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On the way to carbon nitride

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Abstract. The available data on the problem of hypothetical crystalline carbon nitride are considered. These involve the crystal structure, the nature of chemical bonding, and physical properties of carbon nitride of which the most interesting is its predicted high hardness comparable with that of diamond. The experiments aimed at synthesising carbon nitride are described, and properties of the materials obtained are characterised. The results of thermodynamic calculations pertinent to carbon nitride and processes of its synthesis are discussed. The bibliography includes 144 references.

I. Introduction

An extensive class of materials have been synthesised on the basis of metal and non-metal nitrides, and these materials have wide application in various areas of science and technology.[1,2] The existence of carbon nitride is highly probable, since carbon and nitrogen can form strong chemical bonds with each other, in particular, single bonds. Various chemical compounds (including polymers) composed solely of carbon and nitrogen are known.[3,4] Elements, such as boron, aluminium, silicon, and phosphorus readily form nitrides, which are used to produce valuable ceramics. However, for carbon surrounded by the above-mentioned elements in the Periodic Table no corresponding nitride has been obtained so far. It is surprising that until very recently the problem of carbon nitride synthesis had not even been raised. An exception is the work of Franklin[5] who heated mercury thiocyanate to obtain a voluminous solid residue close in composition to C_3N_4, though containing from 0.6% to 2.4% hydrogen. The author called this product carbon nitride but did not study its structure and properties.

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II. Theoretical analysis. Chemical bonding, crystal structure, and predicted properties

The fundamental studies of Cohen and Liu[6–8] were initially aimed at the development of methods allowing prediction of some properties of solids on the basis of readily accessible data. One of such important properties is the bulk modulus (B) determined by the relation

$$B = -V\frac{\mathrm{d}p}{\mathrm{d}V} = V\frac{\mathrm{d}^2u}{\mathrm{d}V^2}, \qquad (1)$$

where V, p, and u are volume, pressure, and energy, respectively. Theoretical analysis of the effect of covalence on the bulk modulus of semiconductors and insulators of the type of diamond and zinc blende with the tetrahedral structure showed that for the compounds composed of elements situated in the middle of the Periodic Table the magnitude of B depends only on the distance d between the nearest-neighbour atoms and is determined by a very simple relation[6]

$$B = 1761d^{-3.5}, \qquad (2)$$

where B is expressed in GPa and d, in Å. For compounds composed of Group III and IV elements, this formula provides fairly acceptable values: as a rule, deviations from the experimental data are close to 2% (*e.g.*, 2.6% for gallium arsenide). At the same time, for materials including Group II and VI elements the deviation is markedly larger: for example, it reaches 14.4% for zinc sulfide. The deviations are due to the fact that formula (2) has been proposed[6] only for compounds with non-polar bonds. If the chemical bonds in a crystal are polar, the bulk modulus is determined not only by the distance between the nearest neighbours but also by the above-mentioned polarity, which is taken into account by introducting an empirical term into the formula (2)

$$B = (1971 - 220\lambda)d^{-3.5}. \qquad (3)$$

Here, B is expressed in Mbar, and the parameter λ accounts solely the extent of bond ionicity: $\lambda = 0$ for the elements of Group IV (*e.g.*, for carbon in the diamond form); $\lambda = 1$ for materials composed of Group III and V elements (boron nitride, gallium arsenide, indium phosphide, *etc.*); finally, $\lambda = 2$ for compounds

including Group II and VI elements (cadmium and zinc sulfides, selenides, tellurides). Comparison of experimental data for 25 materials (chemical elements and binary compounds of the AB type) has shown [7] that formula (3) allows the prediction of the magnitude of bulk moduli with a fairly acceptable accuracy.

The importance of the formula (3) is determined not only in that it allows the calculation of bulk moduli, but also in that it indicates the direction of search for new superhard materials: obviously, one should seek for minimum interatomic distances and nonpolar chemical bonds. Already in 1985 it was mentioned that the above requirements may be met by a hypothetical carbon–nitrogen compound with the tetrahedral structure;[6] however, only in reports,[8,9] which stimulated all subsequent studies, the problem of crystalline carbon nitride synthesis was clearly formulated with the prediction of its unusual chemical properties.

The crystal of β-silicon nitride has served as the prototype. In this compound, formal substitution of carbon atoms for silicon leads to a hypothetical structure called by analogy β-carbon nitride. In this crystal, the unit cell is hexagonal and contains 14 atoms (*i.e.*, it is a dimer of carbon nitride C_3N_4 with the stoichiometric formula C_6N_8). The carbon atoms are in the centres of slightly distorted tetrahedra, whereas the nitrogen atoms have a nearly planar-trigonal configuration. This results in a complex array of CN_4 tetrahedra linked through their apexes. In this lattice, the carbon and nitrogen atoms are in sp^3- and sp^2-hybridisation, respectively. Alternatively, this structure, belonging to the hexagonal space group C_{6h}^2 may be regarded as a combination of distorted layers. It may also be considered as a network of 6-, 8-, and 12-membered rings of alternating carbon and nitrogen atoms [10] and as the structure of the phenacite (Be_2SiO_4) type of 3-, 4-, and 6-membered rings formed by the CN_4 tetrahedra.[11]

Non-empirical quantum-mechanical calculations of β-C_3N_4 carried out by the pseudopotential method within the framework of localised orbitals formalism [8,9] have shown that the length of the C—N bond is 1.47 Å. This magnitude correlates well with the sum of the tetrahedral covalent radii of carbon and nitrogen. The energy of cohesion was found to be 81 eV per unit cell or 5.8 eV per atom (see Ref. 8) (the value of 81.5 eV for the energy of cohesion per unit cell was given in Ref. 9). Representation of the total energy as a function of volume in the Murnaghan and Birch equation of state has permitted computation of the bulk modulus, which proved to be 4.27±0.15 Mbar. The determination of the bulk modulus requires that formula (3) be refined taking into account that the carbon and nitrogen have different coordination numbers equal to 4 and 3, respectively. The resulting formula [12] is

$$B = \frac{N_c}{4}\,\frac{1972 - 220\lambda}{d^{3.5}}, \qquad (4)$$

where, in contrast to the formula (3), B is expressed in GPa rather than in Mbar and N_c is the mean coordination number. In the case of C_3N_4, $N_c = 3.43$, $d = 1.47$, $\lambda < 1$ and, depending on the λ value and according to work,[12] $B = 410-440$ GPa, which correlates well with the above value.

Thus, the predicted bulk modulus of β-carbon nitride is comparable with that of diamond (443 GPa). It will be shown below that somewhat different calculations give different values of the bulk modulus, and in some cases it proves to be higher than that of diamond. However, even if it is not so, most of the calculations indicate that β-C_3N_4 shifts boron nitride, the second hardest compound after diamond ($B = 369$ GPa [7]), to the third position. To get a more complete picture, note that for solidified noble gases $B = 1-2$ GPa, for ionic solids $B = 10-60$ GPa, for non-transition metals $B = 2-100$ GPa, for transition metals $B = 100-300$ GPa, and finally for covalent solids $B = 100-443$ GPa.[12] It is the high predicted hardness of carbon nitride (close to a record value) that stimulated further studies. According to the formulas (3) and (4), such a high hardness is due to small interatomic distances and low polarity of the C—N bond.[13] The predicted very high energy of cohesion of β-carbon nitride gives hope that its existence may well be realised, at least as a metastable phase.

