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Defective and amorphous structure of carbon nitride

J. E. Lowther
Department of Physics, University of the Witwatersrand, Johannesburg, South Africa

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There has been enormous interest in preparing the superhard material C_3N_4, with the large nitrogen concentration being one factor limiting preparation. Using an *ab initio* supercell approach we simulate the electronic structure about a N vacancy and investigate the effect it has on the bulk modulus of the material. We compare this with a relaxed cubic C_3N_3 structure with one N atom removed. The ability of the superlattice to model the electronic structure of the crystalline material is used to deduce properties of an amorphous structure within the *ab initio* framework. The amorphous form has a bulk modulus significantly lower than its crystalline counterpart and comparison of various structures suggests that the final strength of carbon nitride will ultimately depend upon the number of C-N bonds that can be formed during synthesis of the material. [S0163-1829(98)02309-1]

I. INTRODUCTION

Since the suggestion that carbon nitride has a phase with a larger bulk modulus than diamond,[1] there have been additional theoretical investigations confirming the prediction.[2,3] Several phases of carbon nitride have been considered as possibilities for the superhard nitride material. One of the predicted phases, β-C_3N_4, has a hexagonal form with space group $P6_3/m$ and possibly the highest bulk modulus. Another form that has been considered is cubic C_3N_4 with space group $P\overline{4}3m$. This form has a bulk modulus marginally less than the β phase. In each of these structures, carbon atoms are in a four-fold coordination by nitrogen atoms, the nitrogen atoms in three-fold coordination by carbons. Both structures are predicted to be stable. Still a further form of the material with near-graphite structure has been considered. This has space group $R3m$ but now the calculated bulk modulus[2] was significantly less than either of the previous forms. The graphitic form is a possible precursor to the formation of the harder β or cubic phases[3] and other crystalline structures for stoichiometries different from C_3N_4 have recently been examined.[4,5]

This theoretical interest has sustained an intense effort to synthesize the material. Mostly the material has been found in apparent amorphous or disordered phases[6–8] tentatively with a hardness higher than that of a carbon film[9] and there have been some reports of crystalline phases.[10] Ion-beam-enhanced deposition has produced thin carbon nitride films[11] and closer studies suggest that a tetrahedrally bonded C_3N_4 phase is present in the film, the quantity increasing with nitrogen concentration. Laser ablation[12,13] of carbon and nitrogen also shows the importance of nitrogen stoichiometry in the production of the carbon nitride phase, with deposition temperatures affecting the ultimate local environment of the nitrogen atoms. The laser technique seems to be one of the most promising for the synthesis of crystalline carbon nitride and to date various phases of C-N-bonded structures have been observed.[14,15] Deposition techniques[16–18] have also been able to obtain crystalline C-N phases and sputtering of a graphite target with nitrogen has produced carbon nitride film with fairly high yield strength.[19,20]

The synthesis of carbon nitride has, despite some measure of success with an apparent amorphous form, not yet been able to firmly answer the question about whether a crystalline form of the material is possible that is harder than diamond. Possible technological reasons for the difficulty to produce carbon nitride relate to the large amounts of nitrogen required to interact with carbon to give the desired structures. This is displayed by various nitrogen-bonded structures that have been observed[15] following laser ablation. An alternative theoretical problem suggested is that, given the ideal crystalline case, what is the role played by nitrogen vacancies and what are the properties of an amorphous structure of C_3N_4? This paper attempts to answer some of these problems. We specifically consider the cubic form of the material and examine its properties in the presence of a large nitrogen vacancy dilution and then a weak dilution using a supercell approach. The supercell is seen to model properties of the crystal structure quite well and this cell is applied to an amorphous network. Unlike recent attempts to model this network using a tight-binding-based approach[21] or rigid potentials,[22] inclusion of explicit bonding interactions through an *ab initio* computation gives a realistic picture of the structure and its relation to the crystalline phase. The calculation estimates the potential hardness of the amorphous form of C_3N_4.

