PHYSICAL REVIEW B VOLUME 59, NUMBER 18 1 MAY 1999-II

ARTICLES

Relative stability of some possible phases of graphitic carbon nitride

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(Received 4 November 1998)

Various graphitic phases of C_3N_4 are examined using the local-density approximation plane-wave-pseudopotential approach. These are three forms of *p* graphite and the $P\bar{6}m2$ graphite structure. Each differs only in planar stacking and character of planar C-N bonds. Two forms of *p* graphite are predicted to be stable with energies very close to the $P\bar{6}m2$ structure. This suggests a strong phase instability of the graphite structures and material softening along the *c* axis. [S0163-1829(99)09217-6]

I. INTRODUCTION

Despite continuing numbers of reports of the synthesis of the super-hard material C_3N_4 the difficulty to produce large enough samples for a precise structural characterization is proving problematic. Several forms of the material have been suggested for carbon nitride with super-hard forms being β-C_3N_4 (Refs. 1–3) (hexagonal structure and space group $P3$), cubic or defect zinc-blende C_3N_4[2] ($P\bar{4}3m$), and another cubic form[4] ($I43d$) suggested to be the hardest as measured by the calculated bulk modulus. In each of these structures, carbon atoms are in fourfold coordination by nitrogens, the nitrogens in threefold coordination by carbons. All structures are predicted to be stable.

From the experimental point of view the material has been observed to exist in apparent amorphous or disordered phases[5–7] although there are several reports of crystalline phases[8,9] being dispersed in the amorphous matrix. Laser ablation[10,11] appears to be a promising technique for the synthesis of crystalline carbon nitride and to date various C-N bonded structures have been observed.[12,13] Vapor deposition has recently proven to be promising[14,15] as has ion-beam deposition.[16,17] Possibly the technological difficulties to produce carbon nitride relate to large amounts of nitrogen required to interact with carbon to give the desired structure—this is displayed by various nitrogen-bonded structures that have been observed[13] following laser ablation techniques.

Graphite is an important starting point for the synthesis of diamond. It exists in several forms and as such through applied pressure leads to other structures such as hexagonal diamond and then finally diamond. It is likely that carbon nitride will also need intermediate structures for a successful synthesis route to the superhard form. Graphite structures for carbon nitride have been considered theoretically as possible forms of the material.[18,19,4] These all consist of C_3N_4 layers in a hexagonal planar lattice in which a C atom is missing. This form is not as hard as diamond but the location of the missing C atom in the C_3N_4 layer suggests there could be several ways of stacking in much the same way as, for example, graphitic boron nitride.[20] A rhombohedral[2] form of the material in graphitic form is predicted to be stable at a material density lower than the β phase and more recently other graphitic forms with still lower density have been suggested as being possible precursors to the formation of the super-hard phase.[4,18] High-energy amorphous structures have also been investigated[21,22] and these have shown competition between the C-C, C-N, and N-N bonds in forming such a structure. Possible crystalline structures with stoichiometries different from C_3N_4 (Refs. 23,19) have also been examined.

The purpose of the present work is to apply the local-density approximation (LDA) plane-wave pseudopotential approach to examine the relative stability of several forms of stacking in the graphitic phases of C_3N_4 and then compare with other, especially super-hard, phases. The intention is to attempt some identification of possible synthesis routes toward the super-hard material involving graphitic structures—if indeed such a route is at all feasible.

II. COMPUTATIONAL DETAILS

Soft Troullier Martin[24] pseudopotentials with plane waves of 64 Ry were used throughout with *k*-point sampling using a [444] Monkhorst-Pac k grid[25] giving about 16 special *k* points in the case of the graphitic phases. Energy-volume relations were calculated using a standard plane-wave algorithm[26] for each of the various relaxed structures and the results fitted to a standard equation of state[27] from which an estimate of the bulk modulus can be obtained. From the equation of state, derivatives at the common energy of phase intersection were derived giving predicted transition pressures. Apart from the amorphous phase,[22] which essentially was modeled through a high-temperature anneal of a cubic

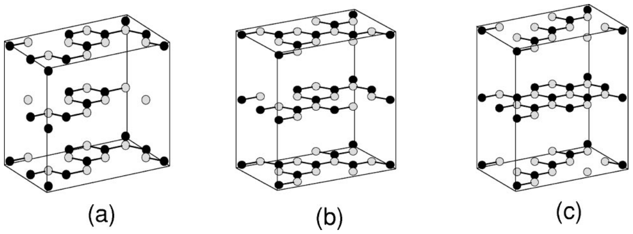

FIG. 1. *p* structures of hexagonal graphite C_3N_4. (a) out-of-phase structure, (b) in-phase structure, and (c) the C_2N_4-C_4N_4 planar structure. C atoms are shown in black.