The above-mentioned quantum mechanics calculations of the β-C_3N_4 crystal (see Refs 8 and 9) yielded maps of the electron density distribution. In particular, it turned out that the valence electrons are localised between the carbon and nitrogen atoms in such a way as to form two electron density maxima: the larger maximum near the nitrogen atom and the smaller one near the carbon atom. The values of electron density normalised to the number of valence electrons in a unit cell are 4.6 and 2.7, respectively. It also fallowed from the calculations that, as regards its polarity, the C—N bond in β-C_3N_4 is intermediate between the bond in the purely covalent diamond and that in the partially ionic boron nitride. It is of note, that the local electron density maximum near the carbon atom is nearly the same as in diamond. Consequently, no substantial charge transfer along the C—N bond takes place in carbon nitride, and this in turn means that the charge density asymmetry along the C—N bond is due to the non-bonding electrons of nitrogen.

Yet another interesting property is the high mean volumetric sound velocity in β-C_3N_4 making up 1.1×10^6 cm s^{-1}.[9] This is 20% higher than in β-Si_3N_4 and is also indicative of high thermal conductivity of β-C_3N_4 determined by its high Debye temperature.[12]

It has been noted (see, *e.g.* Ref. 14) that the nitrogen atoms in β-C_3N_4 are not equivalent. There are two sorts of these atoms — N_1 and N_2. Atoms N_1 (they account for a quarter of all nitrogen atoms) are in the centres of equilateral triangles with their apexes occupied by the carbon atoms. The nitrogen atoms are surrounded by three carbon atoms whose location is little different from the planar one. The distances between N_1-N_1 and N_2-N_2 are 2.46 and 2.69 Å, respectively. These distances are not large; therefore, repulsive interactions are possible for the pairs of unshared electrons of the nearest nitrogen atoms. The above interactions were determined by non-empirical quantum-mechanical calculation and found to be 1.13 and 0.67 eV for N_1-N_1 and N_2-N_2, respectively.[14] As a result, the crystal is destabilised by 2.14 eV per monomer chain of C_3N_4. The above statement does not rule out the possibility of β-C_3N_4 existence as a metastable phase, though it is indicative of its definite energy loading.

The structure of β-C_3N_4 was the first that has been proposed for the crystalline carbon nitride. It is not, however, the only possible one. Although it has been noted [8] that a simple structure of the zinc blende type is energetically unfavourable, because the first antibonding zone is occupied, subsequent quantum-mechanical and molecular-dynamic calculations pointed to the possible existence of rather diverse crystalline modifications of carbon nitride.

α-Carbon nitride, which is topologically equivalent to α-silicon nitride, was studied by the method of density functional in the approximation of the local density for the exchange and correlation of electrons.[11] Its structure may be described as an ABAB... sequence of packed layers of β-C_3N_4 (A) and their mirror reflections (B). The unit cell contains 28 atoms, *i.e.* it corresponds to the formula $C_{12}N_{16}$ (tetramer of C_3N_4). The dependences of total energy on volume for α- and β-C_3N_4 are very similar. Nonetheless, the α-form was found to be somewhat more favourable energetically, by 0.266 eV per monomer unit.

Analysis of α- and β-C_3N_4 has been carried out [15] by the non-empirical Hartree–Fock method in the 6-31G^{**} basis set . In this case, special attention was given to the optimisation of geometry of the molecule and to the realisation of a pyramidal configuration of the nitrogen atom as, for example, in trimethylamine rather than of a planar one as has been assumed.[8,9] On the one hand, optimisation of the β-C_3N_4 geometry did not lead to substantial changes in its configuration: it still remained close to the planar one. Accordingly, the crystal energy was not strongly changed: it decreased in the optimisation by 4.4 kcal per monomer unit. On the other hand, considering the possibility of pyramidal configuration of the nitrogen atom in α-C_3N_4, the optimisation was

found to result in the lowering of the crystal energy by 54.0 kcal per monomer unit. It was inferred from the calculations that α-C_3N_4 is more stable than β-C_3N_4.[11,15] However, the difference of energies reported in Ref. 15 proved to be larger than that in Ref. 11: it was 25.1 kcal per monomer unit for the optimised structures. The values of bulk moduli calculated recently[15] are noticeably lower than those found in the previous studies. For example, for the optimised and non-optimised structures of β-C_3N_4 they were 250 and 357 GPa, respectively. Certainly, these values are also rather high but still they are much smaller than for diamond. Yet another important result of the studies cited[15] is that the bulk modulus proved to be very sensitive to the geometric configuration of the nitrogen atom.

Optimisation of the geometry of α-C_3N_4 yielded yet another interesting result. The calculations have shown that the tetrahedral lattice of α-C_3N_4 contains spheroid cavities 4.1 – 5.2 Å in diameter with pyramidal nitrogen atoms inside. This crystal should be characterised by a negative Poisson ratio: stretching of crystal in any direction should lead to its expansion in the perpendicular direction. The phenomenon of the negative Poisson ratio is known. It was observed, for example, for α-cristobalite, when it was stretched in definite directions.[16,17]

The conclusions made in the work cited[15] are interesting but not indisputable because of insufficient accuracy of the current computational techniques. The results of molecular-dynamic simulation[18] (in accordance with the data of Refs 8 and 9) confirmed the planar configuration of the nitrogen atom in β-C_3N_4. In the case of α-C_3N_4, one half of nitrogen atoms proved to be in the planar configuration, whereas the second half was found to be in the pyramidal configuration with a bond angle C – N – C of 115°, high values of the bulk moduli being obtained for both α- and β-C_3N_4. Thus, the problem of the structure of α-C_3N_4 remains to a considerable extent open.

Cubic carbon nitride[11] is similar to willemite-II (high-pressure phase of Zn_2SiO_4). It can be obtained when zinc and silicon in willemite-II are replaced by carbon, and oxygen is replaced by nitrogen. Relevant calculations show that the pressure of the α-C_3N_4 transition to the cubic form is 68 GPa. Of all C_3N_4 modifications, cubic carbon nitride should posses the highest density (0.2957 atom-mol cm^{-3}). Such a high density and the topology of bonds in cubic carbon nitride suggest its high heat conductivity. The mechanical stability of cubic carbon nitride under normal and high pressures also follows from the calculations.[11]

Pseudocubic carbon nitride (in a number of publication, it is this modification that is called cubic) has a structure of the α-$CdIn_2Se_4$ type.[11] It may be classified as a structure resembling zinc blende with one carbon vacancy per cubic cell.[10] The pseudocubic carbon nitride is similar to β-C_3N_4 in that each carbon atom has four neighbouring nitrogen atoms and each nitrogen atom has three neighbouring carbon atoms. However, the CNC angle in the pseudocubic carbon nitride is close to 109.47°, which is characteristic of sp^3-hybridisation, and not to 120° characteristic of sp^2-hybridisation as in β-C_3N_4. β-C_3N_4 was reported[10,11] to be somewhat more stable than the pseudocubic form, whereas the opposite result was obtained in another study.[18] This is due to the insufficient accuracy of calculation techniques.

