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Stability of carbon nitride solids

Amy Y. Liu*
NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

Renata M. Wentzcovitch†
The Royal Institution of Great Britain, 21 Albemarle Street, London W1X 4BS, United Kingdom
and Department of Geological Sciences, University College London, Gower Street,
London WC1E 6BT, United Kingdom

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An *ab initio* variable-cell-shape molecular-dynamics algorithm is used to investigate the stability of three carbon nitrides with composition C_3N_4. The hexagonal β-C_3N_4 structure, which has been the subject of earlier investigations, is refined and its metastability is verified. Two other metastable structures are identified: a structure resembling zinc-blende CN with one C vacancy per cubic cell and a structure resembling graphitic CN with one C vacancy per four N sites. Both the refined β phase and the cubic phase have compressibilities comparable to that of diamond. The graphitic and the β phases lie very close in energy and are slightly favored over the cubic phase.

Carbon nitrides have recently been proposed as candidates for new hard materials.[1,2] This suggestion was based on a combination of an empirical model[1] and an *ab initio* calculation.[2] The model indicated that short covalent bonds like those that form between C and N are favorable for achieving low compressibility. A local-density-approximation-based (LDA) calculation of the structural and electronic properties of a hypothetical C-N solid called β-C_3N_4 supported this view. The calculation predicted the bulk modulus of β-C_3N_4 to be very large and nearly equal to that of diamond. In addition, the cohesive energy of β-C_3N_4 was found to be moderately large, suggesting that it might be an energetically favorable phase in the C-N system.

Motivated by these results, several groups have attempted to synthesize covalent C-N solids such as β-C_3N_4.[3–6] In one study,[3] amorphous carbon-nitride films were synthesized, and indentation tests found the N-rich films to be extremely hard. In other studies,[4,5] small crystallites were found embedded in amorphous C-N films. Electron diffraction indicates that β-C_3N_4 is a viable structure for these crystallites. As yet, however, adequate samples for quantitative measurements of the bulk modulus and hardness of the crystalline material have not been produced.

In this paper, we expand the theoretical search for low-energy carbon-nitride solids. We refine the β-C_3N_4 structure and examine its metastability. We also investigate two additional structural phases with composition C_3N_4. In both forms, the network of short C-N bonds differs considerably from that in the β structure. The compressibilities and energetics of all three phases are compared, and the Born stability criterion is checked in each case to test for elastic stability.

Throughout this work an *ab initio* molecular dynamics (MD) with variable-cell-shape (VCS) algorithm[7,8] is used to efficiently optimize structures under pressure. This scheme, which has been used to optimize complex structures under arbitrary pressures[9] as well as to simulate structural transitions at finite temperatures,[10] is a combination of two methods: a VCS dynamics derived from a symmetric Lagrangian[8] that automatically keeps structural trajectories within ensembles of preselected space groups, and a plane-wave-based *ab initio* MD[7] that converges the electronic-structure calculation of forces and stresses before updating the dynamical variables, allowing for time steps similar to those used in classical MD. Reliable total-energy differences are obtained as the cell shape changes by fixing the plane-wave cutoff (64 Ry). The electron-ion interaction is represented by soft separable pseudopotentials,[11] and the electron-electron interaction is treated within the LDA with the Ceperley-Alder exchange-correlation potential.[12] The special point scheme[13] is used for integrations over the Brillouin zone.

The three structural phases investigated here can be thought of as C-N networks with varying ratios of sp^2 to sp^3 bonding. The β-C_3N_4 phase, which is C_3N_4 in the β-Si_3N_4 structure (space group $P6_3/m$), is shown in Fig. 1(a). It has the appearance of three-dimensional chicken wire with six-, eight-, and 12-fold rings of alternating C and N sites. Each C is approximately tetrahedrally coordinated by N's, and each N is nearly planarly-three-fold coordinated by C's. The hexagonal Bravais lattice contains two formula units and six free parameters. In the earlier *ab initio* investigation of β-C_3N_4, the complexity of the system prevented a complete optimization of the structural parameters.[2] In the present work, the VCS MD algorithm is used to relax the structure.

