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Abstract

The phonon spectrum of C_3N_4 with defect zincblende-type structure (δ-C_3N_4) was calculated by density functional theory (DFT) techniques. The results permit an assessment of important mechanical and thermodynamical properties such as the bulk modulus, lattice specific heat, vibration energy, thermal expansion coefficient, and thermal Grüneisen parameter. The thermal Grüneisen parameter of δ-C_3N_4 is calculated to be about 1.19 at 300 K, comparable to that of diamond. The coefficient of linear thermal expansion of this structure is calculated to be about 2.2×10^{-6} K^{-1} at room temperature. The thermal conductivity coefficient of δ-C_3N_4 is also estimated using Slack's theory to be as high as about 216 W m^{-1} K^{-1}.

1. Introduction

In the field of materials science, much attention has been paid to new hard materials with high thermal conductivity [1, 2]. Carbon nitrides have attracted the attention of both theoreticians [2–8] and experimentalists [9–13]. Recently Morelli and Heremans have used Slack's [1] model to calculate the thermal conductivities of α-, β- and spinel-C_3N_4 [14]. They found that the thermal conductivities of these carbon nitrides all exceed 100 W m^{-1} K^{-1}. The value for β-C_3N_4 is as high as 520 W m^{-1} K^{-1}. Liu and Wentzcovitch predicted the metastable form of C_3N_4 with defect zincblende-type structure (δ-C_3N_4), which contains only one molecule (seven atoms) in a cell [15]. The structure of δ-C_3N_4 has a C–N network composed of CN_4 tetrahedra. The calculated bulk modulus for this form is 425 GPa, close to those of β-C_3N_4 and diamond. Martin-Gil *et al* [16] have prepared carbon nitride using a chemical precursor route and identified these crystals to be δ-C_3N_4. The preparation method creates the possibility of large-scale production of δ-C_3N_4.

A full characterization of the physical properties of carbon nitride is important for applications. Experimentally it is rather difficult to prepare pure samples with relatively large particle sizes. Therefore, theoretical methods, especially first-principles techniques, can help. Rignanese *et al* [17] calculated the vibrational modes at the Γ point of the Brillouin zone (BZ) and the dielectric properties of different forms of C_3N_4. Recently Mattesini and Matar have calculated some mechanical and electronic properties of carbon nitrides, including δ-C_3N_4 [18]. In this paper we report first-principles calculations of the phonon spectrum for δ-C_3N_4. The dispersion curve and the partial phonon densities of states (PDOS) for both C and N atoms are reported. Using the quasi-harmonic approximation (QHA), the thermal properties, including the thermal expansion coefficient, of δ-C_3N_4 are calculated. The thermal conductivity of this compound is estimated using Slack's theory. We hope that this information will help to further an understanding of the relationship between the crystal structure and mechanical and thermal properties of carbon nitride and related materials. Moreover, we hope it may benefit the developments of new materials for industry.

2. Details of the calculations

The calculations were carried out using the first-principles molecular-dynamics computer code VASP (Vienna *ab initio* simulation program) [19–21]. Calculations for structural optimization 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 equilibrium volume and bulk modulus were obtained by a fit to a second-order Murnaghan equation of state [22].

The calculations are first performed for the electronic structure from first principles. Then the interatomic forces are obtained 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 [23] and [24]. Calculations were applied to a cubic $2 \times 2 \times 2$ supercell, which consists of eight primitive unit cells (56 atoms). Periodic boundary conditions were imposed. The positional parameters of the atoms have been fully optimized. Selected atoms were displaced slightly (about 0.01 Å) 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.

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 transverse optic and longitudinal optic (LO–TO) degeneracy of the IR-active modes. Following [25–27] 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 inter-planar force constants were calculated using a $4 \times 2 \times 2$ cell (containing 16 primitive cells), which has a long a-axis (about 13.2 Å). The phonon dispersion curves were calculated along several high-symmetry directions in the BZ. The calculations show that the vibrational modes at Γ have almost the same frequencies as those obtained from a $2 \times 2 \times 2$ supercell except for those modes with LO–TO splitting. 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 electronic structure calculations were carried out in the local density approximation (LDA), using the projector-augmented wave method [28, 29]. The electronic wavefunctions were sampled on a $4 \times 4 \times 4$ k-point mesh in the BZ of the $2 \times 2 \times 2$ 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 wavefunctions was 945 eV (69 Ryd).

Table 1. The lattice parameter (a), coordinates of nitrogen atoms (x), and bulk modulus (B) for δ-C_3N_4 from our calculations compared with those from literature (prediction versus experiments).