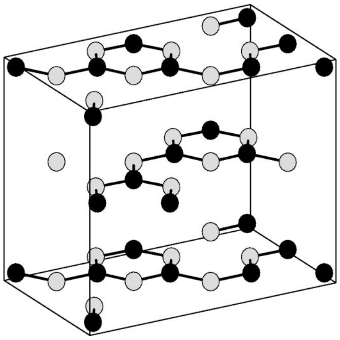

FIG. 2. $P\overline{6}m2$ structure of hexagonal graphite C_3N_4.

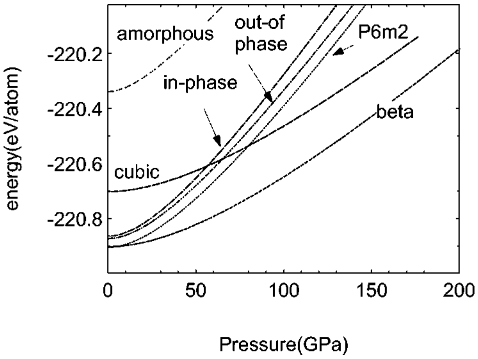

FIG. 3. Energy volume for various phases of C_3N_4.

phase as a super cell, the results presented relate to zero temperature although comparison of the total-energy results will suggest the relative ordering of the phases and synthesis paths.

A. Graphitic carbon nitride structures

Sheets of C_3N_4 that constitute the graphitic phases consist of hexagonal planes of bonded C-N atoms with a missing C atom on one of the sites. There are various possibilities for the ordering of the graphitic planes depending on the relative location of the missing C atom from one plane to another. First is the case where empty C sites are aligned relative to each other along the hexagonal c axis. This structure emphasizes C-C and N-N bonding between the adjacent layers so that all bonds along the c axis are saturated though there is a rather large region (missing C atoms) where bonding is weak. Such a structure was the first type of graphitic structure considered for C_3N_4 and named p-C_3N_4 by Ortega and Sankey.[18] We shall refer to the structure as p-C_3N_4 (in-phase). If we consider that the planes may move relative to one another, another structure can arise with mixed C-N bonding between the layers. This structure we shall name p-C_3N_4 (out-of-phase). Probably there are many possibilities in between. There is also the possibility that one of the planes may have no missing C atoms with the adjacent plane having two missing C atoms—a C_2N_4-C_4N_4 structure. These three possibilities are considered representing the structures of p-C_3N_4 and are each shown in Fig. 1.

The hexagonal unit-cell vectors for all these structures is generated by the unit vectors $a(\frac{1}{2},\pm\sqrt{3}/2,0)$ and $(0,0,c)$, with atoms located at $(\pm x,\pm x,z\pm u)$, $(\pm x,\pm x,-z\mp u)$ such that in the unrelaxed structure $x=\frac{1}{6},z=\frac{1}{4}$ and $u=\frac{3}{16}$. This unit cell is then replicated as $2\times2\times1$ to give a lattice of 16 points. Each of the three p-C_3N_4 structures then corresponds to removal of two C atoms either in two adjacent planes or only one plane indicated in Fig. 1 as discussed earlier. Although not formally necessary for the p-C_3N_4 (in-phase) structure, we always used unit cells that contained 14 atoms for the computations and, especially, k-space sampling.

The other type of graphitic structure considered recently by Teter and Helmley[4] also contains 14 atoms in the unit cell but is somewhat different from the p-C_3N_4 structures as here two possible C-N bond lengths are in the hexagonal plane. This structure is shown in Fig. 2 and emphasizes C-N bonding between layers. The hexagonal unit-cell vectors are $a(\sqrt{3}/2,\frac{1}{2},0)$, $a(0,1,0)$, and $(0,0,c)$, with atoms located at the following unrelaxed positions in the unit cell:

$$\mathrm{C}\ \left(0,\frac{1}{2},\frac{1}{2}\right),\left(\frac{1}{2},\frac{1}{2},\frac{1}{2}\right),\left(\frac{1}{2},1,\frac{1}{2}\right)$$