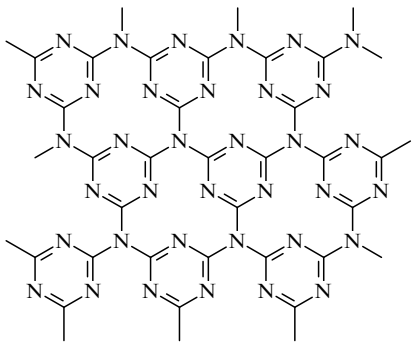


Figure 1. Structure of graphite-like carbon nitride.

Graphite-like carbon nitride has a layered structure and relates to β-C_3N_4, like graphite relates to diamond. The layer structure is shown in Fig. 1. This 'perforated' layer is seen to consist of a series of triazine rings linked through nitrogen bridges. The layers are stacked as ABCABC...,[10] though the ABAB... type in also possible.[11] Non-empirical molecular-dynamic calculations have shown that the interlayer distance is 3.07 Å, which is 8% smaller than in graphite and graphite-like boron nitride.[10] For the two-coordinate nitrogen atom (nitrogen in the triazine ring) the bond angle is 116°, and the mean C – N bond length is 1.36 Å, *i.e.* it is close to the sum of Slater radii of carbon and nitrogen.

Similar results were obtained[18] by the method of density functional in the local density approximation for the exchange and correlation functionals. To simplify calculations, it was assumed that all the nitrogen atoms in the system are equivalent, and the corresponding atoms in the neighbouring layers are strictly one under another. The length of the C – N bond was found to be 1.38 Å and the interplanar distance, 3.2 Å. Both values are in good agreement with the above-cited results.[10] The phase transition pressure of graphite-like carbon nitride in the cubic modification is 12 GPa.[11] Essentially, the graphite-like carbon nitride is the most stable of all modifications analysed so far. The calculated properties of different phases of carbon nitride are presented in Table 1.

Table 1. Characterisation of different phases of carbon nitride.

Parameter	α-C_3N_4	β-C_3N_4	Cubic C_3N_4	Pseudocubic C_3N_4	Graphite-like C_3N_4	Ref.
Space group		C_{6h}^2				9
		$P6_3/m$				20
		$P6_3/m$		$P\bar{4}3m$	$R3m$	10
	C_{3v}^4 [a]	C_3^1 [a]				15
	$P3_1c$(159)	$P3$(143)	$I\bar{4}3d$(220)	$P\bar{4}2m$(111)	$P6m2$(187)	11
Z		2				8 – 10
	4 [a]	2 [a]				15
	4	2	4	1	2	11
a /Å		6.44				9
		6.533				26
		6.41		3.43	4.11	10
		6.47				21
	6.59	6.38				15
	6.35 [a]	6.35 [a]				15

Таблица 1 (continued).

Parameter	α-C_3N_4	β-C_3N_4	Cubic C_3N_4	Pseudocubic C_3N_4	Graphite-like C_3N_4	Ref.
a /Å	6.4665	6.4017	5.3973	3.4232	4.7240	11
	6.46	6.42		3.41	4.09	18
c /Å		2.400				26
		2.45				21
	4.71	2.47				15
	4.64 [a]	2.46 [a]				15
	4.7097	2.4041			6.7205	11
c/a		0.3827				20
		0.375				10
		0.379				21
Length of C–N		1.47				8, 9, 19
bond /Å		1.45		1.48	1.36	10
					1.38	19
Interplanar distance /Å					3.07	10
					~3.2	19
Angle C–N–C /degree	~109.47	112–124		108–110	116 [b]	10
Angle M–C–N	115 [c]					18
/degree		108–112				10
B /GPa		427 ± 15				8, 9
		437		425	51	10
		421				21
	351	357, 366				15
	189 [a]	250 [a]				15
	425	451	496	448		11
	567	557		556		18
B' /GPa		3.7				10
		5.12				21
	3.1	3.3	3.4	3.4		11
E_c /eV per		40.5				8
monomer unit		40.75				9
		47.71		46.56	47.85	10
		41.6				22
	48.9	48.5		49.6	51.0	18
		33.4–35.8				23
E_0 /eV per monomer unit	−1598.669	−1598.403	−1597.388	−1597.225	−1598.710	11
ρ /g cm^{-3}		3.45				26
	3.45	3.50				15
	3.78 [a]	3.56 [a]				15
	3.58	3.58	3.89	3.81	2.33	11
ε		3.2				21
Total valence-		24.8				9
band width		24.5				20
		24.8			24.0	19
Band gap		3.2				9
		3.11				20
		2.1				19
	3.85	3.25	2.90			11

Note. The following designations were used: Z is the number of monomers per unit cell; a and c are unit cell parameters; B' is the pressure derivative of the bulk modulus; E_c is the energy of cohesion; E_0 is the total energy; ρ is density; ε is dielectric constant. To unify the data from different publications, the values of bulk modulus are all expressed in GPa, the energy of cohesion, in eV per monomer unit, and density, in g cm^{-3}.
[a] Calculations included geometry optimisation. [b] Two-coordinate nitrogen. [c] Pyramidal nitrogen.

In conclusion, let us note briefly some other results of theoretical calculations. The geometric coordinates of atoms in the crystal lattices of carbon nitride were determined.[10, 11] Electronic and optical properties of β-C_3N_4 and the dependence of optical properties on pressure were estimated in the local density approximation.[21] The normalised density functions of β-, pseudocubic, and graphite-like C_3N_4 were calculated.[24] Electronic and optical properties of β-C_3N_4 were discussed and an idea of the possible existence of carbon nitride in the form of nanotubes, was suggested.[25]

III. Carbon–nitrogen films: preparation, properties, formation mechanism

After the pioneering studies of Cohen and Liu,[6,8] many attempts have been made to materialise their ideas. Most of the studies concerned with the synthesis of crystalline carbon nitride aimed at preparing carbon–nitrogen films. This was by no means the easiest way to obtain carbon nitride (in our view, it is just the opposite), but rather the direction in which, by the beginning of this series of studies, advanced techniques had been developed and rich experience gained in the synthesis of carbon films, including the diamond-like ones.†

One of the most common ways for preparing thin films is chemical vapour-phase deposition. In its application to carbon–nitrogen materials, it consists essentially in having the initial substances in their specific forms (atomic, molecular, cluster, or ionised) either existing in, or brought into, the gas phase (by vaporisation, or spray) and forming the target films by interaction on the surface of a specially selected substrate.

