

Phonon spectrum and thermal properties of cubic Si₃N₄ from first-principles calculations

Citation for published version (APA):

Fang, C. M., Wijs, de, G. A., Hintzen, H. T. J. M., & With, de, G. (2003). Phonon spectrum and thermal properties of cubic Si₃N₄ from first-principles calculations. *Journal of Applied Physics*, 93(9), 5175-5180. <https://doi.org/10.1063/1.1566473>

DOI:

[10.1063/1.1566473](https://doi.org/10.1063/1.1566473)

Document status and date:

Published: 01/01/2003

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Phonon spectrum and thermal properties of cubic Si_3N_4 from first-principles calculations

C. M. Fang

Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

G. A. de Wijs^{a)}

Electronic Structure of Materials, Research Institute for Materials, Faculty of Sciences, Toernooiveld 1, NL-6525 ED, Nijmegen, The Netherlands

H. T. Hintzen and G. de With

Laboratory of Solid State and Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands

(Received 16 September 2002; accepted 18 February 2003)

The phonon spectrum of cubic Si_3N_4 was calculated by first-principles techniques. The results permit an assessment of important mechanical and thermo-dynamical properties such as the bulk modulus, lattice specific heat, vibration energy, thermal expansion coefficient, and thermal Grüneisen parameter for this compound. The calculated phonon spectrum shows a gapless spectrum extending to a cutoff energy of $\sim 1030 \text{ cm}^{-1}$. The calculated Raman- and infrared-active phonon frequencies are compared with measured data in the literature. © 2003 American Institute of Physics. [DOI: 10.1063/1.1566473]

I. INTRODUCTION

A third modification of silicon nitride in the form of a cubic spinel-type structure ($\gamma\text{-Si}_3\text{N}_4$) was discovered in 1999 by Zerr *et al.*¹⁻³ This new form of silicon nitride has attracted much attention for several reasons. First, in $\gamma\text{-Si}_3\text{N}_4$ the Si atoms are positioned at both the tetrahedral and octahedral sites, i.e., some Si are sixfold coordinated, which is very rare in binary compounds. Second, $\gamma\text{-Si}_3\text{N}_4$ is a semiconductor with an energy gap of about 3.5 eV^{4-7} and has potential applications in electronics.^{8,9} Furthermore, both first-principles calculations and experiments indicate that $\gamma\text{-Si}_3\text{N}_4$ has a hardness comparable to the hardest known oxide (Stishovite, a high-pressure phase of SiO_2),^{1,10-13} and significantly greater than the hardness of the two well-known hexagonal polymorphs.¹⁴ The $\gamma\text{-Si}_3\text{N}_4$ has also a very high resistance in air to oxidation (up to 1600 K).^{15,16} Therefore, $\gamma\text{-Si}_3\text{N}_4$ has the potential to be used as hard materials, next to the two widely used α and β forms. Different preparation methods have also been developed. Recently, Sekine *et al.*^{15,17} have prepared $\gamma\text{-Si}_3\text{N}_4$ by shock-induced transformation of $\beta\text{-Si}_3\text{N}_4$ powder, which may produce $\gamma\text{-Si}_3\text{N}_4$ in large scale.

A full characterization of the physical properties of $\gamma\text{-Si}_3\text{N}_4$ is important for applications. Due to the difficulties in the preparation of pure $\gamma\text{-Si}_3\text{N}_4$ samples,^{15,18} theoretical methods, especially first-principles techniques, can help. For example, Mo *et al.* have calculated the band structure and dielectric properties.⁴ In this article we report first-principles calculations of the phonon spectrum for $\gamma\text{-Si}_3\text{N}_4$. The dispersion curve and the partial phonon densities of states

(PDOS) for both tetrahedral and octahedral Si atoms as well as the N atoms are reported. The Raman and infrared (IR) active modes, which can be used for characterization, are included. Using the quasiharmonic approximation (QHA), the thermal properties, including the thermal expansion coefficient, of $\gamma\text{-Si}_3\text{N}_4$ are calculated. We hope that this information will help to further an understanding of the relationship between the crystal structure on one hand and mechanical and thermal properties of $\gamma\text{-Si}_3\text{N}_4$ and related materials on the other hand, and is expected to benefit the developments of new materials for industry.

