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Electronic density of states, 1*s* core-level shifts, and core ionization energies of graphite, diamond, C_3N_4 phases, and graphitic $C_{11}N_4$

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The full-potential linearized augmented plane wave method has been employed to determine electronic density of states, 1*s* core level shifts, and total 1*s* core ionization energies for the isoelectronic compounds graphite, diamond, C_3N_4, and graphitic $C_{11}N_4$. The C_3N_4 crystal structures studied are the graphitic, α, β, cubic, and pseudocubic configurations. All the C sp^3 bonded structures have band gaps 0.5–1.5 eV smaller than that of diamond. Only the C_3N_4 composition of the C sp^2 phases has a band gap. The core level shifts and ionization energies are compared with x-ray photoelectron energies. The 1*s* energies of C atoms connected to zero, one, two, and three N in $C_{11}N_4$ are close to experimental XPS shifts and peak positions. Nearly all the N 1*s* energies are within the experimental nitrogen XPS energy range. The C 1*s* ionization energies of the tetrahedral carbon C_3N_4 phases are between 288.6–289.5 eV, which is 4.0–4.9 eV higher than the C 1*s* value of pure graphite. β-C_3N_4 has the highest value. This compound has two N 1*s* ionization energies at approximately 400.0 and 400.6 eV. [S0163-1829(99)14239-5]

I. INTRODUCTION

Covalent bonded networks of carbon nitride materials are expected to possess some outstanding physical properties such as high bulk modulus, wide band gap and high thermal conductivity. The C_3N_4 composition has attracted special attention since its β phase, consisting of carbon atoms tetrahedrally surrounded by three coordinated nitrogen atoms, has been proposed by Cohen to have a bulk modulus comparable to that of diamond.[1] Subsequent theoretical works have predicted a high bulk modulus for β-C_3N_4 and that C_3N_4 could exist in different structural forms ranging from the hard and dense cubic and β phases to the soft and less dense graphitic phase.[2–5] The latter is assumed to be the most stable one.[5]

Various experimental efforts have been conducted to synthesize and characterize the β-C_3N_4 phase. By using vapor-phase deposition methods, CN_x films with different amounts of nitrogen have been grown (see, e.g., Refs. 6–13). The overall nitrogen concentration is usually lower than 50%. However, in some works the films are claimed to contain β-C_3N_4 microcrystals embedded in an amorphous matrix.[6–9] These results have been questioned since the characteristics of the electron diffraction pattern and the x-ray photoelectron spectra could be explained by carbon phases and by other carbon-nitrogen bonded systems than the β-C_3N_4 phase.[13]

The x-ray photoelectron spectroscopy (XPS) technique has been frequently used to characterize bonding configuration in CN_x films. In a recent work, which also includes a review of previous works, Ronning *et al.* show that 1 to 5 Lorentzian lines had to be used to obtain a proper fit with the C 1*s* core level spectra of different samples.[13] The energy range of the peak positions is 284.5–289.9 eV. The peak centered at the lowest energy was assigned to carbon atoms in a pure C environment, and it was present in all samples. The next two peaks were close to 285.6 and 286.6 eV. They were assigned to tetrahedral carbon atoms connected to one and two nitrogen atoms, respectively. The two high-energy peaks at approximately 288 and 290 eV were not discussed. Peaks at similar high energy positions are shown in. Refs. 10–12. The peak around 288 eV is assumed to arise from C sp^3 in a C_3N_4 environment,[6] whereas the peak at almost 290 eV is considered to belong to C–O species.

For the N 1*s* spectra, Ronning *et al.* used three Lorentzian lines to achieve a proper fit. The energy range of the core level peaks is 398.2–400.8 eV, and the positions of the peaks shift with up to 1.2 eV for different samples. When the deposition temperature was kept at 350°C, the three peaks were located at 400.8, 399.1, and 398.2 eV, respectively. The highest energy is interpreted as originating from a nitrogen atom with three neighbors in a predominant C sp^2 chemical environment. The peak at 398.2 eV is assumed to belong to two coordinated nitrogen atoms. An additional peak at approximately 403–404 eV was detected in Refs. 10–12. It has been assigned to a nitrogen-oxygen species.

In the above experimental XPS studies, an appreciable fraction of the C atoms are assumed to be sp^3 hybridized. XPS observations of surface chemical structures of polyethylene and polyimide treated in N_2 and NH_3 plasma produced similar energy ranges for the C 1*s* peak positions.[14] These CN_x structures are assumed to contain C sp^2 mainly. Thus it seems hard to confidently connect a chemical shift with a definite bonding configuration in compounds that consist of both sp^2 and sp^3 hybridized carbon atoms. Especially, since it is difficult to synthesize well-ordered structures of CN_x films and pure crystalline forms of C_3N_4. Hence, it becomes important to use theoretical methods and models to obtain further quantitative characterization and trends of the bonding configurations in CN_x structures.

