

Ab initio studies of novel carbon nitride phase $C_2N_2(CH_2)$



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ABSTRACT

First principles calculations are used to study the structural, mechanical, and electronic properties of $C_2N_2(CH_2)$. Due to the large bulk modulus and shear modulus, $C_2N_2(CH_2)$ can be regarded as a potential candidate of incompressible and hard material. For the first time, the tensors of the elastic constants were calculated and used for the analysis and visualization of the directional dependence of the Young's modulus and shear modulus. The maximal value of the Young's modulus is along the [001] direction. The calculated band structure is typical for insulator. The quasi-harmonic Debye model is applied to the study of the thermodynamic properties. The thermal expansions, heat capacities, Grüneisen parameter on the temperature and pressure are obtained in the pressure range from 0 to 100 GPa and temperature range from 0 to 2000 K.

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1. Introduction

In the past few decades, the fact that diamond [1] and cubic boron nitride (c-BN) [2] are superhard materials has been accepted; meanwhile, extensive experimental and theoretical efforts have been devoted to the search of new superhard materials, particularly to the covalent compounds formed by light elements (B, C, N, and O), such as BC_2N [3], BC_7 [4], B_6O [5,6], etc. These compounds attain their hardness from strong covalent bonds and isotropic structure. The strengthening mechanism of these compounds have been studied detailedly in Refs. [7–9,6]. Carbon-nitride-related materials attract much attention [10,11] by boasting their bonds which is slightly shorter than the C–C bonds in diamond, especially for β - C_3N_4 [12] which has been a particular focus of synthetic work due to the predicted ultra-high modulus (~ 430 GPa). Many synthetic studies on superhard C_3N_4 have been conducted over the last two decades, including chemical and physical vapor depositions [13], the implantation of nitrogen ions into graphite [14], and direct synthesis under high pressure [15,16]. But no conclusive report has been obtained, hitherto. In the course of synthetic studies on superhard carbon nitride, Horvath-Bordon et al. [17] reported the synthesis $C_2N_2(NH)$ prepared from the dicynamide molecules as precursor in a laser-heated diamond anvil cell at high pressure and high temperature. Later, Salamat et al. [18] produced the high-density dwur-structured compound

$C_2N_2(NH)$ by heating $C_2N_4H_4$ as a molecular precursor at high pressure. $C_2N_2(NH)$ is the first material obtained having the definite C–N single bond expected in the superhard C_3N_4 . Recently, Sougawa et al. [11] synthesized $C_2N_2(CH_2)$ nanoplatelet by subjecting a precursor $C_3N_4H_xO_y$ nanoparticle in a laser-heating diamond anvil cell to the pressure of 40 GPa and temperature of 1200–2000 K. The crystal lattice constants and internal atomic positions are determined by X-ray diffraction and first principles calculations. Compared to $C_2N_2(NH)$ [19], the detailed physical properties of $C_2N_2(CH_2)$ including structural, elastic, electronic, and thermodynamic properties are least studied so far. Therefore, as another new kind of carbon nitride phases, one might expect the excellent physical properties mentioned above. In the present work, using first principles calculations, we find that $C_2N_2(CH_2)$ is a wide band-gap insulator. The influence of elastic properties on the plastic deformation behavior and the role of the possible anisotropy of interatomic bonding are also studied. These would provide new insight into the excellent mechanical properties of $C_2N_2(CH_2)$. In addition, the effects of pressure and temperature on the thermodynamic properties of $C_2N_2(CH_2)$ are systematically investigated, and this can help us to understand its potential application under high pressure and high temperature further.

2. Computational methods

The density functional theory (DFT) [20] calculations have been performed within the generalized gradient approximation (GGA) [21] and local density approximation (LDA) [22], as implemented in the Vienna *ab initio* simulation package (VASP) [23]. The electron

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and core interactions were included by using the frozen-core all-electron projector augmented wave (PAW) method [24], with H: $1s^1$, C: $2s^2 2p^2$, and N: $2s^2 2p^3$ treated as the valence electrons. The energy cutoff of 800 eV and appropriate Monkhorst–Pack k points mesh $10 \times 10 \times 10$ were chosen to ensure that energy calculations are converged to better than 1 meV/atom. The elastic constants were determined from evaluation of stress tensor generated small strain. Bulk modulus, shear modulus, Young's modulus, and Poisson's ratio were estimated by using Voigt–Reuss–Hill approximation [25]. And the quasi-harmonic Debye model was applied to investigate the lattice thermal expansion [26].

3. Results and discussion

3.1. Structural properties

The experiment has demonstrated that $C_2N_2(CH_2)$ adopts orthorhombic structure with the symmetry of the space group $Cmc2_1$ [11] as shown in Fig. 1. There are four formula units (f. u.) in a unit cell, in which C1 is tetrahedrally coordinated with three N and one C2 atoms, C2 bridges those two tetrahedrons, and N atoms are connected to three C1 neighbors. We optimized both lattice geometry and ionic positions to get a fully relaxed structure of $C_2N_2(CH_2)$. The calculated equilibrium lattice parameters and bond lengths within GGA and LDA method are listed in Table 1, together with corresponding experimental data and theoretical values. It is clear that the predicted lattice constants and bond lengths within LDA method are smaller than those within GGA method, as the usual cases. The predicted structural constant a , b , and c deviate from