II. DETAILS OF THEORETICAL CALCULATIONS

The calculations were carried out using the first-principles molecular-dynamics computer code VASP (Vienna *ab initio* simulation program).¹⁹⁻²¹ This program first calculates the electronic structure from first principles, and then the interatomic forces via the Hellmann-Feynman theorem. The phonon frequencies and eigenvectors were obtained by diagonalization of the dynamical matrix. Details of the methods can be found in Refs. 22 and 23. Calculations were applied to a conventional unit cell ($1 \times 1 \times 1$), which consists of four primitive unit cells. Periodic boundary conditions were imposed. All internal coordinates of the atoms have been fully relaxed. Selected atoms were displaced slightly (about 0.01 \AA) away from their equilibrium positions, and the corresponding interatomic forces were calculated. From the calculated forces and the displacements the interatomic force constants were obtained. Using these force constants, the phonon frequencies were determined. Long-range effects on the force constants have been neglected. These long-range effects have no effect on the modes at Γ , as well as a few

^{a)} Author to whom correspondence should be addressed; electronic mail: dewijs@sci.kun.nl

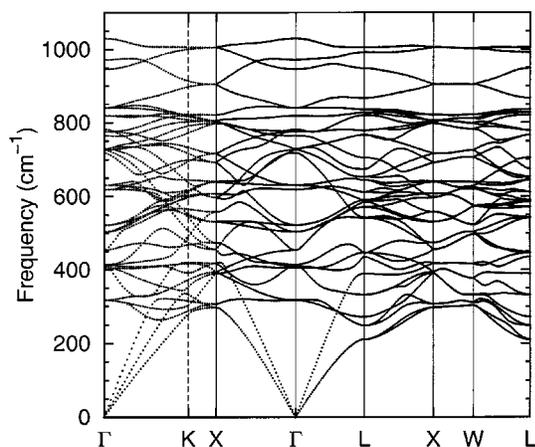


FIG. 1. Calculated phonon dispersion curves along high-symmetry directions in BZ for γ - Si_3N_4 .

other high-symmetry points in the Brillouin zone, which are exact. In a related study (on MgAl_2O_4 spinel, Ref. 23) we found only a minor influence of this approximation on the PDOS. In principle, the phonon spectrum of Fig. 1 should be most severely affected (except for the exact, high-symmetry points Γ and X). In our checks on elongated cells (these included the long-range effects, see below) we, however, found that the deviations from the converged values are small (typically 5 cm^{-1}).

This method does not account for the effect of the macroscopic electrostatic field that arises for certain longitudinal optic (LO) modes in the long-wavelength limit ($k \rightarrow \Gamma$). This field lifts the longitudinal optic and transverse optic (LO-TO) degeneracy of the IR-active modes. Following Refs. 24 and 25 we corrected for the effect of the macroscopic field and the calculated frequency shifts of the LO modes. For the determination of the LO frequencies the interplanar force constants were calculated using a $3 \times 1 \times 1$ cell (containing 12 primitive cells), which has a long a axis (about 23 \AA). The phonon dispersion curves were calculated along several high-symmetry directions in the Brillouin zone (BZ). The phonon density of states (PDOS) was obtained by linear tetrahedron integration of the phonon frequencies over a $10 \times 10 \times 10$ k -point mesh. The symmetry representation of the zone-center modes was examined following White and De Angelis.²⁶

The electronic structure calculations were carried out in both the local density approximation (LDA) and the generalized gradient approximation (GGA), using the projector-augmented wave method.^{27,28} The electronic wave functions were sampled on a $2 \times 2 \times 2$ k -point mesh in the BZ of the conventional unit cell. Additional calculations were carried out for an elongated cell using a consistent k -point mesh as far as possible. The kinetic energy cutoff on the wave functions was 945 eV (69 Ry). Convergence of the total energy as well as of frequencies with the number of k points and the plane-wave cutoff has been checked.

Calculations were carried out for a fixed volume with relaxation of the atomic positions. This procedure was repeated for several volumes in order to obtain a set of total energies as a function of the cell volume. From these data the

TABLE I. The lattice parameter (a), coordinates of nitrogen atoms (x) and bulk modulus (B) for cubic Si_3N_4 from our calculations compared with those from literature (prediction vs experiments).