II. CRYSTALLINE AND DEFECTIVE C_3N_4

Using soft Troullier-Martin[23] pseudopotentials with plane waves of a cutoff of 64 Ry at six reduced k points and the local density approximation[24] we have optimized the cubic structure. The pseudopotentials used in the present work were generated using s and p channels with cutoff radii of $1.50, 1.52a_0$ and $1.12, 1.20a_0$ for C and N, respectively. Cubic C_3N_4 has a space group $P\overline{4}3m$ and calculations[2] have suggested that it should occur with a lattice constant of 3.43 Å. Our results concur with these calculations. The lattice is shown in Fig. 1 and the calculated electronic charge distribution along one of the C-N bonds shown in Fig. 2. The charge is mainly located about the N atom with large regions lying away from the bond. To a certain extent this electronic structure is not unexpected from simple chemical hybridiza-

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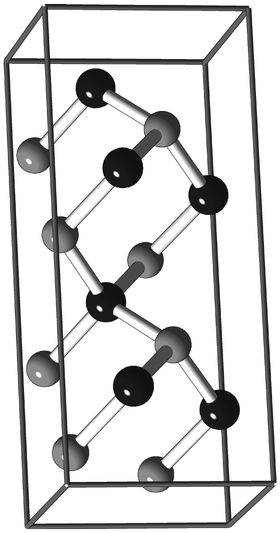

FIG. 1. Two adjacent unit cells of cubic C_3N_4. Carbon atoms are shown schematically as the black atoms.

tion arguments as C probably takes sp^3 hybridization in the nitride while the threefold coordination of the N atoms favors sp^2 bonding. The additional two N electrons, not dissimilar to the case with graphite, enter a weak nonbonding p^2 configuration. These bonds would act as regions for passivation even in a crystalline structure and occupancy of these bonds would affect the nominal insulating structure of the material. Thus the role of H passivation, for example, is likely to be even more complicated in carbon nitride than it is in diamond.

A. Large N vacancy dilution

We removed one of the N atoms in the unit cell and relaxed the trigonal structure. Relaxation was not that large with N atoms moving inward toward the C atoms in such a way as to create a near-planar-bond structure between the adjacent three C atoms. Total energies under an isotropic compression of the cubic unit cell of the N vacancy unit cell are compared with the exact defect-free structure in Fig. 3. From such curves we obtain the bulk modulus through a least-squares fit to the Murnaghan equation of state.[25] Such a calculation represents quite a large concentration of N vacancies but to some crude extent approximates the onset of a chemically disordered amorphous structure.

B. Low N vacancy dilution

To model a more dilute distribution of N vacancies we have employed the 56-atom supercell shown in Fig. 4 and for computational simplicity we only used one k point $(k=0)$. The equilibrium configuration of such a structure is only slightly less than the more accurate unit cell calculation and taken to give quite a good representation of the essential bulk properties. We then placed a N vacancy toward the center of the supercell and repeated the calculation. The variation of energy of both cubic supercells under isotropic compression is shown in Fig. 5.

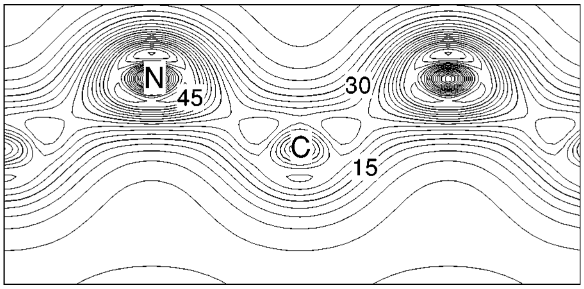

FIG. 2. Charge density distribution along a C-N bond of cubic C_3N_4.