The other two C_3N_4 phases considered here can be described as defect zinc-blende and defect graphite structures that are related to each other by means of a rhombohedral distortion. This is the same distortion that transforms the diamond lattice continuously into rhombohedral graphite. We speculate about the viability of these phases by making an analogy to the isoelectronic compound BN (B_4N_4). The latter exists in both zinc-blende and graphitic forms, and the C_3N_4 phases can be constructed from them by substituting three C's and one vacancy for four B's. These defect structures satisfy electron counting arguments (i.e., two per covalent bond) and are insulating like BN.

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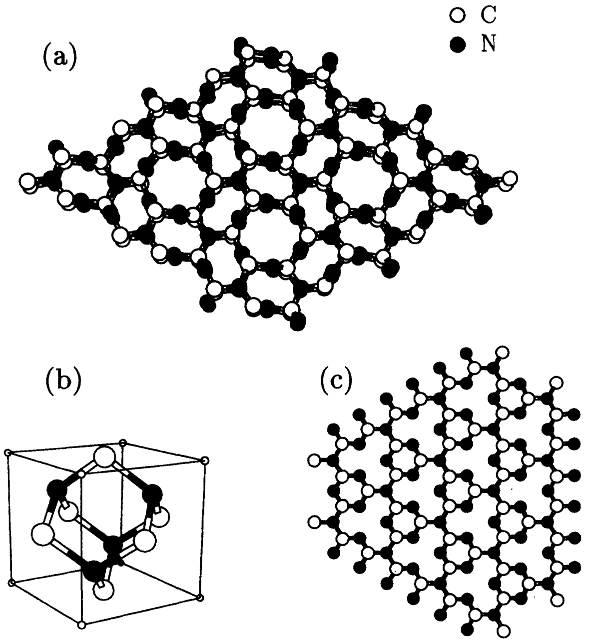

FIG. 1. C_3N_4 crystal structures. (a) Buckled layers in the a-b plane of hexagonal β-C_3N_4. (b) Zinc-blende-like cubic C_3N_4. The small circles at the corners of the cube denote vacant C sites. (c) Single layer of graphitelike rhombohedral C_3N_4.

TABLE I. Equilibrium structural parameters, bulk moduli, and cohesive energies calculated for β-, cubic, and rhombohedral C_3N_4. For the β phase, hexagonal lattice parameters are given by a and c and the positions of the C(N) atoms in lattice coordinates are $\pm(x_{C(N)}, y_{C(N)}, 1/4)$, $\pm(y_{C(N)}-x_{C(N)}, -x_{C(N)}, 1/4)$, $\pm(-y_{C(N)}, x_{C(N)}-y_{C(N)}, 1/4)$. There are also two N atoms located at $\pm(1/3, 2/3, 1/4)$. For the cubic structure, the lattice parameter is given by a. The C atoms are located at (1/2, 1/2, 0) and cyclic permutations, and the N atoms are located at (x_N, x_N, x_N), and $(-x_N, -x_N, x_N)$ and cyclic permutations. The rhombohedral lattice parameter and angle are given by a and α, respectively. The C(N) atoms are located at $(x_{C(N)}, x_{C(N)}, y_{C(N)})$ and cyclic permutations. An additional N atom is at (x'_N, x'_N, x'_N). Cohesive energies are given in eV per formula unit.