As regards the initial substances to be used for the synthesis of carbon nitride, it is natural to rely on its constituent elements, *viz*., nitrogen and carbon. Nitrogen is used either in pure state or in its mixture with argon. Of the carbon allotrops, graphite is most often used, while diamond and glassy carbon are employed on rarer occasions. The latter is a low-density ($\sim$1.5 g cm^{-3}) non-ordered graphite-like material with a microscopically turbostratic structure consisting of an ordered (local order) network of sp^2-hybridised carbon atoms.[37]

As the carbon source for preparing carbon–nitrogen films, various hydrocarbons can be used that, in contrast to graphite, do not require special vaporisation: methane,[38–44] ethylene,[45,46] acetylene,[47,48] cyclohexane,[47] cyclopentane,[49] and benzene.[50,51] Ammonia may well be used as the nitrogen source.[43,44] However, in all of the above-mentioned cases the resulting films contained considerable amounts of hydrogen, which naturally hampered the identification of carbon nitride in them. It is also noteworthy that even when the initial substances were hydrogen-free, it might be present in films as an admixture.[52]

In a number of studies specially devoted to the search for carbon nitride, the sources of carbon were hydrogen-containing compounds, such as the already mentioned methane,[53,54] low-molecular-weight polyethylene,[55,56] and wax.[55] Ammonia was used as the nitrogen source;[54,56–58] incidentally, it was noted[57] that ammonia was to some extent even more convenient than molecular nitrogen because its chemical bonds are markedly weaker than those in N_2.

The transfer of carbon to the gas phase and the preparation of chemically active particles necessary for vapour-phase deposition are energy-consuming processes. In the preparation of carbon–nitrogen films, this is achieved in a few ways. Of these, the most popular seems to be magnetron discharge.[58–76] In yet another method the graphite to be volatilised is used as an electrode to which voltage is applied[24,58,70,77–84] so that the process is as a rule realised in an electric arc mode. Also rather widespread are the methods of laser ablation of graphite[85–96] and glassy carbon,[71] graphite vaporisation under the action of an electron beam[97–100] or a beam of argon ions,[57,101–103] and radiofrequency diode spraying.[104–113] A beam of carbon ions was also used to prepare carbon–nitrogen films.[114,115] The films can also be obtained by pyrolysis (see below).

† Furthermore, irrespective of the carbon nitride problem, investigations have continued on the synthesis of carbon films doped with nitrogen to enhance their performance. In this connection no effort was made to introduce the maximum amount of nitrogen in films (it amounted, as a rule, to a few atomic percent and sometimes to percent fractions), and no measurements intended to detect carbon nitride were carried out. Therefore, when citing some recent publications on this topic,[27–36] we do not discuss them in detail.

In most cases, silicon is used as a substrate on which the process of film formation takes place, see, for example, Refs 53–58, 60–71, 75–78, 80, 83, 85, 87–90, 92, 94–103, 106–108, 111, 113–115 The role of the substrate is also played by sodium chloride,[56–59,62,72,101] potassium chloride,[58,70] glass,[24,59,91,94,104,106,107,109,110,113] quartz,[98,113] potassium bromide,[106,110,112] glassy carbon,[62,107,110] sapphire,[72,74,100] mica,[58,83] copper,[102,115] gold,[115] beryllium,[102] magnesium,[115] zirconium,[59,60,75] germanium,[108] tantalum,[114,115] molybdenum,[114,115] tungsten,[115] nickel,[79,85] steel,[66,67,73,81] tungsten carbide,[97,98] cemented carbides,[67] and a NiP/AlMg system.[105] Alkali metal halides are convenient as substrates because they are readily soluble in water, which facilitates the isolation of films in a pure state. As regards mica, it was noted[58] that some of its lattice parameters are close to those of β-C_3N_4.

Yet another method for the preparation of carbon–nitrogen films is based on ionic implantation. It differs from the methods listed above in that the carbon itself is bombarded with an ionic nitrogen beam and is the substrate on which a film is formed. The corresponding beam is usually generated by an ion gun. Various carbon modifications may be used as substrates: graphite,[115–121] diamond,[121,122] glassy carbon.[24,37,123]

The properties of carbon–nitrogen films were studied in detail. We shall give special attention to the properties that are directly related to the problem of carbon nitride preparation. In this context, two questions seem to be of prime importance: how much nitrogen is incorporated into films and whether these films have a crystalline phase.

Before proceeding to the consideration of the respective data, note that the properties of carbon–nitrogen films depend substantially on both the method of synthesis and the parameters of the process. Therefore, the results reported by different authors differ noticeably.

The concentration of nitrogen in films was determined by the electron energy loss spectroscopy, Rutherford backscattering, Auger electron spectroscopy, *etc*. The content of nitrogen in films varied over a wide range.

Nitrogen content (at.%)	Ref.
20	37, 55, 75, 83, 95, 117, 118, 121
20–30	24, 64, 69, 76, 78, 82, 87, 94, 104, 106, 123
30–40	56, 57, 61, 62, 65, 70, 71, 73, 74, 80, 81, 88, 90, 91
40–50	54, 58–60, 85, 86, 92, 96, 99–101, 103, 105, 107–110, 114, 115, 124

There are only a few papers reporting the contents of nitrogen in films approaching the value of 57.1 at.% corresponding to C_3N_4: 58,[53] 54.6,[68] 57,[72,102,111] 83 at.%.[97] Note that the nitrogen level of 58% was determined disregarding the hydrogen content in the film; furthermore, the accuracy of measurement was 20%. The reason for an anomalously high value of 83 at.% is unclear. The only thing to be mentioned in this connection is that the distribution of nitrogen in the films is far from being always regular: its concentration on the film surface was repeatedly noticed to be higher than inside the film.[83] In particular, this may be due to the fact that not all the nitrogen contained in the film is chemically bound. Thus, in a study[122] unrelated to the problem of carbon nitride synthesis, it was noted that the surface concentration of nitrogen in the film prepared by the bombardment of diamond with nitrogen ions may be as high as 81 at.%, while at a depth of 20 Å it is twice as low. One should bear in mind that all of the above-cited nitrogen concentrations represent the mean values. Therefore, one should not rule out the possibility that even in films with low nitrogen levels its local concentrations may exceed considerably the mean value. Thus it was found[101] that at the mean nitrogen concentration of 45 at.% its local level may achieve 59 at.%.