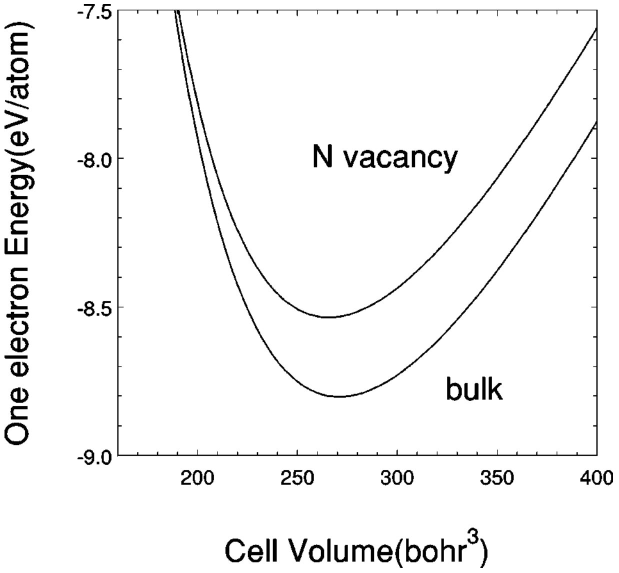

FIG. 3. Equation of state for cubic C_3N_4 and C_3N_3 structures.

III. AMORPHOUS C_3N_4

Although the high N vacancy concentration approach discussed above is a crude attempt to model a chemically amorphous structure, it neglects a disordered topology. Usually computational modeling of an amorphous structure starts from a disordered lattice. We initially attempted generating a disordered lattice from a mathematically randomized system of points with a stoichiometry appropriate to C_3N_4. However, such a procedure introduced a topology with atoms located quite close to each other that, under the subsequent *ab initio* procedure, introduced large kinetic energies intro-

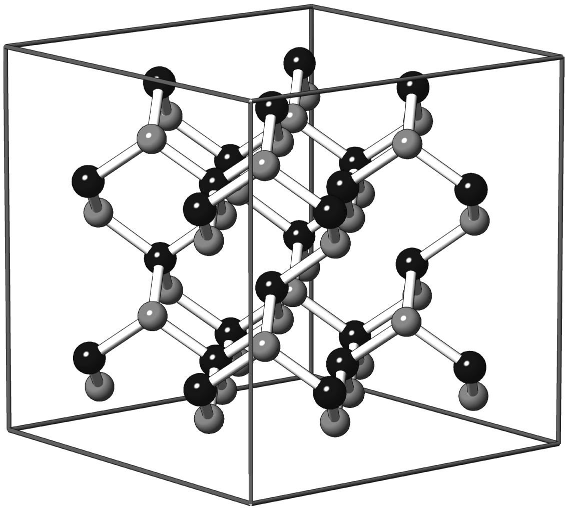

FIG. 4. Cubic $C_{24}N_{32}$ atom supercell.

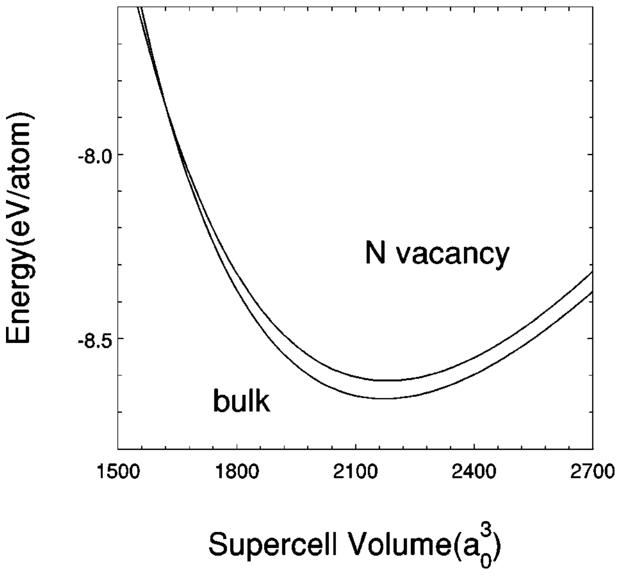

FIG. 5. Equation of state for cubic $C_{24}N_{32}$ and relaxed $C_{24}N_{31}$ cubic supercell structures.

