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Carbon nitride compounds with 1:1 stoichiometry

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We have examined various structures of carbon nitride with 1:1 stoichiometry and determined that for this stoichiometry sp^2 bonding of nitrogen is energetically preferable to sp^3. We found the zinc-blende and rocksalt phases to be mechanically unstable. They relax to a rhombohedral phase composed of buckled carbon nitride sheets with interplanar covalent bonds. The rhombohedral phase has a bulk modulus of 253 GPa. Two other structures made essentially of sp^2 bonds were studied, the H-6 and bct-4 and they have bulk moduli of 345 and 375 GPa, respectively. We also calculate the structure based of the high-pressure phase of GeP and find it to be unfavorable due to its low binding energy. Using the general valence rule, we can state the requirements of a semiconducting or an insulating structure for this compound. Inspired by existing structures, we calculated the phases based on the β-InS and GaSe compounds. Both these structures contain C-C bonds. We find that the β-InS phase has a bulk modulus of 78 GPA. The GaSe structure is made of layers where the C-C bond is perpendicular to the plane of the layers. It is the most energetically favorable of all phases considered and it has a bulk modulus of 199 GPa. [S0163-1829(97)03210-4]

Since the original proposal of[1] and calculations[2] on carbon nitride, considerable effort has been directed towards synthesizing this compound because of its potential use as a hard material. Many experiments have claimed the production of the β-C_3N_4 structure,[3–6] however, it was not possible to measure the bulk modulus of these materials because the samples were too small. Other experiments,[7,8] in which the β-C_3N_4 phase could not be found, still showed evidence of polycrystalline carbon nitride films. In one of these experiments,[7] materials consisting of alternate layers of carbon nitride and TiN yield hardnesses in the range 45–55 GPa. Another experiment[8] where nanoindentation measurements where performed on a $CN_{0.2}$ film a hardness of 60 GPa was found. These values compare favorably with thin films of diamond which have values in the range 55–110 GPa. However, no conclusive measurement of the bulk or Young modulus could be made. These experimental results suggest that there might be structural phases of carbon nitride other than the β-C_3N_4 which may exhibit large values for their bulk moduli and hardness.

On the theoretical side, other carbon nitride structures have been explored[9,10] which show bulk moduli comparable to diamond, except for a soft graphitelike structure. All structures calculated so far have assumed a stoichiometry C_3N_4. However, the experimental data show a wide range of nitrogen concentration.[11,12] Here we investigate possible carbon nitride structures with stoichiometry 1:1. We only study one stoichiometry because we can then compare the binding energies among the different structures calculated. Many more stoichiometries are possible considering the wide range of experimental data. Eight crystal structures are calculated: zinc-blende, rocksalt, rhombohedral, bct-4, H-6, and the structures based on the compounds GeP, β-InS and GaSe. The bct-4 and H-6 structures are three-dimensional networks of pure sp^2 bonded solids.[13]

We use a plane-wave basis pseudopotential total-energy scheme[14,15] with an energy cutoff of 64 Rydbergs. We assume the local density approximation (LDA)[16] and used the Ceperley-Alder interpolation formula[17] for the exchange-correlation energy. *Ab initio* pseudopotentials are generated following the method of Troullier and Martins.[18] The different sets of irreducible k points are generated according to the Monkhorst-Pack scheme.[19] For the zinc-blende, rocksalt and rhombohedral structures, 60 k points are used; we employ 18 k points for bct-4 and the GeP structure, 26 for the H-6 structure, 8 for the β-InS and 12 for the GaSe structure. With these parameters, the calculations have an error of about 1 mRy per atom. The structural parameters were relaxed using a Broyden scheme for the forces and stresses.[20] The relaxation was stopped when the forces were smaller than 0.0003 Ry/a.u. and the stresses in the different directions were within 0.05 GPa of each other.