	β		Cubic	Rhombohedral
	Present	Ref. 2		
a (Å)	6.41	6.44	3.43	4.11
c/a	0.375	0.383		
α (degrees)				70.5
x_C	0.178	0.174		0.509
y_C	0.772	0.766		−0.018
x_N	0.331	0.321	0.254	0.830
y_N	0.033	0.025		0.340
x'_N				0.335
B (GPa)	437	427	425	51
E_{coh} (eV/f.u.)	47.71	40.75	46.56	47.85

The defect zinc-blende structure [Fig. 1(b)] is similar to β-C_3N_4 in that each C atom has four N neighbors and each N atom has three C neighbors. However, the C-N-C bond angle is close to the sp^3 angle of 109.47° rather than the sp^2 value of 120°. This structure (space group $P\bar{4}3m$) has two free parameters: the cubic lattice constant and an internal variable that measures the radial relaxation of the first shell of neighbors around the vacancy. Like β-C_3N_4, this three-dimensional, partially tetrahedral network of covalent C-N bonds is expected to be favorable for low compressibility.

The defect graphitic phase [Fig. 1(c)], which belongs to the $R3m$ space group, consists of "holey" graphitelike sheets with rhombohedral stacking order ($ABCABC\ldots$). Each C atom is three-fold coordinated, as is one of the four N atoms per cell. The other three N atoms are near neighbors of the missing C atom and hence are only two-fold coordinated. The structure is specified by five internal structural coordinates, as well as the lattice parameter and rhombohedral angle. Since the interlayer bonding in this graphitic structure is expected to be weak, this phase is not a likely candidate for low compressibility. However, it is of interest as a possible low-energy structure. In the case of both C and BN, the layered graphitic phases and the dense tetrahedral phases lie extremely close in energy; a similar situation may exist for C_3N_4.

Each of the three structures has been optimized as a function of pressure using damped dynamical simulations. Approximately 20 time steps were required to obtain structural parameters converged to the level displayed in Table I, at which point the forces and the differences between the internal and external pressures were less than 10^{-4} Ry/au and 10^{-6} Ry/au^3, respectively. A plot of the calculated volume as a function of pressure for all three phases is displayed in Fig. 2. As expected, the layered phase is the least dense and the most compressible, while the cubic phase is the most dense. The compressibilities of the cubic and β structures appear to be close in value over a large range of pressures.

The zero-pressure structural parameters calculated for β-C_3N_4 are listed in Table I together with the unrelaxed

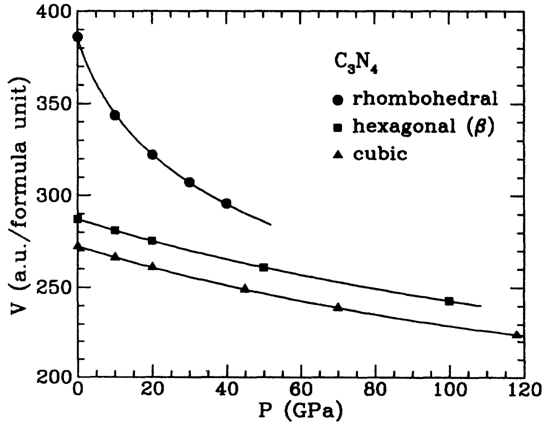

FIG. 2. Pressure dependence of the volume calculated for β-, cubic, and rhombohedral C_3N_4. The curves are fits of the calculated points to the Birch equation of state.

values assumed in the earlier work.[2] Overall, the differences between the relaxed and unrelaxed parameters are small. The structural optimization lowers the energy by about 0.37 eV per formula unit. The remainder of the difference between the binding energy reported here and the result of Ref. 2 is attributable to the use of different basis sets. As in Ref. 2, all the C-N bonds are found to be close in length, and the average bond length of 1.45 Å is slightly smaller than estimates based on the covalent radii of the constituent atoms ($r_C=0.77$ Å, $r_N=0.70$ Å). Since covalent radii are inferred from tetrahedral structures, it is reasonable that bonds formed between sp^2 and sp^3 orbitals such as the C-N bonds in β-C_3N_4 are shorter than the sum of the radii. The bond angles range from 108° to 112° around the C sites, and from 112° to 124° around the N sites.