Method	$a(\text{\AA})$	x	$B(\text{GPa})$
Theoretical			
LDA (this work)	7.696	0.3824	321
LDA-OLCA ^{a,b}	7.8367	0.3843	280
LDA-OLCA ^{c,d}	7.8372	0.3844	280.1
LDA ^e	7.687		308
GGA (this work)	7.789	0.3823	285
GGA ^f			314
GGA ^g	7.7925		284
HF- <i>ai</i> PI ^g	7.419	0.3754	407
Force field ^h	7.692		411.9
Experimental			
Electron diff. ⁱ	7.80(8)		
XRD ^{j,k}	7.744		
Electron diff. ^l	7.75		300(10)
EDXD ^m	7.737(6)		290(5)
			302(6) ^q
XRD ⁿ	7.7381(2)	0.38468	
XRD ^o	7.744(11)		317 (11)
			309(3) ^q
XRD ^e	7.74 (3)		308
XRD ^p	7.7339	0.3833	

^aReference 4.

^bReference 36.

^cReference 5.

^dReference 6.

^eReference 33.

^fReference 43.

^gReference 39.

^hReference 40.

ⁱReference 1.

^jReference 15.

^kReference 17.

^lReference 34.

^mEnergy dispersive x-ray powder diffraction (EDXD), Reference 12.

ⁿReference 18.

^oReference 31.

^pReference 32.

^qFits with first-pressure derivative fixed to be 4.0.

equilibrium volume and bulk modulus were obtained by a fit to a second order Murnaghan equation of state.²⁹

III. CALCULATED RESULTS FOR γ - Si_3N_4

A. Bulk properties

The crystal structure of γ - Si_3N_4 is isostructural with the mineral spinel MgAl_2O_4 ,³⁰ i.e., it is cubic with space group $Fd\bar{3}m$. There are eight formula units per conventional unit cell, which consists of 32 anions (N ions) and 24 cations (Si ions). The Bravais lattice of an ideal spinel structure consists of a fcc sublattice of N with the Si ions occupying both one eighth of the interstitial tetrahedral sites and one half of the octahedral sites. The crystal structure of spinel is completely defined by the lattice parameter a and the anions' positional parameter x .

There are several calculations on the crystal structure and bulk modulus of γ - Si_3N_4 , as summarized in Table I. Experimental results are also included in the table for comparison.^{1,4-6,15,17,18,31-40} It is apparent that the experimental values are generally in good agreement with each other. As shown in Table I, the calculated lattice parameters from different methods are also in good agreement with the experimental values. The differences of our calculated data (7.696 \AA for LDA and 7.789 \AA for GGA) from the experimental values (about 7.74 \AA) are small and typical for the

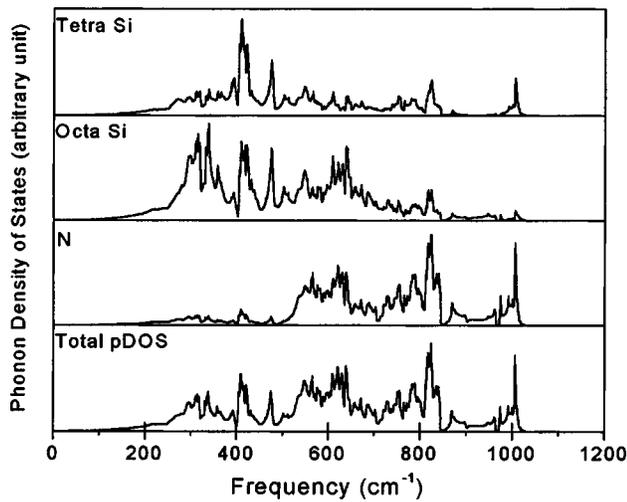


FIG. 2. Partial and total PDOS for γ -Si₃N₄ calculated from first principles.

density functional theory (DFT).⁴¹ The only exception is the value (7.419 Å) by Mori-Sánchez *et al.* using the *ab initio* Hartree-Fock aiPI code.³⁹

However, the values of the bulk modulus calculated by the *ab initio* Hartree-Fock aiPI code³⁹ as well as that from classic pair-potential methods⁴⁰ (~410 GPa) are much larger, as compared with those from experiments (~300 GPa) and DFT methods. Our value of the bulk modulus calculated from the LDA (321 GPa) is slightly larger than that predicted by Ching *et al.* using the LDA-orthogonalized linear combination of atomic orbitals (OLCA) approach.^{4-6,36} However, our value is close to that obtained by Soignard *et al.*³³ Our value of the bulk modulus calculated using the LDA is slightly larger than the experimental data, which were measured at room temperature, while the value (285 GPa) from the GGA is slightly smaller. In all subsequent calculations, the optimized calculated values of *a* and *x* using the LDA were used. The bulk modulus

TABLE II. Calculated frequencies *f* of the optical modes of γ -Si₃N₄ at the Γ point of the primitive cell. The LO modes of the infrared-active species are between brackets.