The objective of the present study is to compare calculated electronic properties of C_3N_4 phases with those of graphite, diamond, and graphitic $C_{11}N_4$. The reasons for choosing graphitic $C_{11}N_4$ as one of the investigated compounds are twofold. First, it is isoelectronic with diamond and C_3N_4, and has been suggested as a potential hard material.[15] Second, the composition is close to the carbon-nitrogen ratio observed by e.g. Sjöstrom *et al.*[10] for buckled

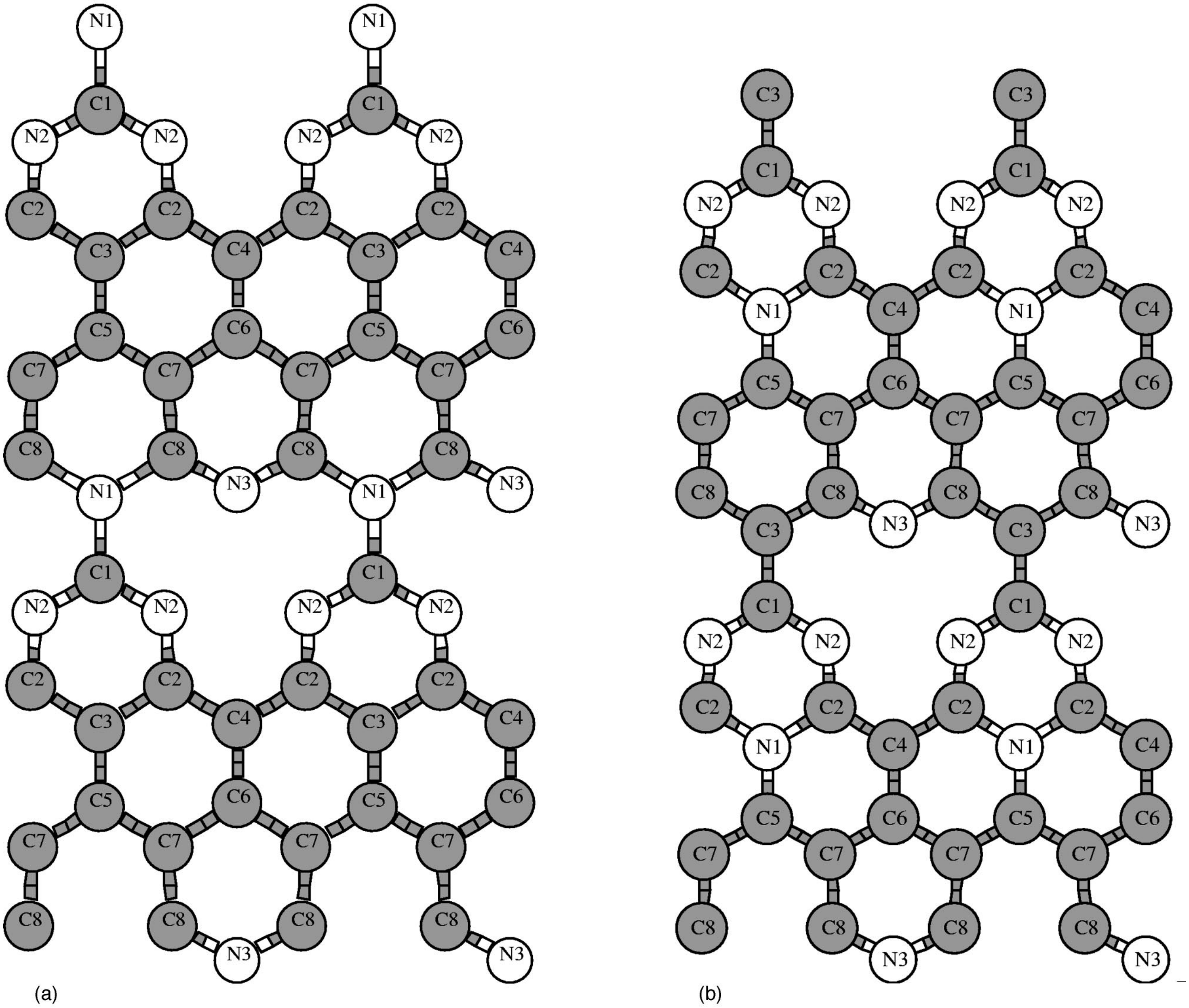

FIG. 1. One layer of graphitic $C_{11}N_4$ A (a), and of graphitic $C_{11}N_4$ B (b).