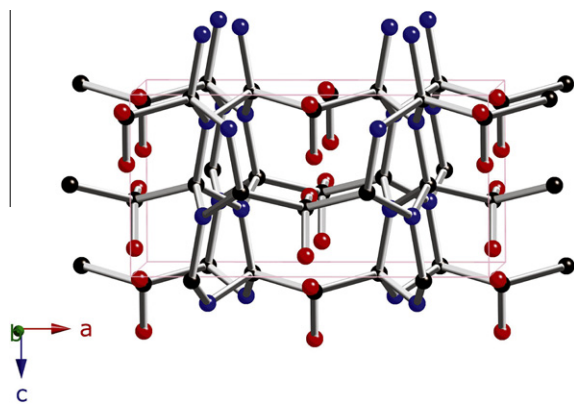


Fig. 1. Crystal structure of $C_2N_2(CH_2)$, the large, middle, and small spheres represent N, C, and H atoms, respectively.

the corresponding experimental values within 4.9%, 1.7%, and 0.5%, respectively, and agree well with the previous theoretical values performed by the same authors at LDA level. Furthermore, it should be noted that the bond lengths are also consistent with those of experimental results in Table 1. In order to provide some insight into the pressure behaviors of $C_2N_2(CH_2)$, the total energy of $C_2N_2(CH_2)$ was minimized as a function of the selected unit cell volume at different pressure. By fitting the E–V data at different pressures into the third-order Birch–Murnaghan equation of states (EOS) [27], we obtained the values of equilibrium bulk modulus and its pressure derivative for $C_2N_2(CH_2)$ are 239/263 GPa and 3.57/3.51 at GGA/LDA level. To compare the incompressibility of $C_2N_2(CH_2)$ and $C_2N_2(NH)$ under pressure, the volume compressions as a function of pressure are plotted in Fig. 2. One can see that the incompressibility of $C_2N_2(CH_2)$ is little smaller than that of $C_2N_2(NH)$.

3.2. Mechanical properties

3.2.1. Elastic constants

The elastic properties (including elastic constants, elastic moduli, elastic anisotropy, etc.) give important information concerning the nature of the forces operating in solids. Particularly, they provide information on the stability and stiffness of materials. To our knowledge, there are no experimental data or other theoretical studies available about the elastic constants of $C_2N_2(CH_2)$. In the present work, the strain–stress method was used in calculating

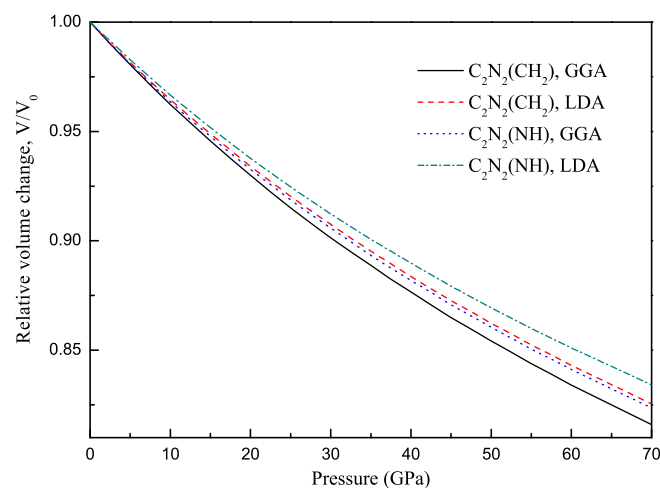


Fig. 2. Variation of ratio V/V_0 as a function of pressure.

Table 1

Calculated equilibrium lattice parameters a , b , c , bond length (in Å), EOS fitted bulk modulus B_0 (in GPa), and its derivative B'_0 for $C_2N_2(CH_2)$.

Method	a	b	c	B_0	B'_0	d_{C1-N1}	d_{C1-C2}	d_{C-H}
GGA ^a	8.1259	4.6381	4.1178	239	3.57	1.5050, 1.4760, 1.4691	1.5535	1.0835, 1.0793
LDA ^a	8.0168	4.5662	4.0667	263	3.51	1.4818, 1.4596, 1.4521	1.5323	1.0913, 1.0867
Experimental ^b	7.625	4.490	4.047			1.503, 1.501, 1.444	1.456	1.075, 1.064
Theoretical ^b	8.1222	4.6430	4.1177			1.505, 1.476, 1.469	1.551	1.084, 1.080

^a This work.

^b Ref. [11].

Table 2
Calculated elastic constants C_{ij} (in GPa) for $C_2N_2(CH_2)$, $C_2N_2(NH)$, c -BN, and B_6O .

Structure	Method	C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
$C_2N_2(CH_2)$	GGA	505	489	728	283	186	143	85	122	99
	LDA	529	510	799	309	201	145	77	142	119
$C_2N_2(NH)$	GGA ^a	597	567	804	335	221	222	89	107	79
	LDA ^a	616	576	871	347	221	218	80	103	71
c -BN	GGA ^b	786			445			172		
B_6O	GGA ^b	603		459	179			109	50	

^a Ref. [19].

^b Ref. [6].