$$\left(\frac{1}{3},\frac{1}{6},0\right),\left(\frac{5}{6},\frac{1}{6},0\right),\left(\frac{5}{6},\frac{2}{3},0\right),$$

$$\mathrm{N}\ (0,0,0),\left(\frac{1}{2},\frac{1}{2},0\right),\left(\frac{1}{2},0,0\right),\left(1,\frac{1}{2},0\right)$$

$$\left(\frac{2}{3},\frac{1}{3},\frac{1}{2}\right),\left(\frac{1}{6},\frac{1}{3},\frac{1}{2}\right),\left(\frac{1}{6},\frac{5}{6},\frac{1}{2}\right),\left(\frac{2}{3},\frac{5}{6},\frac{1}{2}\right).$$

Starting from the above coordinates the cell structure was optimized for each of the cell dimensions allowing atoms to relax within the unit cell. Each structure was then subject to

TABLE I. Structure, bulk modulus, and relative energies of some phases of C_3N_4 using the Birch equation of state. LW=Ref. 2, TH=Ref. 3.

Phase	Shortest C-N distances (Å)	Interplanar distance (Å)	B (GPa)	Energy (eV/atom) (64 Ry cutoff)
Beta	1.45		432 (437LW) 448(TH)	−220.903
Cubic (defect zinc-blende)	1.48		428 (425LW) (451TH)	−220.703
Amorphous [a]			128	−220.339
$P\overline{6}m2$ graphite	1.32−1.45	3.29	253	−220.905
p graphite (out-of-phase)	1.37	3.37	205	−220.874
p graphite (in-phase)	1.37	3.72	198	−220.865

[a] From Ref. 23.

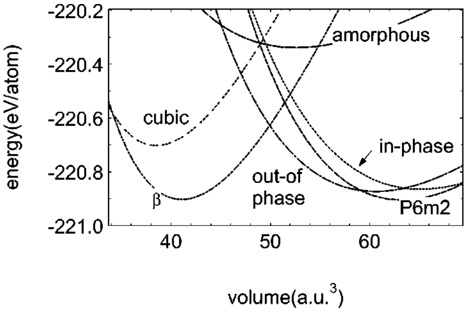

FIG. 4. Energy variation for a c-axis compression of various phases of hexagonal graphite C_3N_4.

a uniform volume compression and the total energy calculated. The energy-volume curve shown in Fig. 3 was then fitted to a Birch equation of state[27] from which the bulk modulus can be estimated. These results are given in Table I.

B. Relative stability

TABLE II. Binding energies for interplanar formation of graphitic carbon nitride.

	$P\overline{6}m2$ graphite	p graphite (out-of-phase)	p graphite (in-phase)
binding energy (eV/atom)	0.041	0.022	0.008

Of the four situations considered we found that stacking involving C_4N_4-C_2N_4 sheets was unlikely; when the molecular-dynamics cycle first initiated movement in the system an unstable diverging situation relating to rapid interlayer charge fluctuations developed suggesting this phase is unstable. On the contrary each of the p-graphite phases were found quite stable and with relative energies lying very close to each other. One point always evident during the calculations was that forces between adjacent planes were very small suggesting that graphitic carbon nitride may be extremely soft along the c axis. However, even with small forces there still may be some finite stress.[28] This softness therefore is quantified through an investigation of the energy dependence of the structures on inter-layer spacing, and this is shown in Fig. 4. The most stable structure has a spacing between adjacent layers of 3.29 Å that is comparable to a similar interlayer spacing in carbon graphite [$c=3.34$ Å (Ref. 20)]. Other structures have larger layer separations.

The calculation also gives some indication of the binding energy for cohesion of the planes in the various graphitic phases. As seen from Fig. 4, energies of the p-C_3N_4 phases converge at a layer separation of just over 5 Å. Taking the energy at this distance to represent no interaction between the hexagonal planes leads to values of the interplanar binding energies and these values are given in Table II. There is a very weak interaction between the layers and this weak interaction probably leads to dispersed layers of graphitic sheets in the material. Such a random distribution of graphite layers has recently been observed using high-resolution spectroscopy of carbon nitride thin films.[29]

As the stability of the graphitic phases relates more to the intralayer structure than the interlayer spacing we investigate the layer charge density for the phases. In Fig. 5 we show the charge density of the $P\overline{6}m2$ phase; rather surprisingly most of the charge on N is directed away from the C-N bond toward the vacant site. Likewise in Fig. 6 we show a similar charge density plot for the out-of-phase p-C_3N_4 phase, a similar situation regarding N bonding toward the missing C-atom site is also evident. Although there is slight difference in bonding about the N site that is threefold coordinated by C atoms in the case of the $P\overline{6}m2$ where the C-N bond length is about 1.45 Å, the planar charge distribution shows