Figure 1 shows the calculated total energy per atom versus volume for the eight structures considered. The rocksalt and zinc-blende structures are depicted by dashed lines because they were found to be mechanically unstable; both phases relax to the rhombohedral structure. In Table I, the equilibrium structural parameters for the different phases are given. Only the zero-pressure values of these parameters are listed; however, we note that the structure was relaxed for every volume calculated. In the rhombohedral basis, the carbon atom is located at the origin and the nitrogen atom is at (h,h,h). For $h=\frac{1}{3}$, this arrangement yields an ABC stacking of planar carbon nitride sheets. Values of $h\neq\frac{1}{3}$ reflect buckling of the atoms out of the sheet. It is possible to express the zinc-blende and the rocksalt phases in the rhombohedral basis which allows us to study the relative mechanical stability between these structures. The zinc-blende phase is recovered in this basis by setting the angle between the lattice vectors to $\theta=60°$ and setting $h=\frac{1}{4}$. For the rocksalt phase, the structural parameters are $\theta=60°$ and $h=\frac{1}{2}$. The energy minimization yields a zero-pressure value of $\theta=70.9°$ and $h=0.393$. The angle between inter and intraplanar bonds is 93.8°, compared to 90° for a perfect planar sheet and

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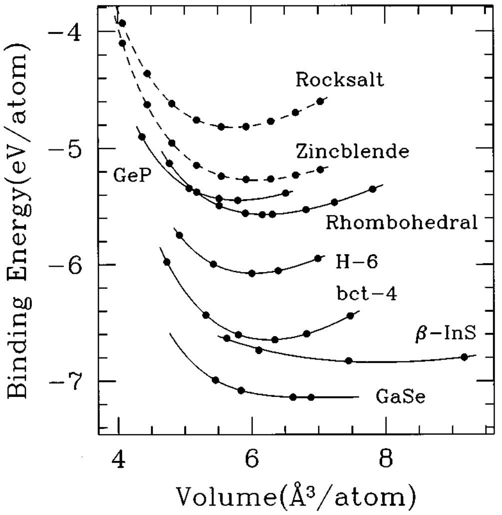

FIG. 1. Total energy versus volume for 1:1 carbon nitride in the rocksalt, zinc-blende, rhombohedral, H-6, and bct-4 structures. The curves are fit to the Murnaghan equation of state (Ref. 27).

109.47° for the zinc-blende structure. This resulting phase is made of slightly buckled CN sheets separated by 1.696 Å which is a little more than the nearest-neighbor distance that we find in the plane (1.631 Å). Note that this interplane distance is about half of the one observed for graphite. The extra electrons which do not contribute to the bonding in the plane form bonds between carbon and nitrogen atoms of neighboring planes. Hence, it is a strong covalent bonding that keeps the sheets together rather than the Van der Waals force found in graphite. For this reason, this phase is much less compressible than graphite. In fact, the angle between the lattice vectors changes by only one degree up to an applied pressure of 125 GPa whereas for rhombohedral graphite, this angle changes by 6° for an applied pressure of 30 GPa. The calculated bulk modulus for rhombohedral carbon nitride is 253 GPa. A recent experiment[8] reported a graphitelike phase of carbon nitride which exhibits extreme hardness. A possible explanation for these observations is the presence of interplanar covalent bonds of the type described above. However, their interplanar distances measured using selected area electron diffraction do not match our interplanar distance but their sample has a much lower nitrogen concentration.

The fact that the zinc-blende structure relaxes to the rhombohedral structure also suggests that, at least for this given stoichiometry, the sp^2 electron configuration found in the rhombohedral structure is energetically preferable to the sp^3 binding found in zinc-blende materials. We give a qualitative argument for this behavior. Since the electronic charge density of a hybridized carbon sp^2 orbital is closer to the nucleus than an sp^3 orbital,[21] sp^2 bonds will benefit more from the attractive potential of the nucleus than sp^3 bonds. On the other hand, the sp^3 bond takes more advantage of the crystal potential than the sp^2 by extending further. For the carbon atom the two environments discussed above are almost energetically equivalent considering that graphite is only less than 0.01 eV per atom lower in energy than the diamond. As we move to the right of the carbon atom, the ionic potential of the atom becomes stronger, which means that an electron density closer to the atom would be energetically favorable. Therefore, it is logical that the nitrogen atom prefers an sp^2 environment rather than an sp^3. Moreover, in an sp^2 geometry, more interstitial space is available in the nitrogen's neighborhood for the extra electrons which do not contribute to the bonding. Moving down the periodic table introduces a repulsive p-potential in the core which forces valence p-states out of the core, and therefore sp^3 hybridization for Si and Ge is energetically favorable.