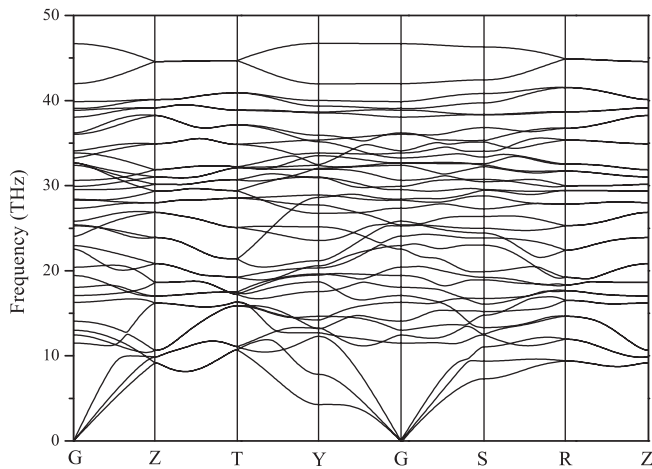


Fig. 3. The calculated phonon frequencies of $C_2N_2(CH_2)$ at the ambient pressure.

Table 3
Calculated elastic constants C_{ij} (in GPa) for $C_2N_2(CH_2)$, $C_2N_2(NH)$, c -BN, and B_6O .

Structure	Method	B_H	G_H	E_H	ν_H	G_H/B_H
$C_2N_2(CH_2)$	GGA	256	210	494	0.178	0.820
	LDA	272	222	524	0.179	0.817
$C_2N_2(NH)$	GGA ^a	276	265	600	0.137	0.960
	LDA ^a	282	270	616	0.135	0.957
c -BN	GGA ^b	376	390			
B_6O	GGA ^b	231	218			

^a Ref. [19].

^b Ref. [6].

the elastic constants. For orthorhombic crystal, there are nine independent elastic constants. The calculated results are shown in Table 2. For comparison, the theoretical value of elastic constants of $C_2N_2(NH)$ [19], c -BN, and B_6O [6] are also listed in Table 2. The calculated elastic constants of $C_2N_2(CH_2)$ satisfy the orthorhombic structural stability criteria, as can be expressed by the following inequalities [28]: $C_{11} > 0$, $C_{22} > 0$, $C_{33} > 0$, $C_{44} > 0$, $C_{55} > 0$, $C_{66} > 0$, $[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})] > 0$, $(C_{11} + C_{22} - 2C_{12}) > 0$, $(C_{11} + C_{33} - 2C_{13}) > 0$, $(C_{22} + C_{33} - 2C_{23}) > 0$, indicating that it is mechanically stable at ambient pressure. To verify its stability further, the phonon dispersion of $C_2N_2(CH_2)$ is calculated and shown in Fig. 3, no imaginary phonon frequency was detected in the whole Brillouin zone, indicating its dynamical stability at ambient pressure.

The bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, which are the most interesting elastic properties for applications, often measured for polycrystalline materials when investigating their hardness. Bulk modulus and shear modulus can be obtained by using the relations given in Ref. [25]. Young's

Table 4
Calculated anisotropy factors $A_1, A_2, A_3, A_{Ba}, A_{Bc}, A_G, A_B$ and directional bulk modulus B_a, B_b, B_c (in GPa) of $C_2N_2(CH_2)$.

Method	A_1	A_2	A_3	A_{Ba}	A_{Bc}	B_a	B_b	B_c
GGA	1.1446	0.7301	0.6942	1.0742	1.8295	670	624	1104
LDA	1.1839	0.7507	0.6554	1.0715	2.0585	685	640	1317

modulus and Poisson's ratio can be calculated by the following expressions:

$$E_H = \frac{9B_H G_H}{3B_H + G_H}, \quad (1)$$

$$\nu_H = \frac{3B_H - 2G_H}{6B_H + 2G_H}, \quad (2)$$

where the subscript H represents Hill approximation. The calculated results are given in Table 3. The calculated bulk modulus is of $C_2N_2(CH_2)$ is 256/272 GPa within GGA/LDA, which agree well with that obtained from the third-order Birch–Murnaghan EOS fitting results listed in Table 1. The results of $C_2N_2(NH)$ are also shown in Table 3 for comparison. One can see that, the bulk modulus of $C_2N_2(CH_2)$ is little smaller than that of $C_2N_2(NH)$, indicating that $C_2N_2(CH_2)$ is more compressible than $C_2N_2(NH)$. This is in accordance with the results shown in Fig. 2. G/B ratio can be used to determine the relative directionality of the bonding in the material. The calculated ratio G/B for $C_2N_2(CH_2)$ is 0.820, which is smaller than that of $C_2N_2(NH)$ at the GGA level. This shows that the directionality of C–N bond in $C_2N_2(CH_2)$ is not as strong as that in $C_2N_2(NH)$. Nevertheless, the calculated mechanical properties show that $C_2N_2(CH_2)$ is a potential hard material.

3.2.2. Elastic anisotropy

Elastic anisotropy can give a prediction of how the atoms arrange in each direction, the bonding properties, and some chemical characters in different directions of materials. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. the shear anisotropic factor for the {100} shear plane between the $\langle 011 \rangle$ and $\langle 010 \rangle$ directions is [29]

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}}. \quad (3)$$

For the {010} shear planes between $\langle 101 \rangle$ and $\langle 001 \rangle$ directions it is

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (4)$$

and for the {001} shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions it is

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}}. \quad (5)$$

The shear anisotropy factors A_1, A_2 , and A_3 must be 1.0 for an isotropic crystal. Any departure from 1.0 is a measure of the degree of elastic anisotropy. The calculated results are shown in Table 4. It can be seen that, the anisotropy of the {001} shear planes between $\langle 110 \rangle$ and $\langle 010 \rangle$ directions is the largest. The bulk modulus along the a -, b - and c -axis are defined as $B_i = i(dP/di)$ with $i = a, b$ and c . Then the anisotropies of the bulk modulus along the a -axis and c -axis with respect the b -axis can be expressed as $A_{Ba} = B_a/B_b$ and $A_{Bc} = B_c/B_b$. The calculated results are also listed in Table 4. One can see that, the directional bulk modulus along the c -axis is much larger than those along a - and b - axis.