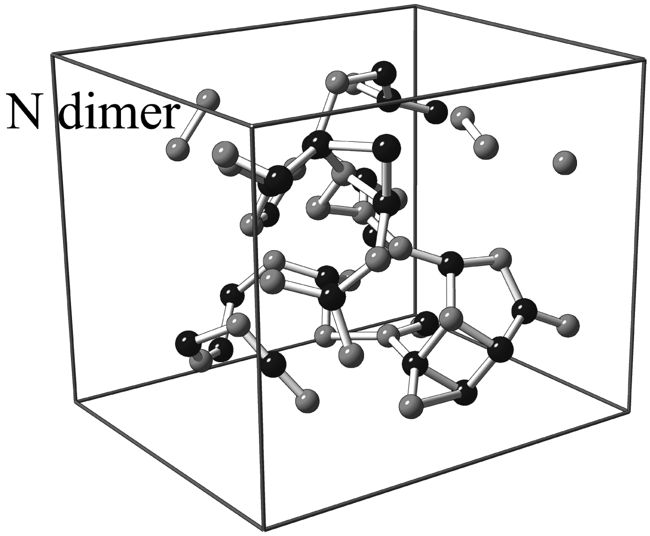

FIG. 6. Amorphous $C_{24}N_{36}$ atom cubic supercell at $V=429.83$ Å^3, very close to equilibrium volume.

ducing convergence problems. An alternative procedure for generating the amorphous lattice, which is the one we follow here, has been to heat the crystalline structure to a very high temperature. *Ab initio* molecular dynamics procedures would be extremely time consuming in adopting this procedure and we chose an empirical rigid molecular dynamics scheme to represent various interactions in the starting configuration. A standard Tersoff potential[26] gives quite an accurate description of carbon and recently various forms of the Tersoff potential have been considered for application to the carbon nitrides.[27] We have chosen standard Tersoff parameters for C and for N those that give best results specifically for the cubic form of C_3N_4, bearing in mind (as pointed out by Kroll[27]) that the Tersoff potential has limitations in describing N-N bonds. The Tersoff potential parameters are given in Table I. The periodic 56-atom cubic cell was equilibrated using these parameters at 10 000 K for several picoseconds, sufficient to ensure a random distribution as measured by the calculated radial distribution of the atoms.

The *ab initio* modeling started from these approximate atom coordinates and this was done for several different volumes of the unit cubic cell. Throughout, the atoms were allowed to relax using a standard gradient technique. The computational procedure was quite time consuming for convergence, this indicating that the initial starting point was indeed a high metastable configuration. Relaxation was monitored throughout and we noted the importance of the various bonding configurations, in particular the buildup of C-N bonds and competition with C-C and N-N bonds. Although the number of atoms in the simulation was small, we did observe that N-N bonds were often not connected into the complete network as much as C-C bonds were. Instead the N atoms tended to group into relatively loosely bonded structures, often isolated from the main continuous network. This can be seen in Fig. 6 which shows the distribution of atoms in the amorphous 56-atom cell at a volume of $V=429$ Å that is very near the stable volume for such a structure. This volume corresponds to a material density of $\rho=2.9$ g cm^{-3}, still relatively high, but far lower than the crystalline hard material, $\rho=3.8$ g cm^{-3}. Specifically at $\rho=2.9$ g cm^{-3}

TABLE I. Tersoff potential parameters used to generate the metastable high-temperature amorphous phase. The parameter notation follows that of Ref. 26.

Parameter	Carbon (Ref. 26)	Nitrogen (Ref. 27)
A(eV)	1393.6	8860.0
B(eV)	346.7	197.09
λ (Å^{-1})	3.4879	5.5237
μ (Å^{-1})	2.2119	2.3704
β (10^{-6})	1.5724	5.8175
n	0.72751	8.2773
c	38049	79126
d	4.384	112
h	-0.57058	-0.99995