With this in mind, we calculate two structures which locally are sp^2 bonded but are three dimensional: the H-6 and the bct-4 structures,[13] depicted in Figs. 2 and 3, respectively. The total energies for these structures are shown in Fig. 1, and as anticipated, they are lower in energy than the zinc-blende, rocksalt, and the rhombohedral structure. The relaxed parameters are given in Table I. The bct-4 structure is in an almost perfect sp^2 geometry with structural parameters $c/a = 3.465$ and $h = 0.086$ which can be compared with 3.4641 and 0.083 for a perfect sp^2 network. The H-6 structure deviates somewhat from ideal sp^2, with $c/a = 2.348$ and $h = 0.108$ as compared with $c/a = 2.598$ and $h = 0.111$ for a perfect sp^2 geometry. Since these structures are sp^2 bonded, the nearest-neighbor distances are much shorter than in the zinc-blende structure. The average bond lengths are 1.42 Å in H-6 and 1.40 Å in bct-4. The calculated bulk moduli for

TABLE I. Equilibrium structural parameters, bulk moduli and cohesive energies calculated for eight phases of 1:1 carbon nitride.

	Rocksalt	Zinc-blende	GeP	Rhombohedral	H-6	bct-4	β-InS	GaSe
V_0(Å^3)	5.729	6.057	5.802	6.208	6.032	6.263	7.900	6.645
a(Å)	3.579	3.646	2.478	2.430	2.611	2.436	4.063	2.364
Lattice Parameters			$c/a=1.523$	$\theta=70.9°$	$c/a=2.348$	$c/a=3.465$	$b/a=1.531$ $c/a=0.580$	$c/a=4.815$
Basis Parameters			$h=0.376$	$h=0.393$	$h=0.108$	$h=0.086$	$x_C=0.124$ $y_C=0.198$ $x_N=0.703$ $y_N=-0.227$	$x_C=0.179$ $x_N=-0.365$
d(Å)	1.789	1.579	1.813	1.631	1.465	1.417	1.384	1.454
d(Å) along c axis			1.421	1.696	1.380	1.387		1.616 (C-C)
B(GPa)	331	253	273	253	345	375	78	199
E_{coh}(eV/atom)	4.817	5.271	5.445	5.566	6.072	6.645	6.842	7.144

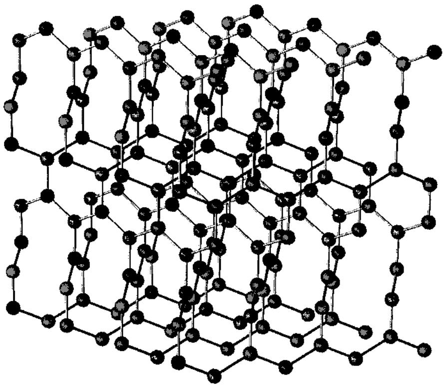

FIG. 2. Ball and stick model of the H-6 structure with alternating C (gray balls) and N (black balls) atoms. The Bravais lattice of the H-6 structure is hexagonal with six atoms per unit cell. The location of the carbon atoms in Cartesian coordinates are $(0,0,0)$, $(a/2,0,c/3)$, $(a/4,-\sqrt{3}a/4,2c/3)$; the nitrogen atoms are located at $(a/2,0,ch)$, $(a/4,-\sqrt{3}a/4,c(h+1/3))$, $(0,0,c(h+2/3))$, where a and c are the hexagonal lattice constants and h is a free parameter. With values $c/a=9/(2\sqrt{3})$ and $h=1/9$ the structure is in a perfect sp^2 geometry.