To illustrate the elastic anisotropy in detail, it is worthy to study the variation of Young's modulus and shear modulus with

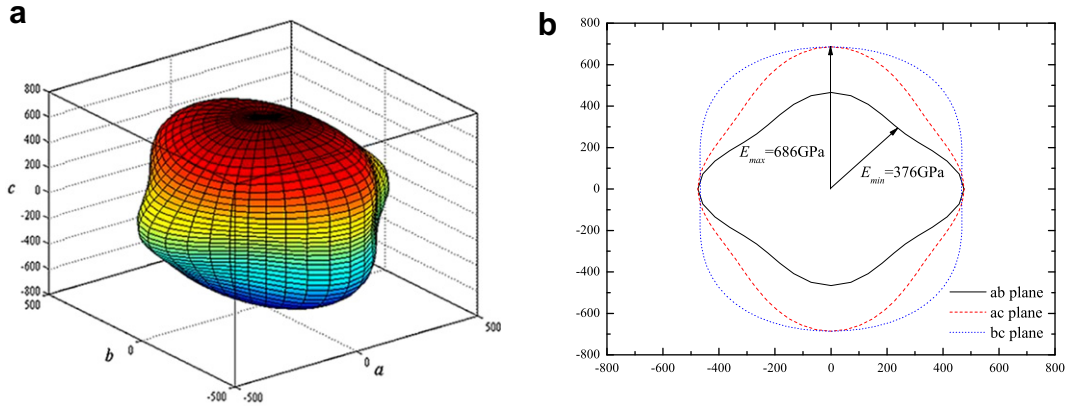


Fig. 4. (a) Directional dependence of the Young's modulus in $C_2N_2(CH_2)$, (b) The plane projections of the directional dependence of the Young's modulus in $C_2N_2(CH_2)$.

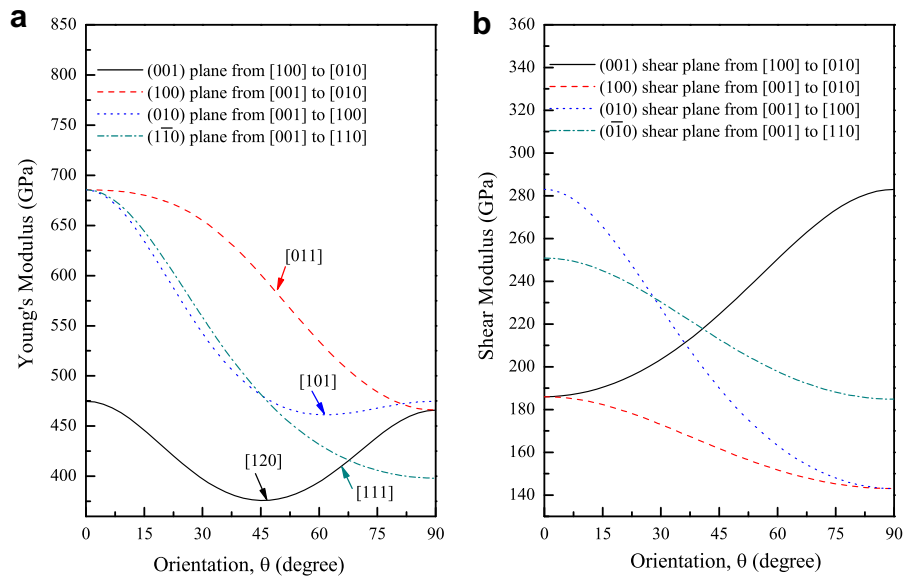


Fig. 5. Orientation dependence of Young's modulus (a) and orientation dependence of the shear modulus (b) in $C_2N_2(CH_2)$.

direction. The variation of Young's modulus along an arbitrary $[hkl]$ direction for orthorhombic symmetry can be written as [29]

$$E^{-1} = s_{11}\alpha^4 + s_{22}\beta^4 + s_{33}\gamma^4 + 2s_{12}\alpha^2\beta^2 + 2s_{23}\beta^2\gamma^2 + 2s_{13}\alpha^2\gamma^2 + s_{44}\beta^2\gamma^2 + s_{55}\alpha^2\gamma^2 + s_{66}\alpha^2\beta^2, \quad (6)$$

where α , β , and γ is the direction cosine of the tensile stress direction, and s_{11} , s_{22} , etc., are elastic compliance constants which are given by Ney [30]. The directional dependence of the Young's modulus is shown in Fig. 4(a), and the plane projections of the directional dependence of the Young's modulus in Fig. 4(b) for comparison. From Eq. (6), we can deduce the expressions of the orientation dependence of Young's modulus when the tensile direction is rotated on specific planes. When Young's modulus for a tensile axis is within the (001) plane, let θ be the angle of between $[hk0]$ and $[100]$. Then the orientation dependence of Young's modulus can be expressed as:

$$E^{-1} = s_{11}\cos^4\theta + s_{22}\sin^4\theta + 2s_{12}\sin^2\theta\cos^2\theta + s_{66}\sin^2\theta\cos^2\theta. \quad (7)$$