Species	<i>f</i> (cm ⁻¹)	Dominant eigen characters ^a
<i>T</i> _{2u}	317	Si ₂ + N
<i>T</i> _{1u} (IR)	406(410)	Si ₁ + Si ₂ + N
<i>T</i> _{2g} (R)	415	Si ₁ + N
<i>E</i> _u	455	Si ₂
<i>T</i> _{1g}	504	N
<i>E</i> _{1g} (R)	522	N
<i>T</i> _{1u} (IR)	619(718)	N + Si ₂
<i>T</i> _{2u}	631	N + Si ₂
<i>T</i> _{2g} (R)	726	N + Si ₁
<i>T</i> _{1u} (IR)	729(764)	Si ₁ + Si ₂
<i>E</i> _u	775	N
<i>A</i> _{2u}	782	Si ₂
<i>T</i> _{1u} (IR)	819(1030)	N + Si ₁ + Si ₂
<i>T</i> _{2g} (R)	840	N + Si ₁
<i>A</i> _{2u}	946	N
<i>A</i> _{1g} (R)	972	N

^aSi₁ represents tetrahedral Si atoms and Si₂ octahedral Si.

TABLE III. Comparison between the calculated and experimental Raman frequencies for γ -Si₃N₄.

Modes	Calculations ^{This work}		Experiments
	(cm ⁻¹)	(cm ⁻¹) ³²	(cm ⁻¹) ^{a,b}
<i>T</i> _{2g}	415	420	
<i>E</i> _{1g}	522	522	522
<i>T</i> _{2g}	726	727	754
<i>T</i> _{2g}	840	845	864
<i>A</i> _{1g}	972	979.5	979

^aReference 1.

^bCorrected according to the Si mode, Ref. 32.

of γ -Si₃N₄ [about 321 GPa (LDA) or 285 GPa (GGA)] is much larger than that for β -Si₃N₄ (about 235 GPa) calculated using the same method.⁴¹

B. Phonon spectrum

Figure 1 shows the dispersion curves along the high-symmetry lines in the Brillouin zone (BZ). The primitive cell of γ -Si₃N₄ contains two formula units (total 14 ions) giving rise to a total of 42 phonon branches. The 42 phonon branches fill the entire energy range, leaving no gap in the PDOS. Figure 2 shows the calculated partial and total PDOS of γ -Si₃N₄. The total PDOS spans up to about 1030 cm⁻¹, which is about 10% smaller than the maximum frequency (1119 cm⁻¹) obtained by Marian *et al.* using the pair-potential approach.⁴⁰

The low energy vibrations (<500 cm⁻¹) originate dominantly from the Si atoms. The N ions are involved in vibrational modes over the high energy range (>500 cm⁻¹). The modes in the high energy part are dominated by N character.

Different vibrational contributions from the two different Si atoms are apparent as shown in Fig. 2. In the very low energy range (between 200 and 400 cm⁻¹) the vibrations are mainly due to the octahedral Si atoms. The tetrahedral Si atoms contribute to the vibrations over the whole energy range with a peak at about 415 cm⁻¹.

C. Vibrations at Γ

The phonon modes at Γ for γ -Si₃N₄ are classified following White and De Angelis²⁶ as

$$\Gamma(k=0) = A_{1g}(R) + E_{1g}(R) + 3T_{2g}(R) + 4T_{1u}(IR) + T_{1g} + 2A_{2u} + 2E_u + 2T_{2u}, \quad (1)$$

where R and IR correspond to Raman- and infrared-active, respectively. The calculated frequencies at Γ and the dominant contributions from the ion species are listed in Table II. The crystal symmetry implies five Raman- and four IR-active modes.

