Low-Compressibility Carbon Nitrides

David M. Teter; Russell J. Hemley


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grals are neglected as a result of the screening techniques (Fig. 5). Thus, a mere \(\approx 1.5\%\) of all interactions in this molecule are treated by analytic integration. However, this computation is costly (Fig. 4).

In the GFMM, the separation between NF and FF is done in terms of uncontracted Gaussian functions because the product of two contracted Gaussians gives a linear combination of Gaussian distributions with different exponents centered at different points. The range criterion explained above thus has to be individually applied to these charge distributions. On the other hand, modern Gaussian integral packages, and in particular the PRISM algorithm (10) used in the Gaussian program (8), utilize contracted basis sets, thereby significantly reducing the computational cost of evaluating integrals over the uncontracted set. We estimate (Figs. 4 and 5) that calculating NF integrals over uncontracted rather than contracted functions for the 3-21G basis increases the computational cost by a factor of 5. This factor imposes a lower bound on the percentage of interactions that must be included in the FF for the GFMM to become competitive with analytic integration. Given an overhead factor of 5 and neglecting the cost of FF evaluation, the GFMM would be more expensive than analytic integration whenever more than 20% of all interactions were included in the NF. In our benchmarks, this break-even point is achieved at small molecular size (Fig. 5).

In a timing comparison in a fully uncontracted basis set, the GFMM became as much as 50 times faster than analytic integration for fairly small-size molecular systems. All results reported in this paper were obtained with contracted bases, because these are commonly used in practical calculations. These results, although limited to benchmark graphene-sheets, are also valid for more complex materials. Given the speed, accuracy, and scaling properties of the GFMM in practical, high-accuracy calculations, this method appears very promising for future electronic structure calculations on large molecular systems.

REFERENCES AND NOTES

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First-principles calculations of the relative stability, structure, and physical properties of carbon nitride polymorphs predict a cubic form of \(\text{C}_3\text{N}_4\) with a zero-pressure bulk modulus exceeding that of diamond. Like diamond, this new phase could potentially be synthesized at high pressure and quenched to ambient pressure for use as a superhard material. The calculations also predict that \(\alpha\)-C\(_3\)N\(_4\) and graphite-C\(_3\)N\(_4\) are energetically favored relative to \(\beta\)-C\(_3\)N\(_4\), and that published diffraction data can be re-indexed as \(\alpha\)-C\(_3\)N\(_4\) with lower error.

Intense theoretical and experimental interest has focused on the possibility of new low-compressibility materials with bulk moduli and hardness exceeding that of diamond. Carbon nitrides have been proposed as superhard materials on the basis of empirical systematics (1). First-principles calculations have suggested that a hypothetical material, \(\beta\)-C\(_3\)N\(_4\), may have a bulk modulus somewhat lower than that of diamond (2, 3). These results have motivated theoretical calculations (4–8) and experimental efforts to synthesize and characterize this compound (10–20). Amorphous C-N films have been synthesized (14, 16, 20), and small crystallites have been found in some of these films (15, 17–19). Electron diffraction patterns of these crystallites were indexed as the \(\beta\)-C\(_3\)N\(_4\) structure. However, these data can also fit to carbon phases (9). Other forms of carbon nitride with high hardness have been suggested, including a fullerene-like carbon nitride (21) and a crystalline carbon nitride composite (22). In this report, we investigate the stability and properties of carbon nitrides using first-principles calculations and show that \(\alpha\)-C\(_3\)N\(_4\) and graphite-C\(_3\)N\(_4\) are energetically preferred over \(\beta\)-C\(_3\)N\(_4\) and describe a cubic form of C\(_3\)N\(_4\) that may have a zero-pressure bulk modulus \(\left(K_B\right)\) exceeding that of diamond and be metastable at zero pressure.

Assuming that a low-energy carbon nitride structure with a high bulk modulus must have carbon four-coordinated with nitrogen, and nitrogen three-coordinated with carbon, we have identified several additional prototype structures by considering chemical systems with this type of bonding topology and by locating dense structures in these systems. Using first-principles pseudopotential total energy techniques (23), we examined a series of C\(_3\)N\(_4\) polymorphs to determine their energetics, structure, and physical properties, including \(K_B\), density, and band gap.