When Young's modulus for a tensile axis is within the (100) plane, let θ be the angle of between $[001]$ and $[0kl]$. Then the orientation dependence of Young's modulus can be expressed as:

$$E^{-1} = s_{22}\sin^4\theta + s_{33}\cos^4\theta + \frac{1}{4}(2s_{23} + s_{44})\sin^2 2\theta. \quad (8)$$

When Young's modulus for a tensile axis is within the (010) plane, let θ be the angle of between $[001]$ and $[h0l]$. Then the orientation dependence of Young's modulus can be expressed as:

$$E^{-1} = s_{11}\sin^4\theta + s_{33}\cos^4\theta + \frac{1}{4}(2s_{13} + s_{55})\sin^2 2\theta. \quad (9)$$

When Young's modulus for a tensile axis is within the $(1\bar{1}0)$ plane, let θ be the angle of between $[001]$ and $[hkl]$. Then the orientation dependence of Young's modulus can be expressed as:

$$E^{-1} = \frac{\sin^4\theta}{(a^2 + b^2)^2} [a^4s_{11} + b^4s_{12} + a^2b^2(2s_{12} + s_{66})] + s_{33}\cos^4\theta + \frac{\sin^2\theta\cos^2\theta}{a^2 + b^2} [a^2(2s_{13} + s_{55}) + b^2(2s_{23} + s_{44})]. \quad (10)$$

The calculated results are plotted in Fig. 5(a). One can see that, the largest value of Young's modulus is 686 GPa when the tensile axis is in the $[001]$ direction. The minimal value of 376 GPa is along the $[120]$ direction. The ratio $E_{max}/E_{min} = 1.82$ is larger than that of $C_2N_2(NH)$ (1.48), indicating that there is a larger anisotropy in $C_2N_2(CH_2)$. From Fig. 5(a), we can obtain the ordering of Young's

modulus when the tensile axis along some specific direction as: $E_{[001]} > E_{[011]} > E_{[100]} > E_{[010]} \approx E_{[101]} > E_{[111]} > E_{[110]} > E_{[120]}$. This means that the crystal is stiffer when deformed uniaxially along the [001] direction.

The study of the dependence of the shear modulus on stress direction is useful in understanding plastic deformation in $C_2N_2(CH_2)$. We choose a shear plane (hkl) and vary the shear stress direction $[uvw]$ within that plane. The axis normal to the (hkl) plane is denoted as $[HKL]$. Thus, the shear modulus on the (hkl) shear plane with shear applied along $[uvw]$ direction can be expressed as [31]

$$G^{-1} = 4s_{11}\alpha_1^2\alpha_2^2 + 4s_{22}\beta_1^2\beta_2^2 + 4s_{33}\gamma_1^2\gamma_2^2 + 8s_{12}\alpha_1\alpha_2\beta_1\beta_2 + 8s_{23}\beta_1\beta_2\gamma_1\gamma_2 + 8s_{13}\alpha_1\alpha_2\gamma_1\gamma_2 + s_{44}(\beta_1\gamma_2 + \beta_2\gamma_1)^2 + s_{55}(\alpha_1\gamma_2 + \alpha_2\gamma_1)^2 + s_{66}(\alpha_1\beta_2 + \alpha_2\beta_1)^2, \quad (11)$$

where $\alpha_1, \beta_1, \gamma_1, \alpha_2, \beta_2,$ and γ_2 are the direction cosines of the $[uvw]$ and $[HKL]$ directions. For shear plane (001) with the shear stress direction rotated from [100] to [010], the direction cosines are $\alpha_1 = \cos\theta, \beta_1 = \sin\theta, \gamma_1 = 0, \alpha_2 = \beta_2 = 0,$ and $\gamma_2 = 1$, where θ is the angle between the [100] and shear stress direction. From Eq. (11), one can deduced the shear modulus can be expressed as

$$G^{-1} = s_{55} + (s_{44} - s_{55}) \sin^2 \theta. \quad (12)$$

For $C_2N_2(CH_2)$, $s_{44} < s_{55}$, the shear modulus is the largest along [010] and the smallest along [001].

When (100) is the shear plane, we rotate the shear stress direction from [001] to [010]. In this case, $\alpha_1 = 0, \beta_1 = \sin\theta, \gamma_1 = \cos\theta, \alpha_2 = 1, \beta_2 = \gamma_2 = 0$, then the shear modulus can be obtained as

$$G^{-1} = s_{55} + (s_{66} - s_{55}) \sin^2 \theta. \quad (13)$$

Since in our case, $s_{66} > s_{55}$, the shear modulus is the largest along [001] and the smallest along [010].

For the shear plane (010) with the shear stress direction rotated from [001] to [100],

$$G^{-1} = s_{44} + (s_{66} - s_{44}) \sin^2 \theta. \quad (14)$$

Due to $s_{44} < s_{66}$, the shear modulus is the largest along [001] with $G_{(010)[001]} = 283$ GPa and the smallest along [100] with $G_{(010)[100]} = 143$ GPa.