these structures are 345 GPa for the H-6 and 375 for the bct-4. These same structures have been previously calculated for pure carbon and boron nitride compounds.[22–24] For pure carbon, bulk moduli were calculated to be 362 GPa for the bct-4 and 372 GPa for H-6 structure. For the boron nitride compounds, the bct-4 structure has a calculated bulk modulus of 268 GPa. It is interesting to note that the calculated bulk moduli for these networks of sp^2 bonding structures have similar values for the carbon nitride and the pure carbon compounds. The lower bulk modulus of the BN bct-4 structure can be associated with the fact that this compound has the most polar bond. In Ref. 22, it was reported that the H-6 structure for pure carbon is unstable with respect to the transformation to diamond. For the carbon nitride compound we do not expect this instability because the zinc-blende structure was itself found to be unstable. However, since both the bct-4 and H-6 structures are metallic, we should investigate the possibility of increasing the unit cell to see if a deformation could not lead to a lower energy structure.

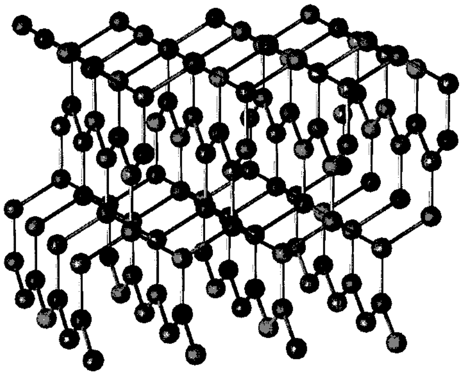

FIG. 3. Ball and stick model of the bct-4 structure with alternating C (gray balls) and N (black balls) atoms. The bct-4 structure has a primitive body-centered tetragonal cell with four atoms per unit cell. The locations of the carbon atoms in Cartesian coordinates are $(0,0,0)$ and $(0,a/2,c/4)$ and those of the nitrogen atoms are $(0,a/2,ch)$ and $(a/2,a/2,c(h+1/4))$. The lattice constants are given by a and c; h is a free parameter. With $c/a=6/\sqrt{3}$ and $h=1/12$ the bct-4 structure is in perfect sp^2 geometry.

We notice that although the rhombohedral structure is an sp^2 bonded material, its bulk modulus is much smaller than the other two sp^2 networks. This difference probably arises because the bonding in the c direction in the rhombohedral structure is due to π orbitals between the planes whereas it is the σ orbitals which give the bonding along all directions in the H-6 and the bct-4 structures.

We have also calculated the structure based on the high-pressure phase of GeP which was proposed in Ref. 25 as a possible candidate for a 1:1 stoichiometry compound. This phase consists of a body tetragonal primitive cell with a two atoms basis; the carbon atom is located at the origin and the nitrogen atom is at $(0,0,2hc)$ in Cartesian coordinates. However we see from Fig. 1 that it is unlikely that this phase should be observed since its binding energy is much less than those of the other structures studied. The structural parameters, the bulk modulus and the binding energy for this structure are given in Table I.

Thus far, all the structures considered are metallic. However, we would expect that if we had a semiconducting or an insulating phase its binding energy will be higher because of the opening of a gap at the Fermi energy. Let's consider the general valence rule[26] which a compound must satisfy in order to be semiconductor:

$$(n_e+b_a-b_c)/n_a=8.$$

In the above expression n_e is the total number of valence electrons, n_a is the number of anions, b_a is the number of electrons involved in forming anion-anion bonds, and b_c is the number of electrons involved in forming cation-cation bonds (including any ''unshared'' valence electrons on the cations). All of these values are calculated per formula unit of the compound. This rule expresses the fact that in a semiconducting compound the valence subshell of the s and p electrons(eight) on the anion is filled. It is a generalization of the $(8-N)$ rule which includes more compounds. In particular for the carbon nitride compounds, it is unfavorable to have N-N bonds since they are so strong they would not contribute to the binding of the structure as a whole and would act as an independent unit. Therefore, we can set $b_a=0$ in the above formula. For an arbitrary stoichiometry, C_xN_y, we can write $n_a=y$ and $n_e=4x+5y$, hence we obtain $b_c=4x-3y$. Consider the case of $b_c=0$ which means that there is no C-C bonds or unshared electrons in the structure. The only stoichiometry which satisfies this requirement is the C_3N_4. For $b_c=1$, we have the stoichiometries CN, C_4N_5, C_7N_9, ... Therefore, for the stoichiometry considered in this study, in order to have a semiconducting phase, we should have C-C bonds or an electron of the carbon atom which do not contribute to the binding with the nitrogen.