turbostratic CN_x microstructures formed at a high substrate temperature. Such carbon-nitrogen systems have been proven to be both hard and elastic. They may to a large extent consist of graphitic-like CN_x structures in which nitrogen atoms are two and three coordinated, and where carbon is linked to different numbers of N as in the graphitic $C_{11}N_4$ models in Fig. 1. The density of electronic states and 1*s* core level energies relative to the Fermi level are calculated for all the structures considered. In order to provide a straightforward comparison with experimental XPS energies 1*s* core ionization energies are estimated for graphite, diamond, graphitic C_3N_4, β-C_3N_4, cubic C_3N_4, and one of the $C_{11}N_4$ configurations. The latter energies are obtained from core-hole calculations including final state relaxation effects.

II. METHODS AND COMPUTATIONAL DETAILS

The calculations were carried out with the full-potential linearized augmented plane wave (FLAPW) program package WIEN97.[16] The electronic structures are determined within the density functional theory (DFT) with the local spin density approximation according to Perdew and Wang.[17] Both valence states and core states are calculated self-consistently in the FLAPW method.

The band structures and the relative energies between 1*s* core levels and Fermi levels (EF) were obtained from unit-cell calculations utilizing full symmetry. The maximum spherical harmonic *l* value of partial waves inside atomic spheres was put to 10. A local *s* orbital was used to improve the flexibility of the basis set. The number of *k* points was increased until differences between Fermi level and core level energies were less than 0.1 eV. The plane-wave cutoff parameter was adjusted so that approximately 100 augmented plane-waves/atom were used. Test calculations with up to 200 augmented plane-waves/atom were performed for some of the species with small unit cells. The energy differences between the 1*s* core level energies and the Fermi level were always less than 0.1 eV.

In order to calculate total core ionization energies comparable with experimental XPS values, a core-excitation procedure was used. Thus, the core-state occupation number of the excited atom was put to 1. The extra electron was placed in the valence band and a self-consistent energy was obtained. By keeping the compounds neutral core-hole interaction between adjacent cells is reduced and the systems are prevented from being over relaxed with respect to the core-hole potential. For graphite and diamond, both unit cell and super cell calculations were performed. The number of k points and the cutoff parameters were in accordance with the full symmetry unit-cell calculations. Local p functions were added at 1.5 Ry to improve the description of the core excited state. Final energies, to be compared with experimental XPS values, were obtained by taking the difference between the total energies of the ground state and the core excited state, and from this value subtract the difference in Fermi levels between the two states. These final energies are denoted as the Fermi level corrected values. It should be noted that introducing a core hole breaks the symmetry of the unit cell. This makes these kinds of calculations computationally demanding, and therefore some of the compounds are not addressed with this technique. However, the non-core-hole and the core-hole approaches complement each other, and together they bring qualitative information about the different bonding configurations in all the compounds.

The geometries of the C_3N_4 compounds were taken from the theoretical work of Teter *et al.*[5] For diamond and graphite experimental geometries were used. $C_{11}N_4$ was geometry optimized with in-plane lattice parameters equal to those of both graphite and graphitic C_3N_4. The out of plane lattice parameter was put to 3.40 Å and $\cdots AAA \cdots$ interlayer stacking was used. The differences in energies between the graphite and graphitic C_3N_4 like unit cells were negligible.

III. RESULTS AND DISCUSSION

A. Geometries

As previously mentioned, the equilibrium structures of the C_3N_4 compounds were taken from Teter *et al.* These structures were determined with a pseudopotential plane-wave approach. Using WIEN97 on the same geometries, some residual atomic forces were obtained for the graphitic, α- and β-C_3N_4 structures in Figs. 2–4. Optimizing the graphitic phase with the same lattice vectors as Teter *et al.* gave the geometries in Table I. It can be seen that the two methods give results that are in reasonable agreement with each other.

In order to evaluate the possibility of having nonplanar graphitic systems, test calculations were carried out in which the three coordinated N in C_3N_4 were shifted somewhat out of the atomic layer. These calculations always produced a considerable energy increase. Presumably, such movements perturb the electronic configuration of the planar six member rings. Thus the graphitic phases are assumed to be planar, or at least they should buckle in such a way that the electronic structures of the six member rings are disturbed as little as possible.

It proved to be rather time consuming to fully optimize the structure of $C_{11}N_4$, and therefore there are still some residual forces acting upon the atoms. Whether this is due to the size and shape of the unit cell, it is not clear. However, the geometries in Table I are not too far from those of pure graphite and graphitic C_3N_4 indicating that the systems, according to their unit cells, are close to their equilibrium positions. Additional changes of the bond lengths and angles are anticipated to be small, and such changes are judged to have a minor effect on the core ionization energies discussed below. The total energy of the A conformation in Fig. 1 is 0.30 eV/unit lower than B.