If the shear plane is $(1\bar{1}0)$, we rotate the shear stress from [001] to $[1\bar{1}0]$, then $\alpha_1 = \frac{a}{\sqrt{a^2+b^2}} \sin\theta, \beta_1 = \frac{b}{\sqrt{a^2+b^2}} \sin\theta, \gamma_1 = \cos\theta, \alpha_2 = \frac{b}{\sqrt{a^2+b^2}}, \beta_2 = -\frac{a}{\sqrt{a^2+b^2}}, \gamma_2 = 0$, where θ is the angle between [001]

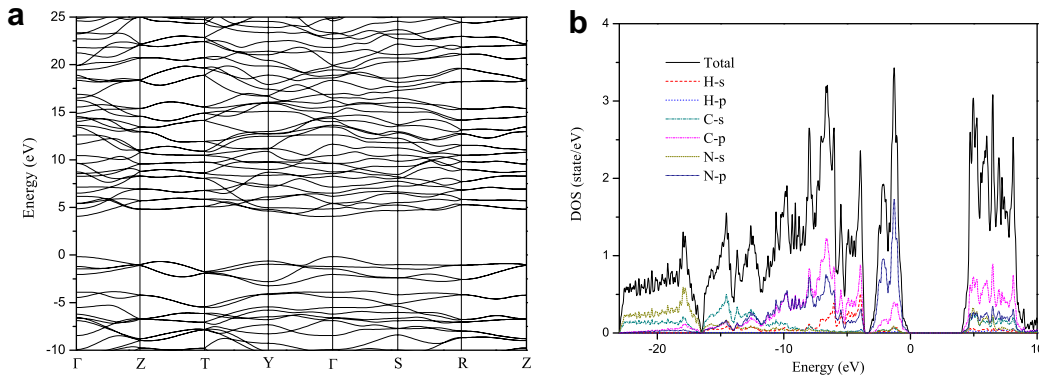


Fig. 6. The calculated band structure (a) and DOS (b) of $C_2N_2(CH_2)$.

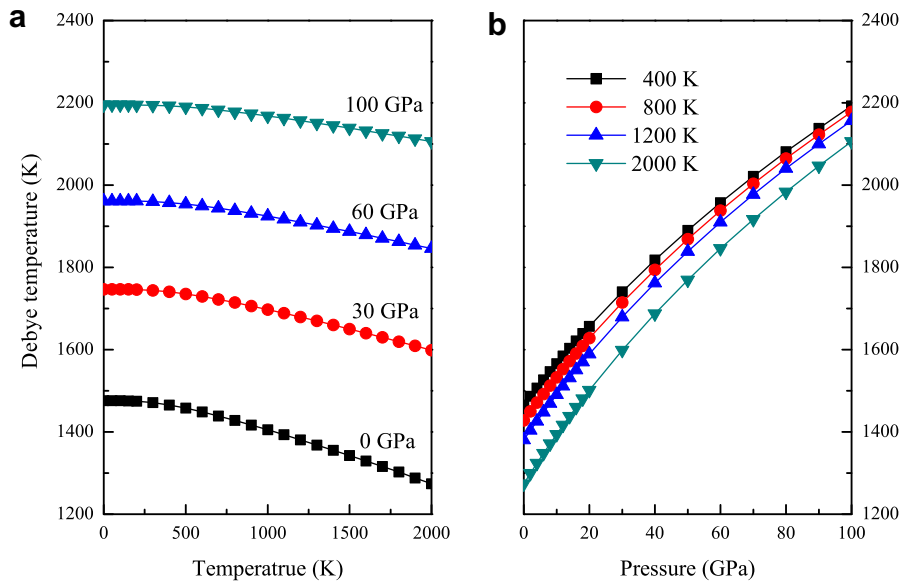


Fig. 7. Temperature (a) and Pressure (b) dependence of the Debye temperature for the $C_2N_2(CH_2)$.

and the shear stress direction, a and b are the lattice constants. Then the shear modulus can be expressed as

$$G^{-1} = \frac{\sin^2 \theta}{(a^2 + b^2)^2} [a^2 b^2 (4s_{11} + 4s_{22} - 8s_{12}) + (b^2 - a^2)^2 s_{66}] + \frac{\cos^2 \theta}{a^2 + b^2} (a^2 s_{44} + b^2 s_{55}) \quad (15)$$

The orientation dependence of the shear modulus for the four cases discussed above is plotted in Fig. 5(b).

3.3. Electronic properties

To understand the mechanical properties of $C_2N_2(CH_2)$ on a fundamental level, the band structure and electronic densities of states (DOS) of $C_2N_2(CH_2)$ were calculated at zero pressure within GGA method, as shown in Fig. 6. It can be seen from Fig. 6(a) that, $C_2N_2(CH_2)$ is insulator characterized by large direct energy gap of ~ 4.24 eV located at G point, which is slightly smaller than that of $C_2N_2(NH)$ (~ 4.36 eV) [19]. It is known that the calculated band gaps with DFT usually underestimate by 30–50%, the true band gap must be larger than the calculated result. The wide band gap means $C_2N_2(CH_2)$ can be a good optical material. The total DOS and the partial wave DOSs projected onto different atoms at 0 GPa are plotted in Fig. 6(b). The main features of $C_2N_2(CH_2)$ can be summarized as follows: (a) the peak present in the lower energy part (-23 to -16.5 eV) of the DOS is mainly due to contributions of the s electrons of N and C; (b) the states from -16.5 eV to Fermi energy (0 eV) mainly originate from C-p and N-p orbitals with slight contributions of C-s and H-s. Moreover, the partial DOS profiles for both C-p and N-p are very similar in the range of -16.5 to 0 eV, reflecting the significant hybridization between these two orbitals. This fact also shows that a strong covalent interaction between the C and N atoms; (c) In the conduction band region of DOS, the peaks are mainly superimposed by the C-p. Mulliken atomic population, which is a useful tool in evaluating the nature bonds in a compound. Although the absolute magnitudes of Mulliken populations have little physical meaning, the relative values can still offer some useful information [32]. The ionicity in C–H bond is mainly featured by the charge transfer from H atom to C atom. The number of charge transfer in two C2–H bonds is 0.23 and