X-Ray and electron diffraction studies were undertaken to detect crystalline phases in carbon–nitrogen films. Some films proved to be totally amorphous,[24, 62, 71, 72, 74, 77, 80, 83, 91, 98, 113] whereas crystallites were also detected in a background of predominantly amorphous phase, see *e.g.* Refs 54–61, 64, 71, 78, 85–90, 99, 102, 104, 107–109, 112, 114, which were attributed directly to β-C_3N_4 on the basis of diffraction measurement results.[56, 75, 78, 85, 86, 88–90, 99, 102, 108, 109, 112, 114, 119] The formation of β-C_3N_4 was also confirmed by the results of X-ray photoelectron,[75] Raman,[78] and IR spectroscopy.[55] Crystallites proved to vary in size: from very small, not exceeding 10 nm,[58, 60, 61, 64, 85, 86] to markedly larger with a size of 100 nm,[59, 102] and even up to 0.4 μm (see Ref. 99) and 0.5 μm.[108] Needle-shaped crystallites 300 nm in size were obtained.[54] Their diffraction pattern was found to be similar to that of α-C_3N_4, while β-C_3N_4 was not detected. As a result of laser-induced microbursts at the interface of frozen ethanol and liquid nitrogen layers, microcrystals up to 100 μm in size were obtained;[71] however, their composition was not established.

Despite the fact that in some of the above-cited studies fairly definite conclusions on the existence of C_3N_4 crystallites in carbon–nitrogen films have been made, they nonetheless should be considered with caution. These films have complex structures, they may include different phases, and finally, they often contain admixtures of other elements (hydrogen, oxygen, *etc.*) affecting the results of measurements. For example, it was noted [125] that some data on electron diffraction in such films are closer to the analogous data for the carbon phase of lonsdelite than to C_3N_4. In this context, one should agree with the arguments of Fang [126] that the available evidence of the formation of crystalline carbon nitride is rather ambiguous.

Let us analyse other properties of carbon–nitrogen films. Numerous measurements of the thickness of such films [53, 55–58, 61, 63, 66, 69, 72, 74, 75, 81, 83, 84, 92, 94, 96–100, 105–107, 110, 115] show that it varies within wide limits ranging from tens of angstroms [53] to micrometers. The thickest films were 2 μm (Ref. 66) and 3.9 μm (Ref. 74). A film separated from the substrate (by dissolving NaCl) was found to be 50 nm thick.[72]

Undoubtedly, the formation of films involves chemical bond formation between carbon and nitrogen. This was confirmed by X-ray photoelectron spectroscopy;[53–57, 71, 76, 84, 85, 88–90, 97–99, 101, 103, 105, 106, 114, 116–119, 122] in some cases, certain information was obtained on the character of the bonds formed. Thus the formation of weakly polarised carbon–nitrogen bonds characteristic of C_3N_4 was established.[55–57, 90] It was also shown that the hybridisation of carbon may be sp^2 and sp^3.[57, 75, 99, 101, 105] In general, judging from the X-ray photoelectron spectra, the composition of carbon–nitrogen films is rather complex and may include various functional groups.[37, 77, 117, 121]

Carbon–nitrogen films were analysed in detail by vibrational spectroscopy. One of the most characteristic features of the IR spectra of these films is the presence of a band at 2200 cm^{-1} attributed to the nitrile group (C≡N).[24, 55, 59, 62, 63, 68, 70, 77, 87, 91, 92, 94–96, 98, 106, 109, 111–113] Analogous results were obtained by employing Raman spectroscopy.[60, 73, 81, 82, 84, 89, 90, 95, 109] The formation of nitrile groups was also confirmed by X-ray photoelectron spectroscopy.[37, 55, 65, 90, 98, 121, 122]

The fact that the nitrile groups are present in films obtained by different methods and under different conditions (in particular, the C≡N group is virtually always observed in the IR spectra) makes it possible to conclude that the formation of nitrile groups is a common phenomenon in the preparation of carbon–nitrogen films. However the nitrile group was considered as an admixture,[92, 96, 127] though it appears to be an admixture in relation to a hypothetical carbon nitride.

The formation of nitriles in the interaction of carbon with nitrogen is not surprising because of the strength and energetic advantage of the triple carbon–nitrogen bonds. The high strength of this bond ensures its stability under drastic conditions of film formation (high temperatures, large energies of nitrogen and carbon ions).

It is difficult to characterise nitriles in the carbon–nitrogen films. It is possible that these compounds are of the paracyanogen type, which is a polymer with a complex branched structure.[128] It contains C≡N and C=N bonds. It is noteworthy that, according to the spectral data, the formation of C=N bonds in the carbon–nitrogen films is quite possible.[53, 65, 68] It is also noteworthy that in 1979, when the problem of carbon nitride synthesis was not yet adequately formulated, paracyanogen was prepared by the method of reactive radiofrequency sputtering,[129] which was subsequently often used for the synthesis of carbon nitride. It was also pointed out [72, 90, 130] that paracyanogen structures can be formed in the carbon–nitrogen films. It was found [96] that nitriles can be removed from the film by annealing. After annealing, a material corresponding in its composition to C_2N was obtained. This does not contradict the above-mentioned high strength of the C≡N bond and can be explained by the destruction of nitrile-containing compounds (including paracyanogen) upon prolonged heating without cleavage of the triple bonds.

To conclude the review of nitriles in carbon–nitrogen films, we can mention a study,[80] which suggested the formation in carbon–nitrogen films of a nitrile compound called polycyanimine, which was found to be rather similar to paracyanogen in structure.

The application of vibrational spectroscopy has revealed yet another phase often occurring in the carbon–nitrogen films. In the IR spectra of films obtained by different methods, three commonly occurring peaks were repeatedly found at 1500, 1300, and 700 cm^{-1}.[62, 87, 94, 109, 112] Analogous bands were observed at 1500 and 1300 cm^{-1} in the Raman spectra.[37, 60, 71, 81, 86, 90, 95, 109, 120, 131] The first of them (*G*-branch) is ascribed to graphite-like carbon, the second band (*D*-branch) was attributed to non-ordered carbon, whereas the band at 700 cm^{-1} was ascribed to the extraplanar deformational vibrations of graphite-like regions (in all cases, the carbon atoms are in sp^2-hybridisation). It is important that for symmetry reasons all of these vibrations must be active in the Raman spectra and inactive in the IR spectra. However, the substitution of a few carbon atoms by nitrogen atoms in the graphite rings results in symmetry perturbation and the corresponding vibrations become IR-active. Thus, the carbon–nitrogen films are believed to include graphite-like structures in which some carbon atoms are replaced by nitrogen atoms. This is supported by NMR data.[63] It was suggested that compounds of the composition C_2N and C_5N [63] can be formed, as well as compounds in which one nitrogen atom is linked with three carbon atoms.[24] The possibility of the existence of the above-mentioned graphite-like nitrogen-containing compounds has been long known. For example, they can be prepared by pyrolysis of polyacrylonitrile incorporated into urea.[132]

Interesting ideas were expressed by Sjostrom *et al.*[69, 76] on the basis of data from quantum mechanics calculations, X-ray photoelectron spectroscopy, and electron microscopy: it was concluded that the sp^2-hybridised graphite-like carbon–nitrogen planes are bent and cross-linked by sp^3-hybridised bonds. It is important that the bend of the plane is due to the incorporation of five-membered rings, *i.e.* a fullerene-like carbon–nitrogen structure appears.