Method	a (Å)	x of N	d (C–N) (Å)	B (GPa)
Theoretical				
LDA[a]	3.4097	0.2544	1.47	428
LDA[b]	3.43	0.254	1.48	425
LDA[c]	3.44			430
LDA[d]	3.3988	0.2549		
LDA[e]	3.4087	0.2553		425.9
Experimental				
HRTEM[c]	3.52			
EXLFS[c]	3.41		1.47	

[a] This work.
[b] Reference [15].
[c] Reference [16].
[d] Reference [17].
[e] Reference [18].

Convergence of the total energy as well as of frequencies with the number of k-points and the plane-wave cutoff has been checked.

In the quasi-harmonic approximation (QHA), the Helmholtz energy (F) is given by

$$F(V, T) = U_0(V) + \tfrac{1}{2} \int \hbar\omega g(V, \omega)\,d\omega + \int k_B T \ln\left[1 - \exp(-\hbar\omega/kT)\right] g(V, \omega)\,d\omega \qquad (1)$$

where the first, second, and third terms are the total lattice energy, zero point, and vibrational contributions, respectively. $U_0(V)$ denotes the total energy, ω denotes the phonon frequencies, $g(V, \omega)$ denotes the PDOS, k_B denotes Boltzmann's constant, and $\hbar$ denotes Planck's constant. The values of $U_0(V)$ and the PDOS are calculated for several volumes, and $F(V, T)$ is interpolated to obtain the zero-pressure volume $V_{zp}(T)$. The summation (integration) runs 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 [25, 27, 29]. From equation (1) and standard thermodynamics, the thermal properties, including internal energy, entropy, specific heat, thermal expansion coefficient, etc can be obtained. The phonon densities of states have been calculated for seven different volumes (covering a volume variation of about 12%) with optimized structures to obtain the thermal properties from equation (1).

3. Calculated results for δ-C_3N_4

3.1. Structure optimization

The crystal structure of δ-C_3N_4 is cubic with space group $P\bar{4}3m$ (number 215 in [31]). There is only one formula unit per unit cell. The crystal structure of δ-C_3N_4 is completely defined by the lattice parameter a and the positional parameter x of the N atoms.

There are several calculations on the crystal structure and bulk modulus of δ-C_3N_4, as summarized in table 1. Our results, obtained just by minimizing the total energy, are also listed. Experimental results are also included for comparison [14]. As shown in table 1, the calculated lattice parameters from different methods are also in good agreement with the experimental values [14]. Our value of the bulk modulus is also in good agreement with the former calculations [14–17]. The bulk modulus B (428 GPa) is close to that (437 GPa) of the β-C_3N_4 obtained by Liu and Wentzcovitch [15] and that (about 442 GPa) of diamond as
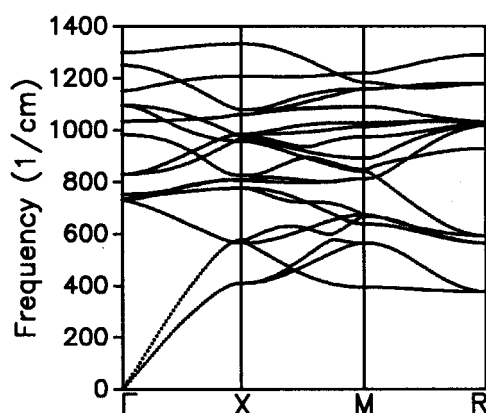
Figure 1. Calculated phonon dispersion curves along high-symmetry directions in the BZ for δ-C$_3$N$_4$.

Table 2. Calculated frequencies f of the optical modes of C$_3$N$_4$ at the Γ-point of the primitive cell. The LO modes of the infrared-active species are in parentheses.

Species	f (cm^{-1}) [a]	f (cm^{-1}) [b]	Dominant eigencharacters
T_2 (IR)	730 (752)	738.3 (752.8)	C, N
T_1	733	741	C, N
T_1	831	828.9	C, N
A_1	993	990.5	N
T_2 (IR)	1035 (1152)	1036.4 (1159.8)	C, N
E	1095	1103.7	N
T_2 (IR)	1250 (1299)	1254.5 (1308.0)	C, N

[a] This work.
[b] Reference [17].

calculated by Cohen *et al* [3]. The C–N bonds in δ-C$_3$N$_4$ (1.47 Å) are close to those (1.45 Å [5]) in β-C$_3$N$_4$ [5, 7], but are much shorter than the C–C bonds in diamond (about 1.54 Å) [2, 30].

The electronic band structure calculations show that δ-C$_3$N$_4$ is an insulator. The calculated energy gap is about 2.8 eV, in good agreement with the former calculations (2.86 eV) by Mattesini and Matar [18].

3.2. Phonon spectrum

The primitive cell of δ-C$_3$N$_4$ contains one formula unit (seven atoms) giving rise to a total of 21 phonon branches (three acoustic modes are included). As shown in figure 1, which shows the dispersion curves along the high-symmetry lines in the Brillouin zone (BZ), the 21 phonon branches fill the entire energy range, leaving no gap in the PDOS. The optical branches are at high frequencies (>400 cm^{-1}).