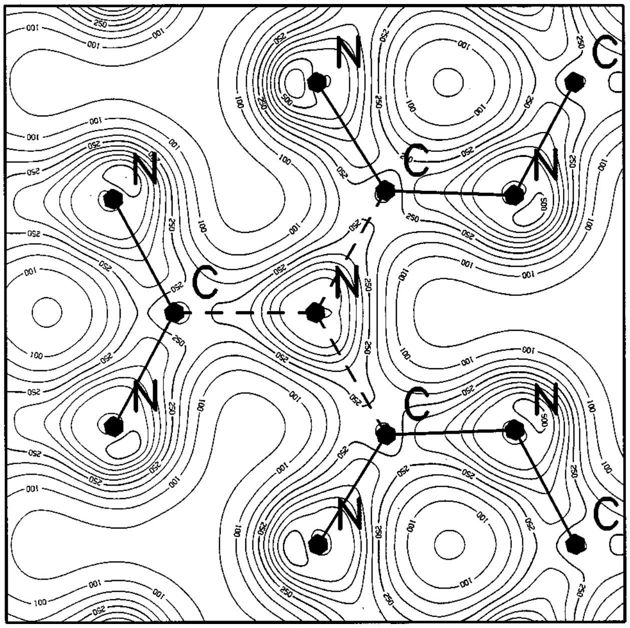

FIG. 5. Charge-density contours in the hexagonal plane of $P\overline{6}m2$ C_3N_4. Bold lines show C-N bond lengths of 1.32 Å, dashed lines show C-N bond lengths of 1.45 Å.

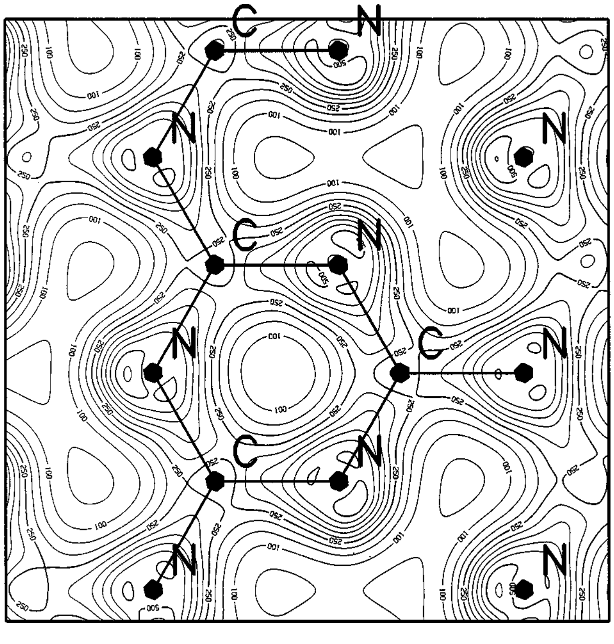

FIG. 6. Charge-density contours in the hexagonal plane of out-of-phase C_3N_4. Bold lines show C-N bond lengths of 1.37 Å.

a strong similarity to that of the p type structures where the bond length is somewhat less at 1.37 Å.

Only modest pressure is needed to overcome the energy barrier separating the graphitic phases and induce a transition between them. Estimating this pressure from the slope at the common energy/volume intersection gives a hydrostatic transition pressure necessary to transfer between the various graphite phases to be less than 5 GPa—a uniaxial compression is far less than this. Hydrostatic pressures that lead to the formation of the super-hard β phase calculated in the same way for graphite phases, however, are much higher. For example, again from the slope at the common energy intersection we calculate that a pressure of about 80 GPa is needed to go from the $P\overline{6}m2$ phase to the super-hard β phase and a little less at about 55 GPa to go from the out-of-phase p-C_3N_4 phase and only slightly more for other graphitic phases. Such transition pressures are well above the value of 12 GPa suggested recently by Teter and Helmley[4] to go from $P\overline{6}m2$ graphite to the super-hard β phase, although the way in which this was estimated is not clear. Very likely this value was based upon a common energy/pressure argument that neglect the importance of intermediate changes in volume of the structures.