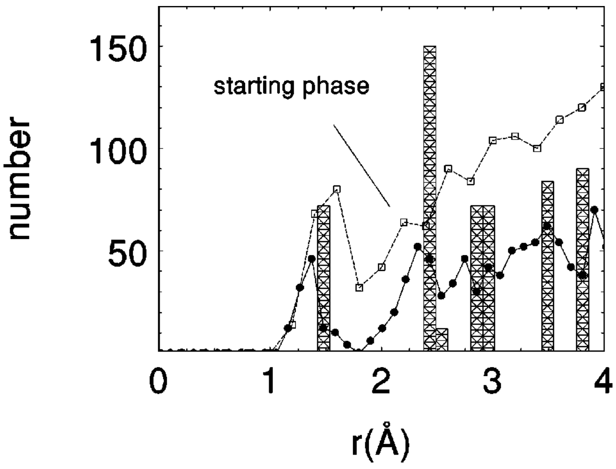

FIG. 7. Radial distribution of the starting phase generated using Tersoff potentials and the relaxed phase using the *ab initio* approach at $V=429.83$ Å^3. Bars show crystal atom locations, and here the number is shown as half the actual value for comparative purposes.

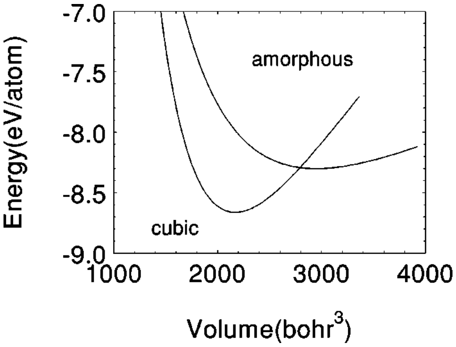

FIG. 8. Equation of state for the final relaxed amorphous $C_{24}N_{32}$ supercell.

TABLE II. Equilibrium volumes and bulk moduli calculated for various defective and amorphous carbon nitride structures. The number of C-N bonds is given for each structure; the crystal supercell has 71 C-N bonds.

	V (Å^3)	Relative number of C-N bonds	B (GPa)	B'
C_3N_4 (bulk)	40.15	1.00	422	3.95
C_3N_3 (N vacancy)	39.36	0.80	355	3.97
$C_{24}N_{32}$ (bulk)	321.89	1.00	402	4.29
$C_{24}N_{31}$ (N vacancy)	323.15	0.95	394	3.44
$C_{24}N_{32}$ (amorphous)	434.33	0.52	113	5.13

there are 11 C-C bonds, 38 C-N bonds, and 5 N-N bonds in the 56-atom cell. The larger number of C-C bonds than N-N bonds is typical of most volumes we considered even up to a material density of 4.5 g cm^{-3}, which corresponds to the smallest volume point at which we did our modeling. Thus the modeling has shown that C-N bond formation is preferred over others.

The final radial distribution at the equilibrium volume is shown in Fig. 7. Assuming the Murnaghan equation is applicable to the amorphous state we can deduce an apparent value of the bulk modulus and equilibrium volume from the energy-volume dependence that is shown in Fig. 8.

IV. SUMMARY

The equilibrium results for the various crystalline, defective, and the amorphous C_3N_4 systems are given in Table II. A steady decrease in the bulk modulus with N vacancy concentration is evident and in the amorphous state the bulk modulus is predicted to be significantly lower than the crystal value. The amorphous structure is also found stable at a density of $\rho = 2.9$ g cm^{-3}, far lower than its crystalline counterpart. We have also shown in the table the number of C-N bonds that are formed in each system. There is clear correlation between the number of C-N bonds and the value of the bulk modulus, suggesting that the final strength of noncrystalline or amorphous carbon nitride will ultimately depend upon the number of C-N bonds that can be formed.

It would appear that the various synthesis techniques that have claimed the formation of superhard carbon nitride do have some foundation but elucidation of the precise structure of the material would help structural identification if at least a lower limit to the hardness of the materials can be estimated. The relatively low value of the bulk modulus of $B = 113$ GPa for the amorphous form that is calculated here will bear a test as to the true identification of the various phases and, more important, which of the various methods of synthesis points the way to the predicted superhard material.

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