Crystalline carbon nitride has been supposed to have high hardness since the very first studies; therefore, it was natural to check this with the carbon–nitrogen films. One could not expect a record hardness because of complex film composition, though the possibility of preparing films with good performance was not ruled out. In practice, it proved to be the case. Mechanical characteristics of films (hardness, elasticity modulus, elastic recovery, friction coefficient, adhesion) were studied in numerous studies.[55, 57, 59, 60, 64, 66, 69–71, 73, 74, 76, 81–87, 89, 90, 97, 98, 103, 113] As a result, it was found that carbon–nitrogen films possess high hardness, large elastic recovery, good adhesion to different

materials (primarily, to silicon), and some other valuable properties. For instance, on the surface of titanium nitride the hardness of a carbon–nitrogen film corresponds to that of diamond and is higher than that of cubic boron nitride.[66] The elastic recovery of films amounts to 84%–85%.[64,76] In the indentation of films, microcracks (as in titanium nitride) are not formed, and plastic deformation occurs instead. On the surface of titanium carbide the film hardness reaches 6500 kg mm^{-2} on Knoop's scale (see Ref. 97). As noted by the authors, no films of such hardness with a thickness of 1 mm have been obtained previously.

The density of films was measured in a number of studies, it was found to be 2.2 and 2.30 g cm^{-3} (see Refs, 59, 65, respectively). A film with a density of 3.4 g cm^{-3} was prepared [102] which is close to the theoretical value of 3.47 g cm^{-3} for β-C_3N_4.

Some other properties of carbon–nitrogen films were also studied. Since they are not of direct relevance to the problem of carbon nitride synthesis, we shall make only a brief mention of them. In a study,[113] the EPR method was employed to study paramagnetic properties of films. The spin density was found to vary from 1.1×10^{18} to 1.1×10^{19} cm^{-3}. It was concluded that the EPR-active centres are localised on carbon atoms. They were attributed to the unordered phase with sp^2-hybridised carbon. The nitrogen contained in the film decreases the concentration of this phase and possibly increases the concentration of the phase with sp^2-hybridised carbon.

Studies [58–60,80,87,91,94,96,106,113] were concerned with the determination and analysis of the electrical conductivity of C–N films, and their optical properties (refractive index, reflection factor, extinction coefficient, width of optical band gap were also studied.[70,73,80,87,91,94,98,104,113]. These films were characterised by high heat conductivity [96] (note that this property had been predicted theoretically). In some cases, the thermal stability was assessed. The films remain stable for 30 min at 350 °C,[63] they can withstand heating up to 800 °C.[85]

Detailed studies of the properties of carbon–nitrogen films have predetermined discussion, in a number of reports, of their performance and prospects of practical uses. There are indications of the possibility of their application as semiconductors with a variable band gap [61] and wear-resistant coatings.[61,87] Such films were reported [105] to be suitable as protective coatings in systems of magnetic registration. In this respect, they are superior to the purely carbon films.

Information about processes occurring during the film formation is very scarce. As a matter of fact, one can speak only about the type of particles involved in these processes.

As the nitrogen interacting with carbon has been subjected previously to energy impact (radiofrequency discharge, electric arc, electron cyclotron resonance, laser radiation, *etc.*), it was always in the ionised or atomic state, the proportion of different active particles being dependent on experimental conditions. Thus, in experiments on ionic implantation, the nitrogen ions had an energy of 160 keV;[123] in analogous experiments [37,118,121] an ion gun produced N_2^+ ions with an energy of 500 eV, whereas the plasma of electron cyclotron resonance yielded low-energy nitrogen ions with an energy of 20–30 eV.[100] In another study [65] ion beams comprised atomic nitrogen and N^+ ions, the latter present in amounts from 2.5% to 25%;[65] or 80% of N_2^+,[102] or 96% of N_2^+ and 4% of N^+.[116]

Carbon also exists in the ionised or atomised state in the process of film formation. The use of beams of C^+ was reported.[114,115] Evaporation in an electric arc leads to the formation of carbon atoms and clusters, as well as C^+, C_2^+, and electrons.[58,82] In experiments on laser ablation of graphite, atomic carbon, C_2, and other carbon clusters were formed.[89] Irrespective of the problem of carbon nitride synthesis, laser vaporisation of graphite was studied;[133] it was shown that atomic carbon, as well as C_2, C_3, and C_4 clusters were formed.

The plasma over substrate contained not only carbon and nitrogen. The formation of CN radicals is also possible.[77] The presence of these particles in the reaction system is important for the understanding of the formation of the above-mentioned nitriles.

Numerous studies were concerned with the measurement of the rates of the film growth.[53,55–60,62,64–66,68,70,71,74,75,81,84,88,92,96,99,100,105,107,113] It was found to vary from 1 Å min^{-1} (see Ref. 53) to 5 nm s^{-1} (see Ref. 64). The growth rate is an important characteristics of both the yield and the mechanism of the process. It was shown [93,96] that the film growth rate determines the nitrogen content in it. It follows that the key stage of the film growth is not the process in the gas phase, but rather the reaction between carbon and nitrogen on the growing surface. This reaction may be preceded by the dissociation of N_2^+ upon its collision with the surface.[102,118]

Summarising the above considerations, it may be stated that the carbon–nitrogen films possess a number of valuable characteristics and are of obvious practical interest. As regards the possibility of preparation of crystalline carbon nitride by non-pyrolytic film formation (in particular, in the form of an individual substance and not as a microphase), we are rather pessimistic despite some progress in this direction. In our view, the major difficulty lies in that the energy of the particles used in the process of film preparation exceeds considerably that of the chemical bonds in the hypothetical carbon nitride. Even when low-energy nitrogen atoms are used, their energy is 20–30 eV, while the strongest chemical bonds have a dissociation energy of 10 eV, and in the case carbon nitride it does not exceed 4 eV (judging from the cohesion energy level, see Table 1). If one uses higher-energy particles, the corresponding energies differ by orders of magnitude. The high energy of the particles involved in the reaction to promote a high rate of the process means that the time for the energy to dissipate is then too short, and the energy is spent in the cleavage of the newly formed C–N bonds. Nonetheless, some bonds have enough time to form, though in the light of what has been said above, the conditions are more favourable for the formation of stronger double and triple bonds, rather than of single C–N bonds, as in carbon nitride, and this was indeed observed experimentally. Apparently, for the same reason even when carbon nitride crystallites are formed, they are very small.