The phonon modes at Γ for δ-C$_3$N$_4$ with space group $P\bar{4}3m$ (number 215 in [31]) are classified as

$$\Gamma(k = 0) = A_1(\text{R}) + E_1(\text{R}) + 3T_2(\text{IR}) + 2T_1 \tag{2}$$

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 2.
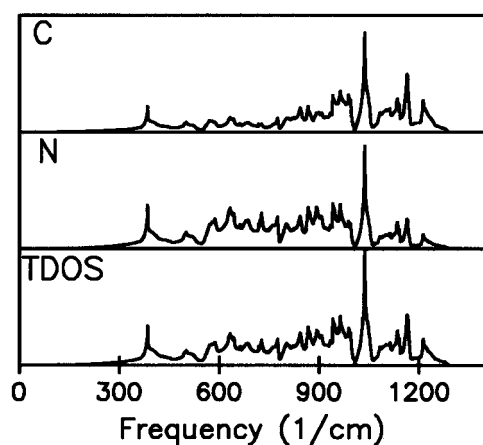
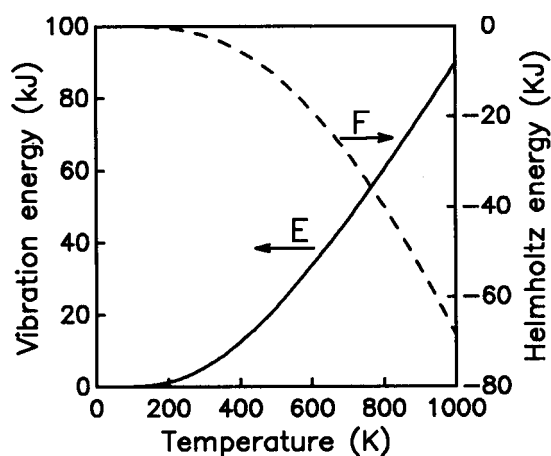**Figure 2.** Partial and total PDOS for δ-C_3N_4.

Figure 3. The internal energy E (full curve) and Helmholtz free energy F (dashed curve) of δ-C_3N_4 calculated from the phonon density of states at equilibrium volume using the QHA. Energies are per formula unit per mole.

The crystal symmetry implies two Raman- and three IR-active modes. The calculated values are in good agreement with those calculated by Rignanese *et al* [17]. For the convenience of the reader the frequencies are listed in table 2.

Figure 2 shows the calculated partial and total PDOS of δ-C_3N_4. The total PDOS spans up to about 1332 cm^{-1}. The partial density of states of the C atom is similar to that of the N atoms, due to the similar masses of both atoms. In fact, most of the vibrational modes, except those with A and E eigencharacters, have contributions from both C and N atoms, as shown in table 2.

3.3. The specific heat and vibrational entropy for δ-C_3N_4

The calculated zero-point energy for the equilibrium volume ($a = 3.4097$ Å) of δ-C_3N_4 is 1122.47 meV/fu (fu represents a C_3N_4 formula unit).

Figure 3 shows the calculated internal energy E and the Helmholtz free energy F at the equilibrium volume as a function of temperature. The value of F decreases rapidly from about
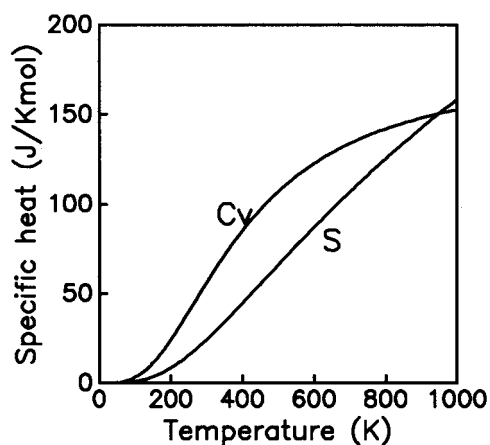
Figure 4. The specific heat C_v and vibration entropy S of δ-C$_3$N$_4$. C_v and S are in the same units.
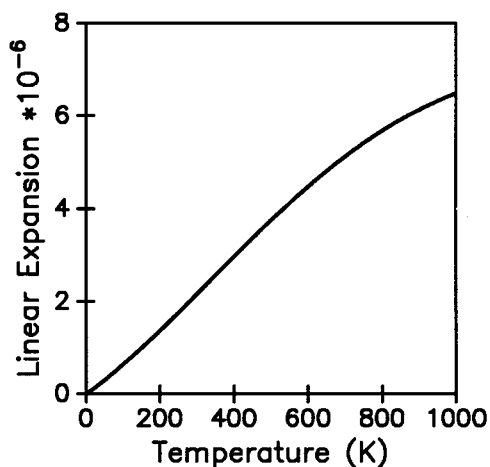

Figure 5. The linear coefficient of thermal expansion α of δ-C$_3$N$_4$.