Our calculations, like those in earlier studies of carbon nitride (4–7), were carried out using density-functional techniques within the local density approximation (LDA) to electron exchange and correlation. We used a preconditioned conjugate-gradient method to minimize the electronic degrees of freedom. The electronic wave

Fig. 5. (C) Percentage of interactions (uncontracted two-electron integrals) included in the FF component of the GFMM for the optimum box-size distribution used in Fig. 2 and treated by the tree hierarchy. (O) Percentage of uncontracted two-electron integrals that were prescreened and neglected in the NF portion of the Coulomb problem using empirical and mathematical bounds.
functions were expanded in a plane-wave basis set with periodic boundary conditions. We used extended norm-conserving and hardness-conserving (ENHC) pseudopotentials (24). This scheme ensures that the total energies of the atom and pseudopotam match to second order with respect to arbitrary changes in valence-state occupancy. This additional condition has been shown to improve pseudopotential transferability in studies of diamond-carbon (24), silica (25), and the linear response properties of free atoms (26). For each structure, we calculated the total energy over a wide range of volumes. At a given volume, we determined the positions of the cations and the anions by minimizing the forces on the ions, and the unit cell edges were determined by minimizing the stress on the cell. We fit the resulting energies to a Birch equation of state (27) to calculate the pressure, \( K_0 \), and pressure derivative of the bulk modulus (\( K'_0 \)).

The \( \beta-C_3N_4 \) structure is based on the \( \beta-Si_3N_4 \) structure, with C substituted for Si. This structure is similar to the phenacite (\( \text{Be}_2\text{SiO}_4 \)) structure and consists of coordinately carbon linked by threefold coordinated N atoms into a network of three-, four-, and sixfold rings of \( \text{CN}_4 \) tetrahedra (Fig. 1A). The unit cell contains 14 atoms and has \( P3 \) symmetry. The \( \alpha-C_3N_4 \) structure can be described as an \( \text{ABAB}\ldots \) stacking sequence of layers of \( \beta-C_3N_4 \) (A) and its mirror image (B). The unit cell contains 28 atoms and has \( P3_1c \) symmetry (Fig. 1B). When the symmetry of the optimized \( P3_1c \) structure was relaxed to \( P3 \), there were no changes in the atomic coordinates of the structure. The graphitic form of carbon nitride consists of an \( \text{ABAB}\ldots \) stacking of the planar structure (28) (Fig. 1C). The unit cell contains 14 atoms and exhibits \( P6m2 \) symmetry. Another candidate suggested by this analysis is the pseudocubic \( \alpha-CdIn_2Se_4 \) structure (31).

![Fig. 1. Representation of the \( \beta-C_3N_4 \) (A), \( \alpha-C_3N_4 \) (B), graphite-\( C_3N_4 \) (C), pseudocubic-\( C_3N_4 \) (D), and cubic-\( C_3N_4 \) (E) structures down the [001] axis. The carbon and nitrogen atoms are depicted as gray and blue spheres, respectively.](image)

### Table 1. Equilibrium structural parameters, bulk moduli, and total energies calculated for \( \alpha-C_3N_4 \), \( \beta-C_3N_4 \), cubic-\( C_3N_4 \), pseudocubic-\( C_3N_4 \), and graphite-\( C_3N_4 \). The differences in total energies are converged to below 0.008 eV per \( C_3N_4 \) unit with respect to \( k\)-point integration and kinetic energy cutoff.

<table>
<thead>
<tr>
<th></th>
<th>( \alpha-C_3N_4 )</th>
<th>( \beta-C_3N_4 )</th>
<th>Cubic-( C_3N_4 )</th>
<th>Pseudocubic-( C_3N_4 )</th>
<th>Graphitic-( C_3N_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>( P3_1c ) (159)</td>
<td>( P3 ) (143)</td>
<td>( I43d ) (220)</td>
<td>( P42m ) (111)</td>
<td>( P6m2 ) (187)</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>4.4665</td>
<td>6.4017</td>
<td>5.3973</td>
<td>3.4232</td>
<td>4.7240</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>4.7057</td>
<td>2.4041</td>
<td>5.3973</td>
<td>3.4232</td>
<td>4.7240</td>
</tr>
<tr>
<td>( \rho_{0} ) (atom/mol/cm(^3))</td>
<td>0.2726</td>
<td>0.2724</td>
<td>0.2957</td>
<td>0.2897</td>
<td>0.1776</td>
</tr>
<tr>
<td>( K_0 ) (GPa)</td>
<td>425</td>
<td>451</td>
<td>496</td>
<td>448</td>
<td>—</td>
</tr>
<tr>
<td>( K'_0 )</td>
<td>3.1</td>
<td>3.3</td>
<td>3.4</td>
<td>3.4</td>
<td>—</td>
</tr>
<tr>
<td>( E_{\infty} ) (eV/unit)</td>
<td>-1598.669</td>
<td>-1598.403</td>
<td>-1597.388</td>
<td>-1597.225</td>
<td>-1598.710</td>
</tr>
</tbody>
</table>

