$ , the phonon lifetimes are approximately half as short as those of the other phases. We will examine this in detail later. As a result,  $d\kappa_{xx}^c/d\omega$  has relatively low intensities. 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  $d\kappa_{xx}^c/d\omega$  of the  $\beta$  phase.

### D. Phonon properties characterizing $\tau_{\lambda,\text{ph-ph}}$

The distribution of phonon lifetimes is qualitatively similar between the  $\alpha$  and  $\beta$  phases, although their group velocities have marked differences. This remains a curiosity. Recalling Eq. (1),  $\tau_{\lambda,\text{ph-ph}}$  in the present form is

dependent on WJDOS and  $|\Phi_{\lambda\lambda'\lambda''}|^2$ . We examine these terms one-by-one.

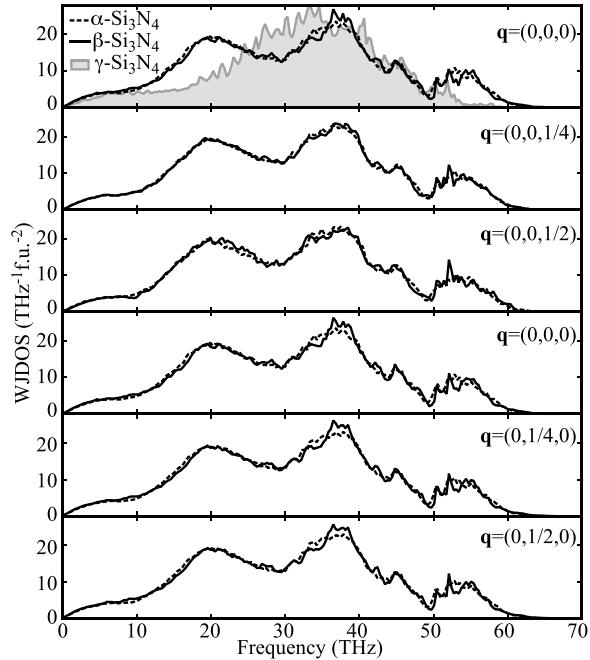


FIG. 5. WJDOS of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  at different  $\mathbf{q}$  points and that of  $\gamma$ - $\text{Si}_3\text{N}_4$  at the  $\Gamma$  point. The WJDOS for the  $\alpha$  and  $\beta$  phases in the first and fourth rows are calculated at the same  $\Gamma$ -point but with the polarization for the non-analytic term correction set along  $c^*$  and  $b^*$ , respectively.

The frequency profiles of WJDOS in Fig. 5 are very similar between the  $\alpha$  and  $\beta$  phases, for each different  $\mathbf{q}$ -points. Their intensities are scaled with  $Z^2$  of which  $Z$  is the number of formula units in the primitive unit cell, to compare WJDOS for structures with different  $Z$ . These profiles show weak  $\mathbf{q}$ -point dependences. The frequency profile for the  $\gamma$  phase is only shown at  $\mathbf{q} = (0, 0, 0)$  because of the different shape of the Brillouin zone from those in the other phases. We checked that the  $\mathbf{q}$  dependence of WJDOS for the  $\gamma$  phase was as weak as those shown in Fig. 5 for the  $\alpha$  and  $\beta$  phases. The intensities of WJDOS below  $\sim 10$  THz in the  $\gamma$  phase are slightly smaller than those in the other phases.

TABLE III. 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 meV<sup>2</sup>.

| Frequency range (THz) | Phase    |         |          |
|-----------------------|----------|---------|----------|
|                       | $\alpha$ | $\beta$ | $\gamma$ |
| 0–15                  | 0.47     | 0.46    | 1.02     |
| 0–35                  | 2.30     | 2.30    | 2.02     |

As for  $|\Phi_{\lambda\lambda'\lambda''}|^2$ , in Table. III, they are averaged over two frequency ranges of 0–15 or 0–35 THz for  $\omega_\lambda$  and all indices in  $\lambda'$  and  $\lambda''$ . 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  $\kappa$ . A small change in the frequency range by a few terahertz did not change the qualitative characteristics of the averages. To compare the averages among the phases having different  $Z$ , as in Ref. 22 we multiply the average by  $(3n_a)^2$  where  $n_a$  is the number of atoms in the primitive unit cell. The averages are very similar for the  $\alpha$  and  $\beta$  phases. With the similar impact of the WJDOS and  $|\Phi_{\lambda\lambda'\lambda''}|^2$ , the phonon lifetimes in these phases are also similar. For the  $\gamma$  phase, the short  $\tau_\lambda$  are attributed to the large  $|\Phi_{\lambda\lambda'\lambda''}|^2$  in the narrower frequency range for  $\omega_\lambda$ .