In Table III the experimental Raman values by Zerr *et al.*¹ and by Jiang *et al.*³² are compared with our theoretical results. Four of the experimental modes agree well with our calculated values (Table III). However, the assignment of the symmetry is different. The calculations show that the mode near 979.5 cm⁻¹ is *A*_{1g} and the mode at 845 cm⁻¹ is *T*_{2g}, that is, an interchange of species, as compared to the assign-

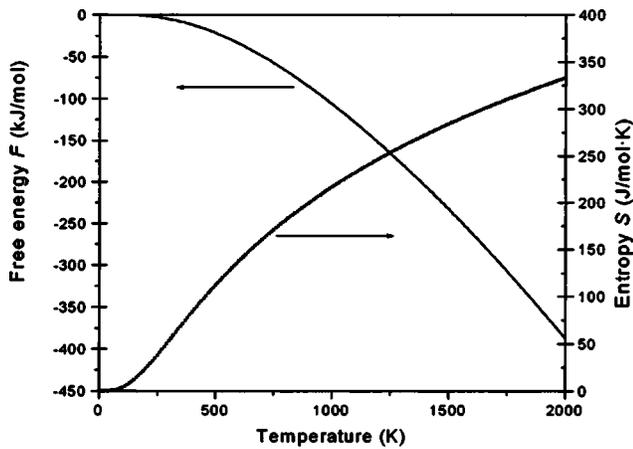


FIG. 3. Vibration free energy F and entropy S calculated from the PDOS using the QHA.

ment by Jiang *et al.*³² The peak at 1331 cm^{-1} is far away from any of our calculations. It originates, we speculate, from an impurity or defect in the sample (the sample used by Jiang *et al.*³² was highly cation deficient). Instead of this peak we find that the (calculated) fifth frequency at 415 cm^{-1} is very close to one (420 cm^{-1}) of the many weak peaks observed by Jiang *et al.*³²

The experimental results on IR active modes for $\gamma\text{-Si}_3\text{N}_4$ are very unclear. Schwarz *et al.*¹⁸ reported IR absorption bands at 1094 , 872 , 702 , and 465 cm^{-1} , which are completely different from the corresponding absorption bands for $\alpha\text{-}$ and $\beta\text{-Si}_3\text{N}_4$. It seems obvious that the bands at 610 and 702 cm^{-1} correspond to the (calculated) TO modes at 619 and 729 cm^{-1} , although there is a small discrepancy. However, assignment of the other bands is problematic. The measured band at 465 cm^{-1} is in between the calculated LO mode at 410 cm^{-1} and the TO mode at 619 cm^{-1} . Therefore it is unlikely that it pertains to spinel $\gamma\text{-Si}_3\text{N}_4$. In the energy range above 800 cm^{-1} there are too many bands as our data suggest only one in that range. For good comparison, a careful measurement on a pure, stoichiometric sample with Kramers–Kronig analysis of frequency dependent reflectivity data is needed.

D. Thermal properties

In the quasiharmonic approximation (QHA), the Helmholtz free energy (F) is given by

$$F(V, T) = U_o(V) + \frac{1}{2} \sum_{q,j} h \omega_j(q, V) + k_B T \sum_{q,j} \ln\{1 - \exp[h \omega_j(q, V)/k_B T]\}, \quad (2)$$

where the first, second, and third terms are the total lattice energy, zero point, and vibrational contributions, respectively. $U_o(V)$ denotes the total energy, $\omega_j(q, V)$ the phonon frequency of branch j at wave vector q for lattice volume V . The values of $U_o(V)$ and $\omega_j(q, V)$ are calculated for several volumes and $F(V, T)$ is interpolated to obtain the zero-pressure volume $V_o(T)$. The summation (integration) runs

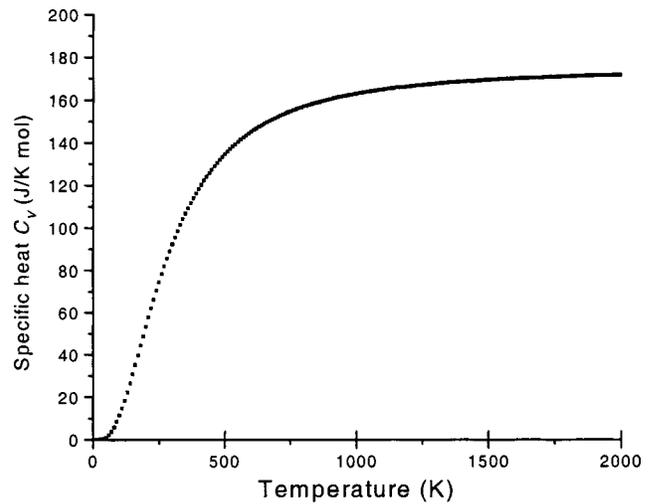


FIG. 4. Specific heat C_v of $\gamma\text{-Si}_3\text{N}_4$ calculated from the PDOS using the QHA.

over the Brillouin zone (BZ). In general, the QHA gives reliable results for temperatures well below the melting point, which is confirmed in several studies.⁴² From Eq. (2) and standard thermodynamics, the thermal properties, including vibrational energy, entropy, and specific heat, thermal expansion coefficient, etc., can be obtained.