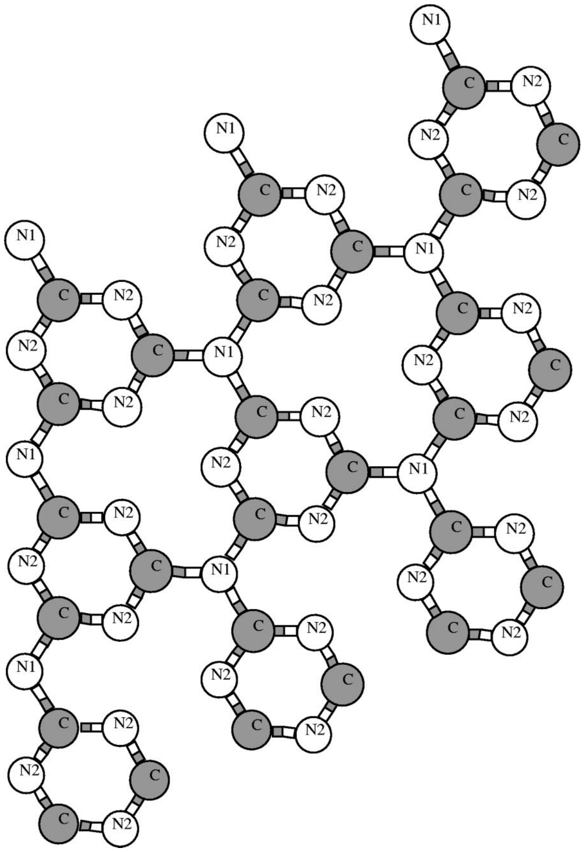

FIG. 2. One layer of graphitic C_3N_4.

B. Total electronic density of states

The total electronic density of states (DOS) of all the compounds is shown in Figs. 5 and 6. In Fig. 5 it can be seen that the only graphitic phase that displays a band gap is C_3N_4. For this compound the occupied states closest to the Fermi level belong to $2p$ states of the two coordinated N atoms [cf. Figs. (2) and 5(b)]. The empty bands closest to the Fermi level consist of C and two coordinated N states. The occupied $2p$ states of the three coordinated N atoms are predominately located below -2 eV.

$C_{11}N_4$, which is isoelectronic with graphite and C_3N_4, should have a zero density of states at the Fermi level. However, if the geometry is constrained to have the same structural parameters as graphite the system is metallic [cf. Fig. 5(c)]. When it is relaxed the DOS approach zero, although there are still some states crossing the Fermi level. These are C $2p$ states mostly. The DOS would most likely drop to zero if a complete geometry optimization is performed. As for graphitic C_3N_4 there are partial states of the two coordinated N just below the Fermi level, whereon they suddenly decrease to zero.

The DOS of the C sp^3 C_3N_4 phases in Fig. 6 exhibit band gaps which are approximately 0.5–1.5 eV smaller than that of diamond. The values are close to those previously obtained.[5] Since DFT usually produces too small band gaps

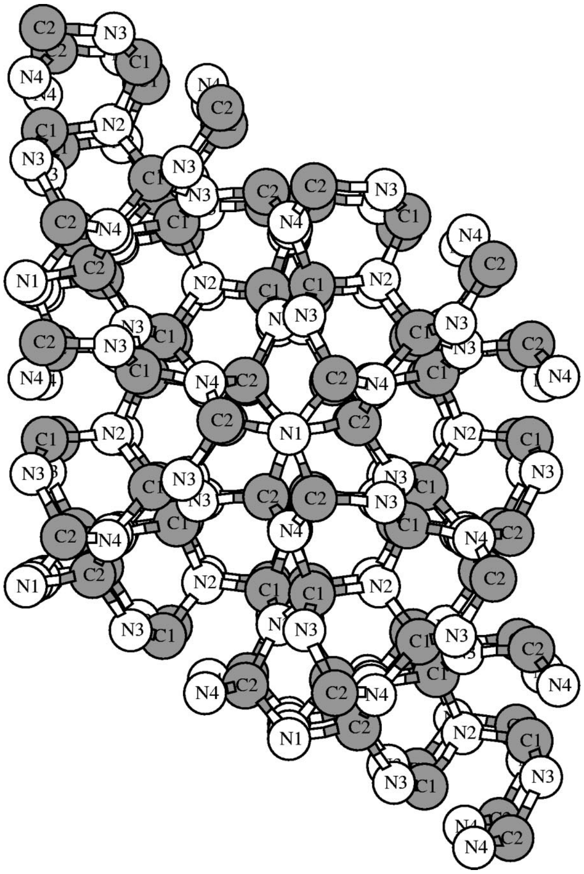

FIG. 3. α C_3N_4 in the 001 direction.