60 K, while the absolute value of E increases rapidly from about 120 K. The calculated values of the Helmholtz energy F for δ-C$_3$N$_4$ are about -2.01 and -68.41 kJ mol^{-1} at 300 and 1000 K, respectively. Figure 4 shows the specific heat C_v and entropy S at the equilibrium volume. The C_v at 300 and 1000 K are about 56.19 and 152.54 J mol^{-1} K^{-1}, respectively. The calculated values of the entropy S for δ-C$_3$N$_4$ are about 68.42 and 158.24 kJ mol^{-1} at 300 and 1000 K, respectively.

From $F(V, T)$ (equation (1)) we also calculate the zero-pressure volume (and lattice constant) as a function of temperature. At 0 K, the lattice constant is 3.4235 Å, which is only slightly larger (0.4%) than the lattice constant obtained from straightforward total energy minimization. This difference is entirely due to the zero-point motion of the atoms. At 300 and 1000 K the lattice constants are 3.4242 and 2.4356 Å, respectively.

The calculated linear lattice thermal expansion coefficient $\alpha(T) = [\mathrm{d}a(T)/\mathrm{d}T]/a(T) = [\mathrm{d}V(T)/\mathrm{d}T]/[3V(T)]$ of δ-C$_3$N$_4$ is shown in figure 5. It increases almost linearly with temperature to approximately 600 K. Above 600 K the increase is gradually reduced. The

calculated linear coefficients of thermal expansion (CTE) are 2.2×10^{-6} and 6.5×10^{-6} K^{-1} at 300 and 1000 K, respectively.

The thermal Grüneisen parameter, which is very important in materials science, is defined as $\gamma_{th} = (V_m \alpha_v B / C_v)$, where V_m is the molar volume, B the isothermal bulk modulus, α_v the volume thermal expansion coefficient ($\alpha_v = 3\alpha$), and C_v the heat capacity. At zero pressure, the calculated values are $\gamma_{th} = 1.194$ and 1.299 for 300 and 1000 K, respectively. These values are close to the corresponding data for γ-Si$_3$N$_4$ (about 1.194 and 1.346 at 300 and 1000 K, respectively) [27], and to that of diamond (about 1.19 at room temperature) [32]. These values are significantly larger than those (about 0.70 at room temperature) for β-Si$_3$N$_4$ and β-C$_3$N$_4$, though it is generally believed that the Grüneisen parameter for the zincblende-type structure is close to that of β-Si$_3$N$_4$-type materials [1, 14].

The maximum thermal conductivity for δ-C$_3$N$_4$ can be estimated from Slack's equation [1, 14]

$$\kappa = \frac{A \bar{M} \delta \theta^3}{\gamma^2 T n^{2/3}} \tag{3}$$

in which A is a constant ($A = 3.04 \times 10^7$ W mol kg^{-1} m^{-2} K^{-3}), $\bar{M}$ (kg mol^{-1}) the mean atomic mass, δ^3 (m^{-3}) the average volume of one atom in the primitive unit cell, θ (K) the Debye temperature, γ_{th} the Grüneisen parameter, and n the number of atoms in the primitive cell.

The Debye temperature can be calculated from the calculated phonon DOS. At room temperature the Debye temperature θ for δ-C$_3$N$_4$ is about 1680 K, close to that of β-C$_3$N$_4$ (1778 K) [14].

From equation (3) we obtain the thermal conductivity for δ-C$_3$N$_4$ to be about 216 W m^{-1} K^{-1}, which is close to that of β-Si$_3$N$_4$, but is smaller than that of β-C$_3$N$_4$ [14].

As shown above, the material is calculated to be a hard insulator with thermal conductivity close to that of SiC and AlN. Therefore δ-C$_3$N$_4$ may be used as a heat sink material for thermal management. Furthermore, the low coefficient of thermal expansion (CTE) makes δ-C$_3$N$_4$ potentially useful for bonding chips.

4. Conclusions

δ-C$_3$N$_4$ has a bulk modulus (about 428 GPa) close to that (442 GPa) of diamond. The phonon spectrum and density of states for δ-C$_3$N$_4$ have been calculated using a first-principles technique. The optical branches are at rather high frequencies (above 400 cm^{-1}). The linear coefficient of thermal expansion is about 2.2×10^{-6} at 300 K. The thermal Grüneisen parameter is about 1.19 at 300 K, which is close to that of diamond. The thermal conductivity has been estimated to be about 216 W m^{-1} K^{-1}.

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