Inspired by existing semiconducting structures which have the same b_c, we calculated two possible semiconducting candidates for carbon nitride compounds with 1:1

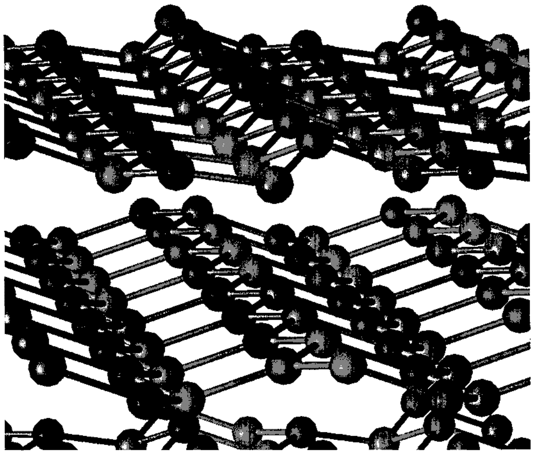

FIG. 4. Ball and stick model of the β-InS structure with C atoms (gray balls) and N atoms (black balls). The β-InS structure has an orthorhombic primitive cell with an eight atoms basis. The C(N) atoms are located at $\pm(x_{C(N)},y_{C(N)},1/4)$ and at $\pm(1/2-x_{C(N)},y_{C(N)}+1/2,1/4)$in terms of the lattice vectors.

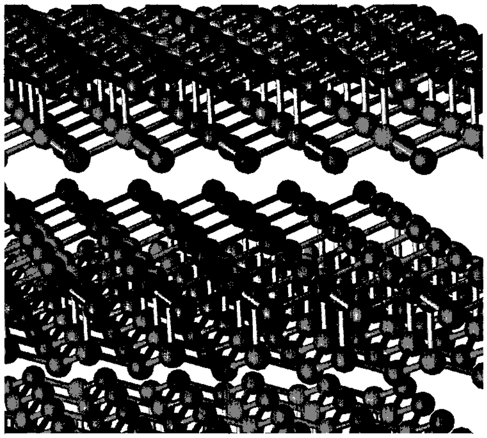

FIG. 5. Ball and stick model of the GaSe structure with C atoms (gray balls) and N atoms (black balls). The GaSe structure has a hexgonal unit cell with an eight atoms basis. The C(N) atoms are located at $\pm(1/3,2/3,x_{C(N)})$ and at $\pm(2/3,1/3,x_{C(N)}+1/2)$ in terms of the lattice vectors.

stoichiometry: the structure based on the β-InS and the GaSe compounds.[26] Figures 4 and 5 show respectively the ball and stick models of these relaxed structures when carbon and nitrogen are substituted. Both these structures have cation-cation bonds. The β-InS has three-dimensional bond arrays, however, upon relaxing the structure with the carbon and nitrogen atoms, it becomes a layer structure and it is actually found to be metallic within the local-density approximation. The GaSe structure is also a layer structure but the C-C bonds are perpendicular to the plane (see Fig. 5) and it is found to have a length of 1.62 Å. This structure is semiconducting and it is the most binding of all those calculated in this study. However, because it is a layered structure, its bulk modulus is only at 199 GPa.

In summary, we have studied eight different structures of carbon nitride with a 1:1 stoichiometry. Two of these structures, the rocksalt and the zinc-blende, are unstable, relaxing to a rhombohedral structure which has covalent bonding across the CN planes. Two other phases with sp^2 bonding were also calculated. These H-6 and bct-4 phases have calculated bulk moduli of 345 and 375 GPa, respectively. Inspired by existing phases, we have calculated the structures based on the high-pressure phase of GeP, and the semiconducting phases of β-InS and GaSe compounds. The GeP phase was found to be unfavorable because of its low binding energy. The most energetically favorable of all phases is the GaSe phase which is semiconducting and consists of a layered structure with C-C bonds perpendicular to the planes. It has a calculated bulk modulus of 199 GPa.

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