As a function of pressure, the internal coordinates and c/a ratio for β-C_3N_4 are found to change very slowly. At $P=100$ GPa, which corresponds to a volume reduction of about 15%, neither c/a nor any of the internal parameters differs from its zero-pressure value by more than 1.5%. A fit of the calculated pressure-volume relation to the Birch equation of state[14] yields a bulk modulus B_0 of 437 GPa and a pressure derivative of the bulk modulus B_0' of 3.7. This B_0 is very close to that of diamond (443 GPa), which has the largest known value. The weak pressure dependence of the internal structural parameters and the fact that B_0 and B_0' are similar to the values reported in Ref. 2 justify the approximation of isotropic compression under hydrostatic pressure made in that work.

The local coordination in cubic C_3N_4 is similar to that in hexagonal β-C_3N_4 except that the N atoms form sp^3 rather than sp^2 bond orbitals, with one lone pair directed at an empty C site. The repulsion between these lone pairs leads to a slight outward relaxation of the N atoms away from the vacant site at low pressures (Table I). The bond angles, which lie between 108° and 110°, are close to the ideal tetrahedral value, and the bond length of 1.48 Å is close to the sum of the C and N tetrahedral radii. Even though the cubic structure is slightly more dense than the β structure, its C-N bonds are longer than those in β-C_3N_4. The bulk modulus of cubic C_3N_4 is calculated to be 425 GPa, which is a few percent smaller than that of the β phase. This is consistent with trends observed in diamond and zinc-blende systems, where the bulk modulus is found to decrease as the bond length increases.[1] Energetically, the cubic phase is less favorable than β-C_3N_4 by 1.15 eV/formula unit.

The cubic structure can be described by a more general rhombohedral cell containing the same number of atoms. Depending on the initial configuration within the $R3m$ space group, the damped VCS dynamics leads to one of at least two local minima. One minimum corresponds to the cubic structure. The other, which lies about 1.29 eV/formula unit lower in energy, is the graphitelike layered structure. Although buckled layers are allowed by symmetry, we find that a nearly flat geometry is preferred. The calculated structural parameters are listed in Table I. The optimal distance between the layers is found to be 3.07 Å, which is about 8% smaller than the measured interlayer distances in graphite and graphitic BN. At least part of this difference may be due to incomplete convergence with respect to basis-set size or k-point sampling. Because of the extreme softness of graphitelike structures along the c-axis, accurate determinations of the interlayer separation require highly-converged calculations.[15] The intraplanar positions, however, are expected to be more accurate. The largest in-plane relaxation is experienced by the C atoms. As can be seen in Fig. 1(c), each C atom is part of one complete hexagonal ring. When the structure is allowed to relax, the C atoms move inward towards the center of the ring. The repulsion between lone pair orbitals leads to a small inward relaxation of the N atoms on the ring as well. The net result is that the bonds along the ring are significantly shorter than those not part of the ring, and the C-N-C bond angle around the two-fold N sites drops to about 116°. The lone pair orbital on the N site acquires more s character than it would have in an ideal sp^2 configuration and thereby lowers its energy. The average bond length of 1.36 Å is close to the sum of the C and N Slater radii ($r_C=0.70$ Å, $r_N=0.65$ Å). This relationship between bond lengths and Slater radii has been observed in other graphitic systems including C, BN, and BC_3.[16]

For all three phases, the binding energy with respect to the isolated atoms is calculated to be moderately large. While the graphitelike phase is the most stable, β-C_3N_4 lies only marginally higher in energy. The cohesive energies of the three phases, which range from 46.56 to 47.85 eV/formula unit, include estimates of -1.40 eV and -2.92 eV for the spin-polarization energies of atomic C and N, respectively. For comparison, the energies of C in the diamond structure and molecular N_2 have also been calculated. In reasonable agreement with other LDA-based calculations,[17,18] the cohesive energies are found to be 8.63 eV per C atom and 11.30 eV per N_2 molecule. Within the LDA, the C_3N_4 solids therefore lie higher in energy by 0.64 to 1.93 eV/formula unit than separated diamond and N_2. Note that zero-point energies, which are likely to be on the same order as these energy differences, have not been included in the present estimates for the binding energies.