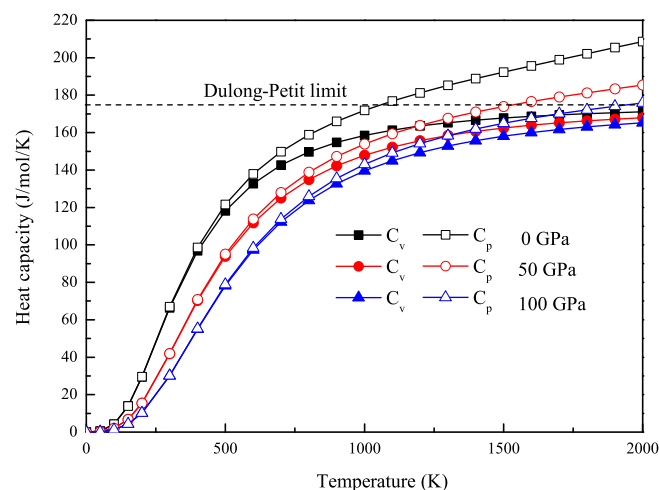


Fig. 9. Temperature dependence of the heat capacity at different pressures for the $C_2N_2(CH_2)$.

0.22, respectively. N atom obtains 0.36 e from its three neighbored C1 atoms. We thus conclude that the C–H and C–N bonds are mixture of covalent and ionic characters.

3.4. Thermodynamic properties

The investigation on the thermodynamic properties of solids at high pressure and high temperature is an interesting topic in the condensed matter physics. The investigations on the thermodynamic properties of the orthorhombic $C_2N_2(CH_2)$ under high temperature and pressure are determined by the quasi-harmonic Debye model [26]. It should be noted that the Debye model of phonon density of states is essentially a linear extrapolation of the sound speed of acoustic branches but not optical branches in order to get density of states. Since this model is very computationally quick and easy, it has been successfully applied to predict the thermodynamic properties of some materials [33–35]. The model has been described detailedly in Ref. [26]. The thermodynamic properties of the $C_2N_2(CH_2)$ are determined in the temperature range

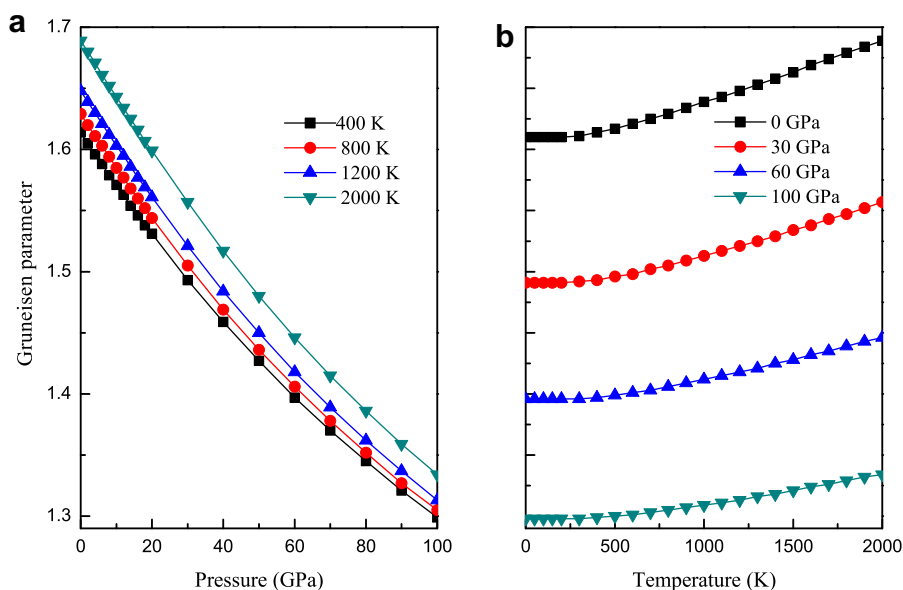


Fig. 8. Pressure (a) and Temperature (b) dependence of the Grüneisen parameter for the $C_2N_2(CH_2)$.