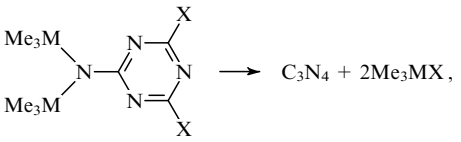
IV. Pyrolysis

Pyrolytic processes underlie the synthesis of numerous materials; therefore, their use for the preparation of carbon nitride appears quite natural. Clearly, it is preferable to use high-nitrogen substances as precursors of carbon nitride. Depending on the conditions of the process, the final product may be obtained in the form of a voluminous mass (*e.g.*, a powder) or as a thin film. The latter case was realised [134] in the pyrolysis of 3,3′-diaminobenzidine and melamine. The corresponding reactions lasted for 1 h at 800 °C (heating to 800 °C was accomplished at a rate of 10 °C min^{-1}). The decomposition products of the above-mentioned substances contained 11.7 mass % and 39 mass % of nitrogen, respectively, and small quantities of hydrogen (0.8 mass% and 2 mass%). The volatile products of the reaction were nitrogen, ammonia, and hydrogen cyanide. This study [134] was not concerned with carbon nitride synthesis, therefore it is not discussed at all. However, this task was already in view in the next study by the same authors.[135] In this case, melamine, 1,2,4-triazole, diaminomaleonitrile, polymerised hydrogen cyanide, dicyanoimidazole, tetracyanoethylene, its mixture with ammonia, and hexaazatriphenylenehexacarbonitrile were subjected to pyrolysis. The reactions were also conducted at 800 °C and yielded a solid residue containing from 25 mass% to 45 mass% of nitrogen.

However, this attempt to prepare carbon nitride failed: the results of X-ray analysis indicated that the product was amorphous, while its pycnometric density was 1.71 g cm^3, which is considerably less than the theoretical value for β-C_3N_4. Judging

by the results of Raman spectroscopy and ^{13}C NMR, the carbon in the synthetic product is in the sp^2- and not in sp^3- hybridisation, while the product itself seems to have a characteristic graphite-like structure in which certain carbon atoms are replaced by nitrogen.

Pyrolysis of triazine derivatives gave interesting results.[136, 137] The reactions proceeded according to the scheme:



where X is chlorine or fluorine and M is silicon [136] or tin.[137]

The process may be regarded as a condensation in which the group Me_3M of one molecule of the substrate interacts with X of another molecule. This results in the elimination of the corresponding silane or stannane, while two triazine rings are linked by a nitrogen bridge. This linkage should lead to the appearance of the structure shown in Fig. 1 and theoretically predicted for the graphite-like carbon nitride (see above). The presence of such structure was confirmed by spectral measurements.[136, 137] Unfortunately, the product obtained in these studies proved to be amorphous. Thermolysis was conducted at 400–500 °C, the tin derivative being thermally less stable than that of silicon. The products were obtained as films up to 0.5 μm thick. The deposition rate achieved was 300 Å min^{-1}. The tin derivative (but not that of silicon) could also be obtained as a powder when the reaction was carred out at 200 °C. Depending on the experimental conditions, the product included small quantities of admixtures. Thus, the pyrolysis of the silicon derivative yielded a film of the composition $C_3N_4O_{0.3}Si_{0.02}F_{0.05}$. The authors [136, 137] were correct in pointing out that the material they had prepared might prove to be a convenient precursor for the synthesis of crystalline carbon nitride (at least, graphite-like). The reason for the optimism is not only the stoichiometric composition of the product, but also that, in contrast to other carbon nitride precursors, it contains only C–N bonds (with no account of admixtures).

Combined pyrolysis of pyridine and chlorine at 800 °C yielded a product of approximate stoichiometry of C_5N.[138] Judging by the results of electron diffraction, it has a layered structure, and it is not ruled out that, as in a number of cases considered above, this is a graphite-like product in which some (one out of six) carbon atoms are replaced by nitrogen.

In conclusion, a study can be mentioned [139] in which the process was not thermal in character and the product was not a film. Etching of diamond or graphite with a microwave nitrogen plasma produced a soft porous low-density carbon–nitrogen material of a structure similar to the turbostratic structure of graphite or the hexagonal structure of boron nitride. This material decomposes at 900 °C or even at lower temperatures.

V. High pressure

The synthesis of numerous carbon materials (including that of diamond) is carried out under high pressure, and it seems natural that higher pressures would favour the preparation of carbon nitride. The expedience of high pressures for the synthesis of carbon nitride was pointed out in a number of papers (see, *e.g.*, Refs 9, 11, 135).

Pyrolysis of 1,3,5-triazine and tetracyanoethylene was carried out at a temperature of 1400 °C and a pressure of 5 GPa, and reaction lasted for 30 min.[140] The product of triazine pyrolysis was found to contain no nitrogen whatsoever, while pyrolysis of tetracyanethylene yielded a graphite-like material of composition $C_{4.66}N$. Judging from electron energy loss spectroscopy, the carbon contained in this product was exclusively in sp^2-hybridisation. Apparently, as in a number of cases considered above, pyrolysis of tetracyanoethylene yielded a graphite-like product in which some of the carbon atoms were replaced by nitrogen.

Other authors [135] described low- and high-pressure pyrolysis (225 MPa) of hexaazatriphenylhexacarbonitrile and tetracyanoethylene for 70 h at 700 °C. However, in this case, too, amorphous products were obtained with nitrogen contents of 36.1 mass % and 39.3 mass %, respectively. Incidentally, it was noted that these products (having the same structure as the low-pressure pyrolysis products) may be convenient precursors for the synthesis of carbon nitride.

Pyrolysis of paracyanogen for 75 h at 725 °C and 0.3 GPa yielded graphite-like carbon as the sole product.[128] The authors noted that paracyanogen is inconvenient for the carbon nitride synthesis because it can undergo decomposition at relatively low temperatures.

As far as we know, there is only one instance of the use of the method of shock-wave compression for carbon nitride synthesis.[26] The product of pyrolysis of melaminoformaldehyde resin and the products of low-temperature combustion of tetrazole and its sodium salt were the objects for the shock impact. These materials were compressed by shock under the conditions typical of the synthesis of diamond and wurtzite-like boron nitride, where the pressure seemed to reach 60–250 GPa. However, no carbon nitride was obtained; instead diamond was detected the structure of which proved to be much more ordered than that of diamond prepared from carbonaceous precursors. It is believed [139] that the reason for unsuccessful attempts [26] to obtain carbon nitride was the presence of hydrogen in the original reagents. The expedience of the use of hydrogen-free compounds was also pointed out in Ref. 135. In our opinion, this is not the only reason. Other reasons will be considered below.

We have already demonstrated that in various attempts to synthesise carbon nitride the final product contained, as a rule, nitrogen at levels below the required 57.1 at.%. In order to overcome this deficit, it was recommended [141] to use lithium azide (or other metal azide) as the nitrogen source and to subject its mixture with a non-diamond form of carbon to shock-wave compression under a pressure of about 100 kbar. As a control, it was proposed to conduct the experiment so as to provide for the synthesis of carbon nitride in one part of the reactor and, in another part separated from the first one, for the analogous synthesis of silicon nitride (the synthesis may also be carried out in a single mixture). This may permit obtaining additionally a new phase of silicon nitride (boron may also be added to the system to obtain the 'elusive' BCN phase). The proposed approach is substantiated by the fact that the shock-wave compression of a mixture of boron with lithium azide allows the synthesis of cubic boron nitride.