they are expected to be larger. As a comparison the calculated band gap for diamond is 4.4 eV which is 1 eV lower than experimental value.[18]

In α-C_3N_4 there are four different N atoms (cf. Fig. 3). They are all bonded in nonplanar configurations. However, the pyramidal conformation is most prominent for N2, presumably since the distance from N2 towards its nearest neighbor in the direction of the lone pair is 4.7 Å. This is long when compared with the other N-N distances, which are approximately 2.4 Å. As a consequence $N2$ has a sharp and high DOS peak located at -1 eV. The DOS closest to the Fermi level are N1 and N4 states.

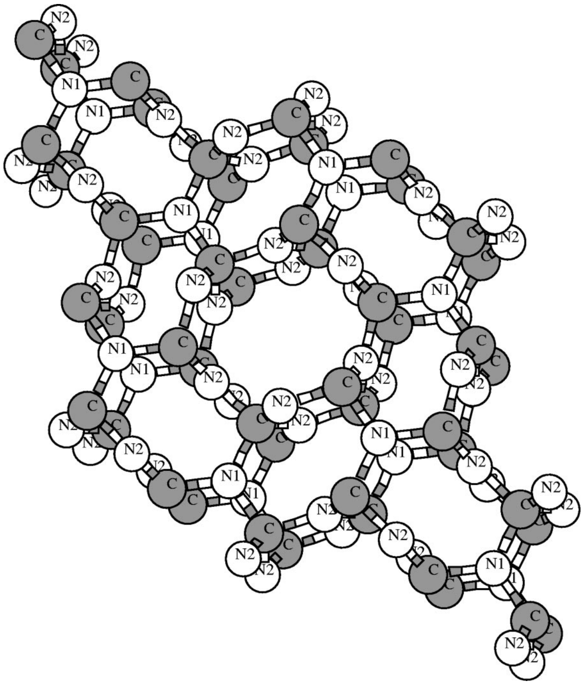

FIG. 4. β C_3N_4 in the 001 direction.

In β-C_3N_4 N1 is forced to have a completely planar position, whereas $N2$ is slightly pyramidal (cf. Fig. 4). The $N1$-$N1$ distance is only 2.40 Å, indicating a rather strong interaction between their lone pairs. This is also reflected by the DOS since the states closest to the Fermi level are $N1$ p states.

C. 1*s* core level energies relative to Fermi level

The energy differences between Fermi levels and core levels obtained from unit-cell calculations are shown in Table II. The discrepancy between values calculated with and without local p functions are generally within 0.2 eV. The exceptions are the nitrogen atoms of the graphitic phases for which the differences are larger. However, the relative chemical shifts between atoms in the same compound are stable. When comparing with experimental XPS data it is evident that the energies of the nitrogen atoms are too low with approximately 3–4 eV. The reason is of course the hole potential that is created in the x-ray photoemission process. Thus atoms with different nuclear charges cannot be compared directly with each other from Fermi-level and core-level energies only. Furthermore, it might be dangerous to apply this method to species with different constitutions, since polarization effects might be erroneously accounted for. It is therefore necessary to perform core-excitation calculations in order to estimate quantitative values. These are provided in the next section. In this section a qualitative analysis of the chemical shifts in Table II is presented.

Following the C 1*s* column in Table II downwards it can be seen that the energy increases by almost 3 eV when going from graphite to graphitic C_3N_4. For the C sp^3 C_3N_4 phases additional shifts of 1–1.8 eV are obtained. The highest values are for the α, β, and cubic systems. Their values are more than 4 eV above that of graphite. This is more than 1 eV higher than previously assumed for tetrahedral C in C_3N_4,[6] indicating a substantial polarization of charge towards the N atoms. The energy difference between the two C in α clearly indicate that these two atoms are nonequivalent.

As a consequence of the lower nitrogen content the C 1*s* values of $C_{11}N_4$ decrease when compared with the C_3N_4 phases. It is notable that for the C atoms bonded to two and three N similar shifts are estimated (cf. C1 and C8 in $C_{11}N_4$ A, and C1 and C2 in $C_{11}N_4$ B). There is a decrease of almost 1 eV when going to the C atoms connected to one N (C2 in A and C5 in B). The C atoms that are not linked to any N exhibit different values. Some are even negative demonstrating that these atoms have acquired some charge when compared with graphite. In order to find an explanation for the variations it could be stressed that the atomic configurations in Figs. 1(a) and 1(b) impose a graphiticlike C_3N_4 electronic structure upon the $C_{11}N_4$ systems. In $C_{11}N_4$ A, $C3$, $C4$, and $C7$ should therefore be in nitrogenlike positions, whereas $C1$, $C2$, $C5$, $C6$, and $C8$ should be in carbonlike positions.