III. CONCLUSION

The present study of the graphite structure of C_3N_4 reveals the existence of several stable structures that are quite close in energy. Only modest pressure is needed to change from one of the graphitic phases to the next either through hydrostatic or especially uniaxial compression. The low-energy $P\overline{6}m2$ graphite phase appears to change to one of the higher energy p-C_3N_4 graphite phases following compression well before the super-hard β phase is reached. However, this p-C_3N_4 graphite phase seems slightly softer than the $P\overline{6}m2$ phase and as such requires less pressure to surmount the energy barrier that leads to the β phase. If a graphitic phase of C_3N_4 can be established it would therefore appear quite fruitful to use pressure (especially uniaxial) techniques to change between the graphitic phases and possibly attain a super-hard phase.

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[1] A. Y. Liu and M. L. Cohen, Science **245**, 841 (1989).

[2] A. Y. Liu and R. M. Wentzcovitch, Phys. Rev. B **50**, 10 362 (1994).

[3] J. V. Badding, Adv. Mater. **11**, 877 (1997).

[4] D. M. Teter and R. J. Hemley, Science **271**, 53 (1996).

[5] A. R. Merchant, D. G. McCulloch, D. R. McKenzie, Y. Yin, L. Hall, and E. G. Gerstner, J. Appl. Phys. **79**, 6914 (1996).

[6] M. Y. Ching, D. Li, X. Lin, V. P. Dravid, Y. Chung, M. Wong, and W. D. Sproul, J. Vac. Sci Technol. A **11**, 521 (1993).

[7] D. M. Bhusari, C. K. Chen, K. H. Chen, T. J. Chuang, L. C. Chen, and M. C. Lin, J. Mater. Res. **12**, 322 (1997).

[8] J. Martin-Gill, F. Martin-Gill, M. Sarlkaya, M. Qian, M. Jose-Yacaman, and A. Rubio, J. Appl. Phys. **81**, 2555 (1997).

[9] K. Yamamoto, Y. Koga, K. Yase, S. Fijiara, and M. Kubota, Jpn. J. Appl. Phys., Part 2 **36**, L230 (1997).

[10] Z. J. Zhang, S. Fan, and C. M. Lieber, Appl. Phys. Lett. **66**, 3582 (1995).

[11] M. Tabbal, P. Merel, S. Moisa, M. Chaker, A. Ricard, and M. Moisan, Appl. Phys. Lett. **69**, 1698 (1996).

[12] A. K. Sharma, P. Ayyub, M. S. Multani, K. P. Adhi, S. B. Ogale, M. Sunderaraman, D. D. Upadhyay, and S. Banerjee, Appl. Phys. Lett. **69**, 3489 (1996).

[13] Z. Ren, Y. Du, Y. Qiu, J. Wu, Z. Ying, X. Xiong, and F. Li, Phys. Rev. B **51**, 5274 (1995).

[14] Y. Chen, L. P. Guo, and E. G. Wang, Philos. Mag. Lett. **75**, 155 (1997).

[15] Kehui Wu, E. G. Wang, Jian Qing, and Guichang Xu, J. Appl. Phys. **83**, 1702 (1998).

[16] C. Ronning, H. Feldermann, R. Merk, H. Hofsass, P. Reinke, and J. U. Thiele, Phys. Rev. B **58**, 2207 (1998).

[17] H. W. Lu, X. R. Zou, and J. Y. Feng, J. Phys. D **31**, 363 (1998).

[18] J. Ortega and O. F. Sankey, Phys. Rev. B **51**, 2624 (1995).

[19] Y. Miyamoto, M. L. Cohen, and S. G. Louie, Solid State Commun. **102**, 605 (1997).

[20] J. Furthmuller, J. Hafner, and G. Kresse, Phys. Rev. B **50**, 15 606 (1994).

[21] F. Weich, J. Widany, and Th. Frauenheim, Phys. Rev. Lett. **78**, 3326 (1997).

[22] J. E. Lowther, Phys. Rev. B **57**, 5724 (1998).

[23] M. Cote and M. L. Cohen, Phys. Rev. B **55**, 5684 (1997).

[24] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[25] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[26] M. Bockstede, A. Kley, J. Neugebauer, and M. Scheffler, Comput. Phys. Commun. **107**, 187 (1997).

[27] F. Birch, J. Geophys. Res. **57**, 227 (1952).

[28] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3780 (1985).

[29] H. Sjostrom, S. Stafstrom, M. Boman, and J. E. Sundgren, Phys. Rev. Lett. **75**, 1336 (1995).