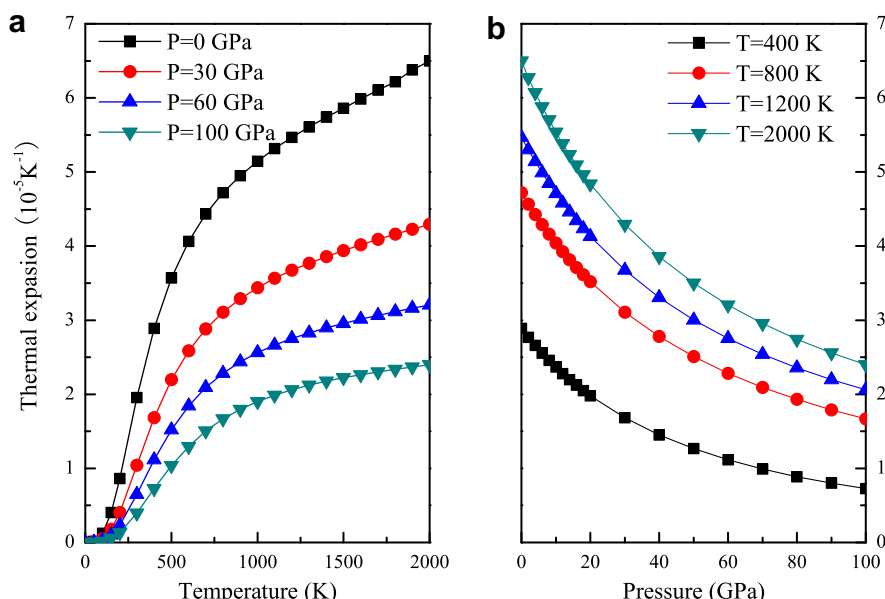


Fig. 10. Temperature (a) and Pressure (b) dependence of the thermal expansion coefficient for the $\text{C}_2\text{N}_2(\text{CH}_2)$.

from 0 to 2000 K where the quasi-harmonic model remains fully valid. Meanwhile, the pressure effect is studied in the range 0–100 GPa. In the quasi-harmonic Debye model, the Debye temperature and the Grüneisen parameter are two key quantities. The Debye temperature closely relates to many physical properties of solids, such as specific heat, dynamic properties, and melting temperature. The calculated relationships of Debye temperature on pressure and temperature are plotted in Fig. 7. It is clear seen that, Debye temperature decreases with temperature at certain pressure. The lower the pressure is, the faster Debye temperature decreases. Varying temperature from 0 to 2000 K, Debye temperature decreases 13.6% at 0 GPa and 4.0% at 100 GPa. From Fig. 7(b), one can see that the Debye temperature increases monotonously at given pressure.

The Grüneisen parameter, which describes the alteration in a crystal lattices vibration frequency, can reasonably predict the anharmonic properties of a solid, such as the temperature dependence of phonon frequencies and lattice volume. Usually, the Grüneisen parameter are positive and lie in the range 1.5 ± 1.0 . The calculated relationships of Grüneisen parameter on pressure and temperature are plotted in Fig. 8. It is found that, Grüneisen parameter increases with temperature at a given pressure, but decreases with pressure at a given temperature. Grüneisen parameter almost decreases lineally with pressure. At low temperature ($T < 300$ K), Grüneisen parameter is constant, as well as increases linearly with temperature at high temperature ($T > 500$ K).

The temperature dependence of the calculated heat capacity C_v and C_p at various pressures are shown in Fig. 9. Due to the anharmonic approximations of Debye model, the heat capacity C_v and C_p increase rapidly with pressure. At low temperature (< 300 K), the difference between C_v and C_p is slight, C_v is proportional to T^3 . However, at high temperature, the C_v approaches a constant value, C_p increases monotonously with increments of the temperature. It is also interesting to note that the values of C_v follow the Debye model at low temperature due to the anharmonic approximations. However, the anharmonic effect on C_v is suppressed and the C_v is close to a constant at sufficient high temperatures, obeying Dulong and Petit's Rule. In a word, one can see that the heat capacity increases with the temperature at certain pressure and decreases with the pressure at certain temperature. The influences of the

temperature on the heat capacity are much more significant than that of the pressure on it. The thermal expansion coefficient α with pressure and temperature for $\text{C}_2\text{N}_2(\text{CH}_2)$ are investigated, as shown in Fig. 10. In Fig. 10(a), one can see that, α increase with increasing temperature. At certain temperature, α decrease monotonically with increasing pressure. The effects of pressure on the thermal expansion coefficient are very small at low temperature, and the effects increase with increasing the temperature.

4. Conclusions

The structural, electronic, elastic and thermodynamic properties of $\text{C}_2\text{N}_2(\text{CH}_2)$ are successfully obtained using first principles calculations in combination with the quasi-harmonic Debye model. The calculated structural parameters agree well with the experimental data and previous theoretical values. Our results show that $\text{C}_2\text{N}_2(\text{CH}_2)$ has high bulk modulus and shear modulus, indicating $\text{C}_2\text{N}_2(\text{CH}_2)$ is a potential low compressible and hard materials. The directional dependence of the Young's modulus in $\text{C}_2\text{N}_2(\text{CH}_2)$ are investigated. The ordering of Young's modulus when the tensile axis along some specific direction is: $E_{[001]} > E_{[011]} > E_{[100]} > E_{[010]} \approx E_{[101]} > E_{[111]} > E_{[110]} > E_{[120]}$. The shear modulus of $\text{C}_2\text{N}_2(\text{CH}_2)$ is the largest on the (001) plane with [010] shear stress direction and on (010) plane with the [001] shear stress direction. Using the quasi-harmonic Debye model, the thermodynamic properties including the Debye temperature, Grüneisen parameter, the heat capacity, and the thermal expansion coefficients of $\text{C}_2\text{N}_2(\text{CH}_2)$ are predicted under high temperature and high pressure. High pressure leads to a smaller Grüneisen parameter, heat capacity, and thermal expansion coefficients at a given temperature. On the contrary, high temperature leads to a larger Grüneisen parameter, a larger heat capacity, and a larger thermal expansion coefficient at certain pressure.

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