TABLE I. FLAPW geometries in Ångstrom for graphitic C_3N_4 and $C_{11}N_4$. See Figs. 1 and 2. Values inside parantheses refer to those of Teter and Hemley.

C_3N_4		$C_{11}N_4$ A		$C_{11}N_4$ B	
N1-C	1.48 (1.45)	N1-C8	1.47	N1-C2	1.43
		N1-C1	1.51	N1-C5	1.40
N2-C	1.31 (1.32)	N3-C8	1.34	N3-C8	1.33
		N2-C1	1.31	N2-C1	1.32
		N2-C2	1.38	N2-C2	1.43
		C-C	1.41–1.42	C1-C3	1.48
				C2-C4	1.45
∠N2CN2	124°(124°)	∠N2C1N2	128°	∠N2C1N2	119°
		∠C8N3C8	122°	∠C8N3C8	125°
∠CN2C	116°(116°)	∠C2N2C1	117°	∠C2N2C1	123°
				∠C2N1C2	115°

This coordinates fairly well with the energies in Table II, since the former group has the lowest values and the latter group has the highest. The same assignments can be done in $C_{11}N_4$ B, and again the energies seem to follow this trend.

The aromatic nitrogen atoms, N2 and N3 in C_3N_4 and $C_{11}N_4$, and the three coordinated nitrogen, N1, in the same systems have the lowest and the highest N 1*s* values, respectively. The energy difference between these two nitrogen configurations vary from 2.4 eV in graphitic C_3N_4 to 3.3 eV in $C_{11}N_4$ B. The energy gaps are in accordance with an experimental value of 3.0 eV for systems containing similar nitrogen bonding configurations.[19] The wide energy difference in $C_{11}N_4$ B together with the geometries in Table I indicate that when N is located in a local carbon graphitic environment it strives to give away some charge in order to fit into the lattice. Some of the charge may have been accumulated on N3.

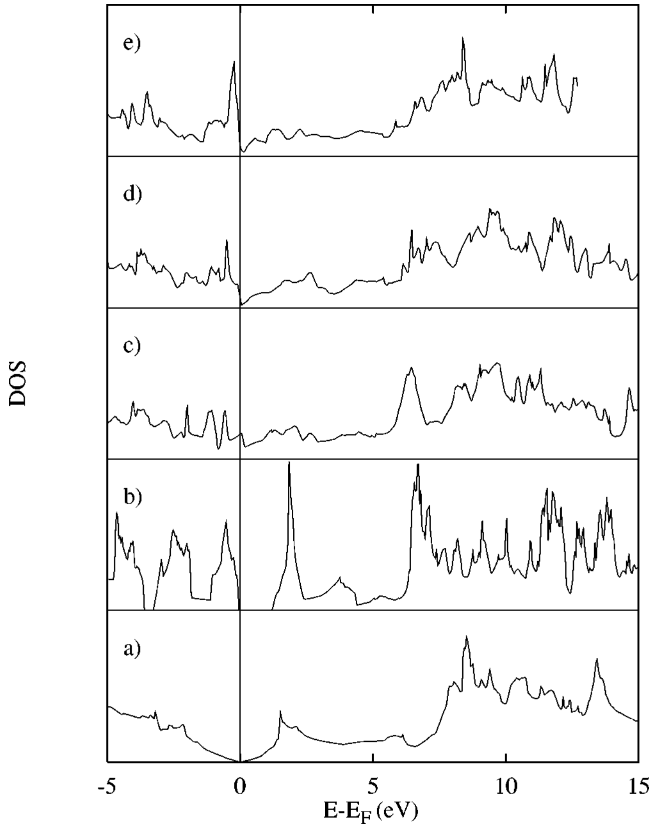

FIG. 5. Electronic density of states of graphite (a), graphitic C_3N_4 (b), unrelaxed $C_{11}N_4$ A (same in-plane lattice parameters as graphite) (c), geometry optimized $C_{11}N_4$ A (d), and geometry optimized $C_{11}N_4$ B (e).