The calculated zero-point energy for the zero-pressure volume of $\gamma\text{-Si}_3\text{N}_4$ is 0.7896 eV/f.u. (f.u. represents a Si_3N_4 formula unit), which is slightly larger than that (0.76 eV/f.u.) reported by Marian *et al.* using the classic pair-potential method.⁴⁰

Figure 3 shows the relationship between the calculated entropy S as well as the free energy F of vibration of the optimized volume (V_o) with temperature. The value of the free energy decreases fast from about 60 K , while the absolute value of the vibrational entropy also increases rapidly from about 120 K . The calculated values of free energy F

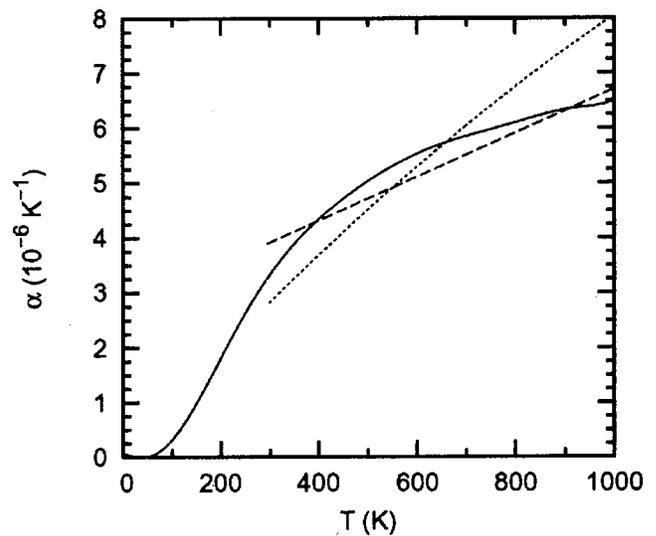


FIG. 5. Linear thermal expansion coefficient α of $\gamma\text{-Si}_3\text{N}_4$ calculated using QHA as compared with experimental values. The broken line represents the data by Jiang *et al.* (see Ref. 32) and the dotted line is the fitted data by Hintzen *et al.* (see Ref. 43).

and entropy S for γ -Si₃N₄ are about -5.13 kJ/mol and 92.39 J/mol K, and -106.40 kJ/mol and 216.72 J/mol K at 300 and 1000 K, respectively.

Figure 4 shows the relationship between the calculated specific heat C_v and temperature. The C_v at 300 and 1000 K is about 92.39 and 162.99 J/mol K, respectively. The C_v value at room temperature is slightly smaller than that (98.2 J/mol K) of β -Si₃N₄.¹⁵

The result for the linear lattice thermal expansion coefficient $\alpha(T) = (da(T)/dT)/a(T) = (dV(T)/dT)/(3V(T))$ of γ -Si₃N₄ is shown in Fig. 5. The coefficient $\alpha(T)$ has very low values in the low temperature range (<50 K). After an initial steep increase (50 – 400 K), the slope changes and $\alpha(T)$ increases gradually with temperature again, but slower, above 600 K. Experimental measurements for the linear thermal expansion coefficient of γ -Si₃N₄ have been performed by Jiang *et al.*,³¹ and Hintzen *et al.*⁴³ (who also took the boundary condition $\alpha(T)=0$ as $T=0$ K) into account. The shape of the calculated curve is slightly different from the experimental results (also plotted).^{31,43} However, the difference between the two experimental curves is of the same order of magnitude as the difference between the experiments and theory. If the experimental uncertainty is taken into account, the agreement between the theoretical calculation and the experiments is good. The scatter between various experiments may, in our opinion, be explained by impurities in the samples, as shown by Jiang *et al.*³¹

The calculated linear thermal expansion coefficient for γ -Si₃N₄ is 3.3×10^{-6} and 6.5×10^{-6} K⁻¹ at 300 and 1000 K, respectively. These values are much larger than the corresponding data for β -Si₃N₄ (1.19×10^{-6} and 3.47×10^{-6} K⁻¹ at 300 and 1000 K,⁴⁴ respectively).