Interesting results were reported [142] on a reaction of carbon with nitrogen. It was carried out at 2000–2500 K and a pressure of 30 ± 5 GPa. The carbon sources were graphite, amorphous carbon, and fullerene C_{60}. This resulted in the formation of a crystalline phase with cubic symmetry. The X-ray diffraction pattern of this phase does not correspond to that for β-C_3N_4, though the very fact of preparation of a crystalline carbon–nitrogen phase is remarkable.

VI. Thermodynamics

The scarcity of our knowledge about the range of thermodynamic stability of carbon nitride determines largely the fact that until now attempts to synthesise crystalline carbon nitride, in particular in the pyrolytic mode, have been unsuccessful. Hence, it is still unclear what process parameters (temperature, pressure) should be 'aimed at' to ensure successful synthesis. Despite the evident topicality of the thermodynamic analysis of conditions of the carbon nitride synthesis, only few studies were concerned with this problem.

Having analysed the available data on the dissociation energies of single C–N bonds (286–305 kJ mol^{-1}), the authors [23] assumed that the cohesion energy of carbon nitride should be $E_c = 858–915$ kJ (mol $C_3N_4)^{-1}$. As noted above, the repulsion

of unshared electron pairs of nitrogen should make a noticeable contribution to the energy of a carbon nitride crystal.[14] Taking into account this repulsion, one obtains a more accurate range of cohesion energy values, $E_c = 806-863$ kJ (mol $C_3N_4)^{-1}$. The cohesion energy is directly related to the thermal effect of the reaction.

$$\tfrac{3}{4}C + \tfrac{1}{2}N_2 \longrightarrow C_{3/4}N\,.$$

Thermodynamic analysis of this reaction allows calculation of the standard enthalpy of carbon nitride formation. It was found [23] that $\Delta H_f^\circ = 147-204$ kJ (monomer unit $C_3N_4)^{-1}$. The entropy of C_3N_4 was calculated using the Latimer rule and amounted to 19 J (K mol $C_{3/4}N)^{-1}$, *i.e.* 77 J (K monomer unit $C_3N_4)^{-1}$. Thus, $\Delta S_f^\circ = -78$ J (K mol $C_{3/4}N)^{-1}$; $T\Delta S = -23$ kJ (mol $C_{3/4}N)^{-1}$ at 298 K; and $\Delta G_f^\circ = 171-227$ kJ (mol $C_{3/4}N)^{-1}$.

Knowledge of the thermodynamic properties of carbon nitride made it possible to follow the dependence of the thermodynamic potential of its formation on pressure.[23] This was done with the aid of the Gibbs–Duhem equation using the Birch–Murnaghan equation of state. As a result, the dependences of the specific volume of carbon nitride on pressure were determined for isothermal conditions (298 K).[23] In a thermodynamically unfavourable case [$\Delta G_f^\circ = 227$ kJ (mol $C_{3/4}N)^{-1}$ under normal pressure], $\Delta G_f^\circ = 0$ (*i.e.* the reaction becomes possible) under a pressure of 150 GPa, and at 75 GPa in the optimal case [$\Delta G_f^\circ = 171$ kJ (mol $C_{3/4}N)^{-1}$]. One should also bear in mind that to permit the reaction at a sufficient rate (it is short conversion times in the shock-wave compression that could be the reason for failure to synthesise carbon nitride [26]) rather high temperatures are required and this necessitates increased pressure. Thus in synthesis at 1300 K (this temperature is characteristic of the high-pressure synthesis of diamond) it is necessary to increase pressure by another 30 GPa to make the reaction possible. Such pressures are considerably higher than those realised in the attempts to synthesise carbon nitride (except for the shock-wave compression). Nonetheless, it was noted [23] that since nowadays static pressures up to 200 GPa are achievable, the potential possibility of carbon nitride synthesis is preserved. Thermodynamic analysis of carbon nitride with stoichiometry C_4N_3 which contains some C–C bonds besides the C–N bonds, has been carried out.[23]

Thermodynamic analysis of the temperature dependence of the pressure of β-C_3N_4 formation in a system containing solely carbon and nitrogen was carried out.[22] In the estimation of the standard enthalpy of carbon nitride formation, it was assumed (based on the equality of bond lengths) that the dissociation energy of its C–N bonds is the same as in methylamine, *viz.*, 80 kcal mol^{-1}. As a result, the enthalpy of β-C_3N_4 formation was found to be 18.6 kJ (monomer unit $C_3N_4)^{-1}$ which is much less than the values used in Ref. 23. The results of calculation are shown in Fig. 2. These were used for elucidating the possibility of carbon nitride synthesis through detonation of explosives. It is known that the detonation may lead to the formation of diamond but not carbon nitride because the pressure of detonation products is considerably lower than the pressure of carbon nitride condensation. Possibly, it is this that was the reason that diamond rather than carbon nitride was formed under the shock-wave compression of a number of substrates.[26]

Yet another approach to the synthesis of carbon nitride has been analysed.[22] It is based on adiabatic explosion with subsequent isochoric cooling of the products formed. It was found that with isochoric cooling the system shifted first to the area of thermodynamic stability of diamond and then to that of carbon nitride. Thus, under the conditions considered carbon nitride should be formed through vaporisation of carbon from diamond and condensation of the vapour formed with nitrogen.

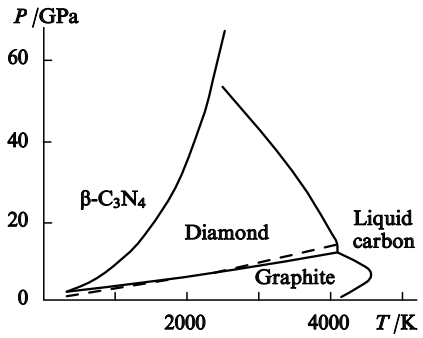


Figure 2. The line of β-C_3N_4 condensation in the carbon phase diagram according to Bundy.[143]
The dashed line shows the calculated graphite–diamond equilibrium.[144]

VII. Conclusion

The properties predicted theoretically for crystalline carbon nitride make this product highly attractive. In our view, the actual situation with carbon nitride is similar to that in which the phenomenon of high-temperature superconductivity was a few years ago and the problem of synthetic diamond several decades ago: there are no theoretical restrictions, but experimental efforts fail until a certain stage is reached. The major difficulties seem to be associated with insufficient knowledge of the optimum conditions of carbon nitride synthesis and with the possibility of occurrence of numerous competitive processes leading to the formation of various carbon phases and C–N compounds that are more stable thermodynamically than carbon nitride under given conditions. Nonetheless, the material discussed above enables one to feel optimistic about the synthesis of crystalline carbon nitride. In this review, we touched only briefly upon the possibility of synthesis of a carbon nitride with stoichiometry different from C_3N_4. However, such a possibility does exist and should be taken into account in relevant studies.

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