The calculations were completed at a kinetic energy cutoff of 60 Hartrees. The structural parameters were considered to be fully relaxed when the forces on the ions were less than 0.02 eV/Å and all Puley-corrected stress tensor components were less than 0.002 eV/Å\(^2\).
Figs. 2. Total energies as a function of volume for the structures studied. The curves were generated from fits to the calculated data points using the Birch equation of state. For the C-N structure, we predict a K vs of 425 GPa. For the B-2 structure, the K vs is 451 GPa and does not change significantly when the symmetry constraints are lowered from P6/m to P3.3. The K vs for pseudocubic C-N structure is also high (448 GPa); although this phase does not appear to be energetically favorable relative to α-C-N, and cubic C-N, it is conceivable that this material could be formed metastably. Transition pressures were determined by taking common tangents.

Hence the structure is predicted to be mechanically stable at high pressures as well as at ambient pressures. We also determined the elastic constants of cubic C-N using established first-principles techniques (34). The structure meets the Born stability criteria for mechanical stability (35).

The widespread interest in carbon nitrides also arises from their predicted wide band gap and high atomic density. The calculated band gap of the cubic C-N phase is 2.90 eV. For α-C-N and B-2 the calculated band gaps are 3.85 and 3.25 eV, respectively. In all cases, the gap is found to be indirect. Because LDA usually underestimates experimental band gaps by 15 to 20%, the actual band gaps of the carbon nitride structures, if they can be synthesized, should be higher. All of these phases except graphite C-N have predicted atomic densities approaching that of diamond (experimental result: 0.2950 mol-atoms/cm3; LDA result: 0.3070 mol-atoms/cm3). We find that the atomic density of cubic C-N is 0.2957 mol-atoms/cm3.

On the basis of the high atomic density and bonding topology of this structure, cubic C-N should be an excellent thermal conductor. Most experimental studies of carbon nitrides have been carried out at ambient or low-pressure conditions. Our results indicate that high-pressure synthesis should be important in the search for new carbon nitrides. The calculated transition pressure to the cubic C-N phase from low-pressure phases (graphite C-N or α-C-N) is within reach of modern high-pressure techniques. Moreover, the predicted transition pressure for synthesis of cubic C-N from the graphite C-N phase is within the reach of large volume presses, which would allow synthesis at an industrial scale. Our results suggest that it may also be possible to synthesize other high-pressure carbon nitrides with low compressibility (for example, pseudocubic C-N) as pressure-quenchable metastable phases.

REFERENCES AND NOTES
32. Our LDA results at the same level of theory and convergence calculate a diamond K vs of 468 GPa. While the predicted bulk moduli of other hypothetical materials, including the high-pressure BC-8 carbon structure, approach that of diamond, the cubic C-N exceeds it.
33. Although a rigorous correlation between bulk modulus and hardness does not exist, it is found empirically that for an isotropic material, hardness is usually proportional to K vs, assuming the absence of plastic deformation. Hence, the hardness of cubic C-N may exceed that of diamond.
35. We determined the elastic constants of cubic C-N using norm-conserving Trouiller and Martins pseudopotentials at a kinetic energy cutoff of 25 Hartrees with a [444] Monkhorst Pack grid. We found c11 = 863 GPa, c12 = 313 GPa, and c44 = 348 GPa. This meets the Born mechanical stability criteria for a cubic crystal, as c11 > 2(c12) and c44 > 0. We thank M. T. Stawowy, O. F. Sankey, M. O’Keeffe, L. W. Finger, R. M. Hazen, C. T. Prewitt, and J. V. Badding for encouragement. Computational results were obtained using a version of the software program Plane-Wave from Biosym Technologies of San Diego.

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