That the crystalline phases of C_3N_4 considered here may not be the lowest-energy phases in the C_3N_4 system does not preclude the possibility of their synthesis in the laboratory. To assess this possibility, it is important to examine the mechanical stability of the structures. To that end, we have computed their zero-pressure elastic constants. These are derived from the linear change in the stress tensor induced by an applied strain. Each strain is applied with both a positive and negative sign and the induced stresses are averaged. The Born criterion for stability stipulates that the matrix of elastic constants must be positive definite. For a hexagonal crystal, which has five independent elastic constants, the conditions for elastic stability are that c_{11}, $c_{11}-c_{12}$, c_{44}, and $(c_{11}+c_{12})c_{33}-2c_{13}^2$ are all greater than zero. A crystal with cubic symmetry has only three independent elastic constants, and it is mechanically stable if c_{11}, $c_{11}-c_{12}$, and c_{44} are positive. Finally, for a rhombohedral structure with six independent elastic constants, the conditions for stability are that c_{11}, $c_{11}-c_{12}$, $(c_{11}+c_{12})c_{33}-2c_{13}^2$ and $(c_{11}-c_{12})c_{44}-2c_{14}^2$ are all positive. As shown in Table II, these conditions are easily satisfied for β-, cubic , and rhombohedral C_3N_4,[19] confirming that all three of the structural phases are mechanically stable. Hence even if they are not the most energetically favorable structures for C_3N_4, they are at least metastable.

TABLE II. Elastic constants calculated for β-, cubic, and rhombohedral C_3N_4. Elastic constants are reported in units of GPa.

	β	Cubic	Rhombohedral
c_{11}	834	840	870
c_{33}	1120	840	57
c_{44}	305	452	14
c_{12}	279	213	148
c_{13}	138	213	−3
c_{14}	0	0	1

Two independent efforts to synthesize covalent C-N solids have produced crystallites embedded in amorphous C-N films.[4,5] While neither the rhombohedral nor the cubic structures investigated here are consistent with the diffraction patterns produced by the crystallites, the β-C_3N_4 structure is a viable candidate. Unfortunately, the crystallites are very small and occupy less than 5% of the volume of the films.[5] The synthesis of larger and higher-quality crystalline samples is needed for better characterization of the material. That our calculations show the β and graphitelike structures to lie extremely close in energy suggests that the large amorphous component of the films may contain significant amounts of energetically favorable sp^2 bonding. One of the problems encountered in the synthesis of diamond films is the competition between graphitelike and diamondlike growth.[20] We speculate that an analogous problem may exist in attempts to synthesize partially tetrahedral C-N solids such as β-C_3N_4.

In summary, we have studied the structural and relative stabilities of three phases in the C_3N_4 system. The structure of β-C_3N_4, a phase that was studied in an earlier investigation, has been refined. The structural optimizations do not lead to large changes in the predicted properties of the material, and, in particular, the bulk modulus of β-C_3N_4 remains very large and comparable to that of diamond. The stability of the β structure has also been verified. Two additional metastable phases of C_3N_4 have been identified: a zinc-blende-like cubic structure that is found to have a large bulk modulus and a layered graphitelike phase. All three phases have moderately large cohesive energies, but the graphitic and β structures are slightly favored over the cubic phase. We hope that our confirmation of the metastability of β-C_3N_4 and identification of other metastable carbon nitrides encourages further efforts to synthesize these potentially useful, low-compressibility materials.

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*Present address: Department of Physics, Georgetown University, Washington, DC 20057.

†Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455.

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