The thermal Grüneisen parameter, which is very important in materials science, is defined as $\gamma_{th} = (V\alpha_v B/C_v)$, where V is the molar volume, B the isothermal bulk modulus, α_v the volume thermal expansion coefficient, C_v the heat capacity. At zero pressure, the calculated value is $\gamma_{th} = 1.194$ and 1.346 for 300 and 1000 K, respectively. These values are much larger than the corresponding data for β -Si₃N₄ (about 0.40 and 0.63 at 300 and 1000 K, respectively).⁴⁴

A measure of lattice anharmonicity can be obtained by the difference between the specific heat C_v at constant volume and the specific heat C_p at constant pressure. The value of the specific heat (at constant pressure) $C_p = (1 + \alpha\gamma_{th}T)C_v$, which is calculated to be 92.72 and 166.95 J/mol K at 300 and 1000 K, respectively.

As shown above, the cubic silicon nitride shows a much larger thermal expansion coefficient and thermal Grüneisen parameter as compared with that of the β form. That indicates larger lattice anharmonicity of the γ -Si₃N₄ than β -Si₃N₄, which is probably due to the particular SiN₆ and NSi₄ coordinations in the cubic form.

IV. CONCLUSIONS

First-principles calculations have been performed for the phonon spectrum of γ -Si₃N₄. The calculations show that the PDOS has a cutoff energy of 1030 cm⁻¹ with the contribu-

tions from Si atoms all over the energy range, while the contributions from the N atoms are mainly in the high energy range (500 – 1030 cm⁻¹).

The interpretation of Raman experiments needs to be qualified. A weak low frequency mode (415 cm⁻¹) is characteristic of bulk γ -Si₃N₄ instead of a strong high frequency mode.

Thermal properties have been obtained using the QHA. At 300 K the specific heat, linear thermal expansion coefficient and thermal Grüneisen parameter are calculated to be 92.39 J/K mol, 3.47×10^{-6} K⁻¹ and 1.194 , respectively. We hope the obtained information will be useful in characterization of γ -Si₃N₄ and for the appraisal of applications.

ACKNOWLEDGMENTS

Dr. G. Kresse (University of Vienna) is acknowledged for technical help in the calculations. The authors thank Professor Ruud Metselaar (SVM, TUE), Dr. Xiao Tang (Element Six B. V., NL) and Dr. Jan Los (KUN) for helpful discussions and the critical reading of this manuscript. A portion of this work represents part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), and the financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) is gratefully acknowledged.

- ¹A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, and R. Boehler, *Nature (London)* **400**, 340 (1999).
- ²A. Zerr, M. Scharz, G. Serghiou, E. Kroke, G. Miehe, R. Riedel, and R. Boehler, *Ger. Offen.* (2000) DE 19855514 A1 (June, 8, 2000).
- ³R. Riedel, A. Zerr, E. Kroke, and M. Schwarz, *Ceram. Trans.* **112**, 119 (2001).
- ⁴S. D. Mo, L. Z. Ouyang, W. Y. Ching, I. Tanaka, Y. Koyama, and R. Riedel, *Phys. Rev. Lett.* **83**, 5046 (1999).
- ⁵W.-Y. Ching, S.-D. Mo, L. Z. Ouyang, P. Rulis, I. Tanaka, and M. Yoshiya, *J. Am. Ceram. Soc.* **85**, 75 (2002).
- ⁶W. Y. Ching, S.-D. Mo, and L. Z. Ouyang, *Phys. Rev. B* **63**, 245110 (2001).
- ⁷I. Tanaka, F. Oba, and W.-Y. Ching, *Mater. Integr.* **14**, 21 (2001).
- ⁸F. Oba, K. Tatsumi, H. Adachi, and I. Tanaka, *Appl. Phys. Lett.* **78**, 1577 (2001).
- ⁹F. Oba, K. Tatsumi, I. Tanaka, and H. Adachi, *J. Am. Ceram. Soc.* **85**, 97 (2002).
- ¹⁰R. J. Brook, *Nature (London)* **400**, 312 (1999).
- ¹¹I. Tanaka, F. Oba, T. Sekine, E. Ito, A. Kuba, K. Tatsumi, H. Adachi, and T. Yamamoto, *J. Mater. Res.* **17**, 731 (2002).
- ¹²A. Zerr, M. Kempf, M. Schwarz, E. Kroke, M. Goken, and R. Riedel, *J. Am. Ceram. Soc.* **85**, 86 (2002).
- ¹³J. Z. Jiang, F. Kragh, D. J. Frost, K. Stahl, and H. Lindelov, *J. Phys.: Condens. Matter* **13**, L515 (2001).
- ¹⁴F. L. Riley, *J. Am. Ceram. Soc.* **83**, 245 (2000).
- ¹⁵T. Sekine, *J. Am. Ceram. Soc.* **85**, 113 (2002).
- ¹⁶T. Sekine and T. Mitsushashi, *Appl. Phys. Lett.* **79**, 2719 (2001).
- ¹⁷T. Sekine, H. L. He, T. Kobayashi, M. Zhang, and F. F. Xu, *Appl. Phys. Lett.* **76**, 3706 (2000).
- ¹⁸M. Schwarz, G. Miehe, A. Zerr, E. Kroke, B. T. Poe, H. Fuess, and R. Riedel, *Adv. Mater.* **12**, 883 (2000).
- ¹⁹G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); **49**, 14251 (1994).
- ²⁰G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ²¹G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²²G. Kresse, J. Furthmüller, and J. Hafner, *Europhys. Lett.* **32**, 729 (1995).
- ²³G. A. de Wijs, C. M. Fang, G. Kresse, and G. de With, *Phys. Rev. B* **65**, 094305 (2002).
- ²⁴G. Kern, G. Kresse, and J. Hafner, *Phys. Rev. B* **59**, 8551 (1999).
- ²⁵K. Kunc and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982).
- ²⁶W. B. White and B. A. De Angelis, *Spectrochim. Acta, Part A* **32**, 985 (1967).