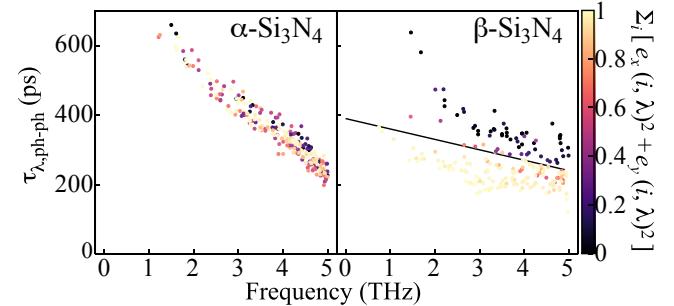


FIG. 6. (color online) Distribution of phonon lifetimes for  $\omega_\lambda \leq 5$  THz shown in color with respect to the fraction of the eigenvector component (a) along  $\mathbf{q}$  and (b) parallel to the  $ab$  plane (b).

Finally, we examine the striking difference in Fig. 4 (d) below  $\sim 5$  THz between the  $\alpha$  and  $\beta$  phases. Fig. 6 enlarges that part. In the  $\alpha$  phase,  $\tau_{\lambda, \text{ph-ph}}$  below  $\sim 5$  THz are distributed around a single smooth line, while for the  $\beta$  phase, they are scattered much more largely. In this figure, each plot is shown with a color specified by  $\sum_i [e_x(i, \lambda)^2 + e_y(i, \lambda)^2]$ , the fraction of the eigenvector component parallel to the  $ab$  plane.

From Fig. 6, we find that, for the  $\beta$  phase, a phonon mode of the atomic vibration parallel to the  $ab$  plane is more hindered by the other phonons than a phonon mode of the vibration perpendicular to the plane. A straight line is inserted in the graph for  $\beta$  phase in Fig. 6. The numbers of the phonon modes below and above the line are 145 and 67, whose ratio is reasonable as the population ratio between the two groups of the phonon modes whose atomic vibrations are, respectively, parallel and perpendicular to the  $ab$  plane.

#### IV. SUMMARY

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

- 1) In  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$ , of which the crystal structures are characterized by the stacking manner of the basal

layer structures,  $\kappa$  is largely altered due to the differences in the harmonic band structures induced by the different stacking manners. This is in contrast with the zincblende and wurtzite structures in the previous study<sup>15</sup>.  $\kappa$  for  $\alpha\text{-Si}_3\text{N}_4$  is rather isotropic, while  $\kappa_{zz}$  for the  $\beta$  phase is twice or more larger than the other  $\kappa_{ii}$  of the three phases.

2) In the  $\alpha$  phase, the acoustic-mode phonons below 6 THz are the main heat carriers, while in the  $\beta$  phase, the phonons below 12 THz contribute to  $\kappa$ . Their group velocities are confirmed to characterize the behavior of  $\kappa$ .

3) In the  $\gamma$  phase, the frequency distribution of the phonon mode contributions to  $\kappa$  is similar to that for  $\kappa_{xx}$  of  $\beta\text{-Si}_3\text{N}_4$ , which is attributed to its large phonon-phonon scattering strength and steep longitudinal acoustic branches.

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for Structural Materials (ESISM) of Kyoto University.

## Appendix A: Dependence of the lattice thermal conductivity of $\gamma$ -phase on pressure

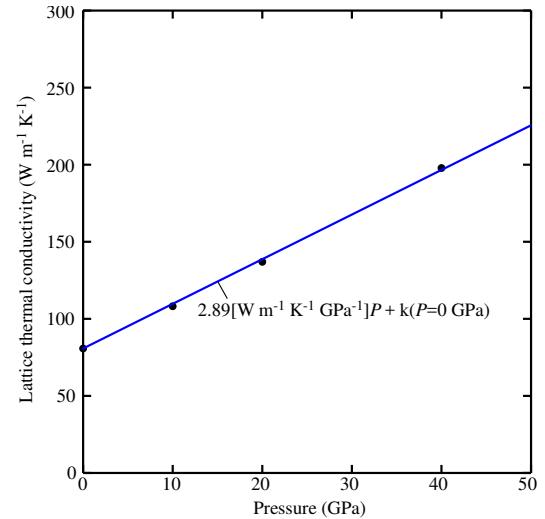


FIG. 7. (color online) Lattice thermal conductivity of  $\gamma\text{-Si}_3\text{N}_4$  as a function of pressure.

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