The variations of the N 1*s* energies within the carbon sp^3 compounds are less then 1 eV, and the values are in between those of the graphitic systems. It can be noticed that the nonequal nitrogen atoms in α and β have different values. Thus they are all subjected to somewhat different bonding conditions. This has been previously established to be the

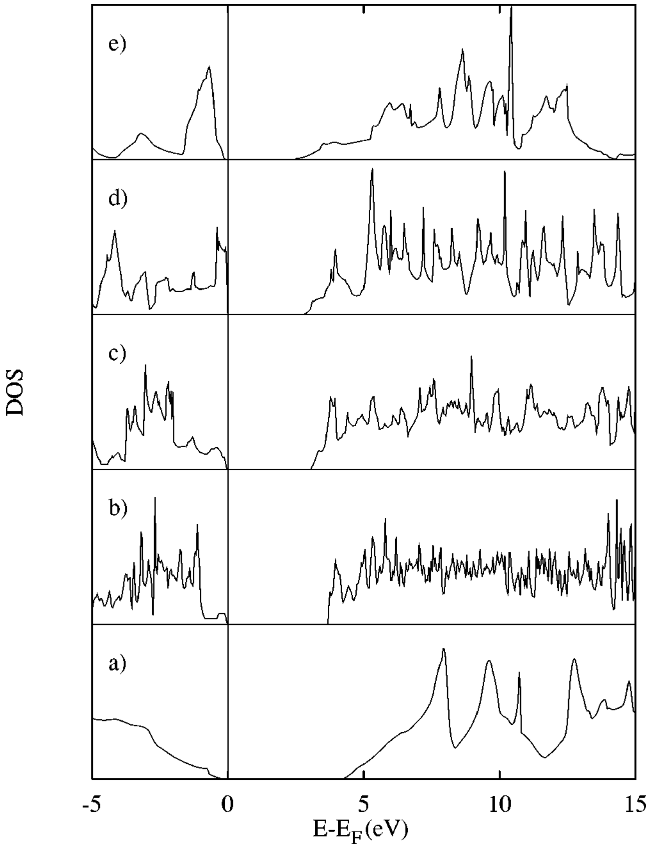

FIG. 6. Electronic density of states of diamond (a), α C_3N_4 (b), β C_3N_4 (c), cubic C_3N_4 (c), and pseudocubic C_3N_4 (e).

TABLE II. Differences in *EF*—1*s* core-state energy (eV) obtained from unit cell calculations. Graphite is used as reference. Values inside parantheses refer to calculations with local *p* orbitals.

Species	Atoms in unit cell	C 1*s* atom	C 1*s* energy	N 1*s* atom	N 1*s* energy
Graphite	4	C1	0.00 (0.00)		
		C2	−0.03(−0.06)		
Diamond	8	C	−0.18(0.00)		
Graph-C_3N_4 [a]	14	C^1	2.64 (2.44)	N1 [e]	112.80 (112.39)
		C^2	2.60 (2.42)	N1 [f]	112.85 (112.43)
				N2 [e]	110.52 (110.12)
				N2 [f]	110.48 (110.08)
α-C_3N_4 [b]	28	C1	3.71	N1	111.62
		C2	4.12	N2	110.80
				N3	111.50
				N4	111.47
β-C_3N_4 [c]	14	C	4.28 (4.28)	N1	111.05 (110.98)
				N2	111.71 (111.61)
cubic-C_3N_4	14	C	4.04 (4.06)	N	111.34 (111.29)
pscub-C_3N_4	7	C1	3.54	N	111.03
		C2	3.53		
$C_{11}N_4$ A [d]	15	C1	2.10 (1.85)	N1	113.00 (112.49)
		C2	1.11 (0.80)	N2	110.36 (109.86)
		C3	0.10(−0.10)	N3	110.68 (110.17)
		C4	0.20(−0.02)		
		C5	0.50 (0.27)		
		C6	0.57 (0.34)		
		C7	0.30 (0.07)		
		C8	2.20 (1.97)		
$C_{11}N_4$ B [d]	15	C1	2.05	N1	113.50
		C2	2.30	N2	110.38
		C3	−0.10	N3	110.20
		C4	0.45		
		C5	1.55		
		C6	0.72		
		C7	0.20		
		C8	0.85		

[a] See Fig. 2.
[b] See Fig. 3.
[c] See Fig. 4.
[d] See Fig. 1.
[e] Layer 1.
[f] Layer 2.

case for β-C_3N_4.[20] The lowest value is obtained for N2 in α, which is the most pyramidal nitrogen atom in its compound. The low value for the planar N1 in β is presumably an effect of the short distance between its lone pairs. In the cubic and pseudocubic compounds the nitrogen atoms in the latter are the most pyramidal ones. These atoms have also rather low values.