- ²⁷P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
- ²⁸G. Kresse and J. Furthmüller, Phys. Rev. B **59**, 1758 (1999).
- ²⁹F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).
- ³⁰N. W. Wyckoff, *Crystal Structures* (Interscience, New York, 1962), Vol. 2.
- ³¹J. Jiang, H. Lindelov, L. Gerward, K. Stahl, J. M. Recio, P. Mori-Sanchez, M. Mezouar, E. Dooryhee, A. Fitch, and D. J. Frost, Phys. Rev. B **65**, 161202 (2002).
- ³²J. Z. Jiang, K. Stahl, R. W. Berg, D. J. Frost, T. J. Zhou, and P. X. Shi, Europhys. Lett. **51**, 62 (2000).
- ³³E. Soignard, M. Somayazulu, J. J. Dong, O. F. Sankey, and P. F. McMillan, J. Phys.: Condens. Matter **13**, 557 (2001).
- ³⁴M. Zhang, H. L. He, F. F. Xu, T. Sekine, T. Kobayashi, and Y. Bando, J. Appl. Phys. **88**, 3070 (2000).
- ³⁵H. L. He, T. Sekine, T. Kobayashi, and H. Hirosaki, Phys. Rev. B **62**, 11412 (2000).
- ³⁶W. Y. Ching, S. D. Mo, L. Ouyang, I. Tanaka, and M. Yoshiya, Phys. Rev. B **61**, 10609 (2000).
- ³⁷W. Y. Ching, S. D. Mo, I. Tanaka, and M. Yoshiya, Phys. Rev. B **63**, 064102 (2001).
- ³⁸D. Bagayoko and G. L. Zhao, Physica C **364365**, 261 (2001).
- ³⁹P. Mori-Sánchez, R. Franco, A. M. Pendás, V. Luña, and J. M. Recio, Europhys. Lett. **54**, 760 (2001).
- ⁴⁰C. M. Marian, M. Gasteich, and J. D. Gale, Phys. Rev. B **62**, 3117 (2000).
- ⁴¹C. M. Fang and R. Metselaar, J. Mater. Chem. **13**, 335 (2003).
- ⁴²S. Baroni, S. de Gironcolli, A. Dal Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001), and references therein.
- ⁴³H. T. Hintzen, M. R. M. M. Hendrix, H. Wondergem, C. M. Fang, T. Sekine, and G. de With, J. Alloys Compd. **351**, 40 (2003).
- ⁴⁴R. J. Bruls, Ph.D. thesis, Technische Universiteit Eindhoven, 2000; *CRC Materials Science and Engineering Handbook*, 2nd ed., edited by J. F. Shackelford, W. Alexander, and J. S. Park (CRC, Boca Raton, 1994).