D. 1*s* core excitations and XPS energies

As can bee seen in Table III the Fermi level corrected values of graphite and diamond vary with the size of the unit cells. This is natural since interaction between and within unit cells caused by the corepotential and the extra valence electron depends on the size and the total number of valence electrons of the cells. As the cells increase in sizes the values will converge. However, it is not possible to obtain converged values. This is the reason why Fermi level corrected values have to be used. Of course the technique inherently includes some errors. The main ones can be listed as follows: (a) core-potential inter unit-cells interaction; (b) inter unit-cells interaction caused by the extra valence electron: and (c) intra unit-cell interaction between the extra electron and the other valence electrons. As mentioned above (a) is reduced by the presence of the extra valence electron, which keeps the compound neutral. The Fermi level correction reduces the effect of (b), and having the same number of valence electrons in all the unit cells investigated with the core-excitation procedure minimizes (c). The difference in energy

TABLE III. Total energies for core excitations, TE (eV), difference in Fermi level between ground state and core excited state, ΔEF (eV), and Fermi level corrected values, $TE—\Delta EF$. Values inside parentheses are relative to graphite.

	Atoms in	C 1s				N 1s		
Species	unit cell	TE	ΔEF	$TE-\Delta EF$		TE	ΔEF	$TE-\Delta EF$
Graphite (C1[a])	16	287.7	0.79	286.6 (0.00)				
Graphite (C1[a])	4	288.1	1.86	286.2(−0.40)				
Diamond	32	291.5	4.43	287.1 (0.50)				
Diamond	16	291.3	4.64	286.7 (0.10)				
Diamond	8	291.4	5.33	286.1(−0.50)				
Graph-C_3N_4[b]	14	290.3	0.79	289.5 (2.87)	N1	404.8	1.59	403.3 (116.6)
					N2	402.1	1.19	400.9 (114.2)
β-C_3N_4[c]	14	294.2	2.72	291.5 (4.85)	N1	405.5	3.47	402.0 (115.4)
					N2	405.6	3.05	402.6 (116.0)
cubic-C_3N_4	14	293.9	2.79	291.1 (4.42)		405.3	3.29	402.0 (115.4)
$C_{11}N_4$ A[d]	15							
C1		289.5	0.69	288.8 (2.13)	N1	403.6	0.80	402.8 (116.1)
C2		288.1	0.51	287.6 (0.92)	N2	401.1	0.71	400.4 (113.7)
C3		287.4	0.76	286.5(−0.10)	N3	401.7	0.82	400.9 (114.2)
C5		287.5	0.45	287.0 (0.39)				
C8		289.1	0.34	288.7 (2.11)				

[a] Unit cell coordinates 0,0,0 and 0,0,0.5.

[b] See Fig. 2.

[c] See Fig. 4.

[d] See Fig. 1.

when compared with experiment is expected to be almost the same for all the iso electronic unit cells.

The XPS measurements performed by Ronning *et al.* show that the energy difference between the C 1*s* core level in the pure carbon compound and the N 1*s* core levels in CN_x films should be in the range of 115.9–113.3 eV. The core-ionization Fermi level corrected N 1*s* values in Table III are in good agreement with this finding. It is notable that the super cell ionization energies of graphite and diamond are close to 287 eV. This is almost 2 eV higher than the experimental XPS value. Thus, it is suggested that all the Fermi level corrected values in Table III should be decreased by 2 eV when comparing with XPS energies.

The Fermi level corrected values for C in Table III show that the C shift of graphitic C_3N_4 is somewhat larger but close to that in Table II. The XPS value should be approximately 287.5 eV. Shifting the N1 value by 2 eV gives 401.3 eV, which is above the highest experimental value obtained by Ronning *et al.*

The C 1*s* shifts for β and cubic C_3N_4 are also above those in Table II. This suggests that the C 1*s* values for α- and pseudocubic C_3N_4 in Table II should be shifted to higher values, and that the XPS values for C sp^3 in C_3N_4 environments should be between 288.6–289.5 eV. This energy range is clearly higher than the XPS values estimated for graphitic C_3N_4. An explanation in accordance with the arguments in Refs. 21 and 22 is that the electronic charge density of C sp^3 is less confined to the C nucleus than in sp^2 hybridization and therefore prone to be more polarized towards the N atoms.

The relative difference between the core excited N 1*s* values of β and cubic C_3N_4 have not changed considerably when compared with the values in Table II, and XPS energies should be within 400.0–400.6 eV. Thus, the N 1*s* core ionization energies for all the C sp^3 C_3N_4 compounds are supposedly within the experimental range. However, when comparing with experimental results it seems difficult to correlate nitrogen energies in this range with C energies located at 288.6–289.5 eV, and therefore it is concluded that C_3N_4 phases are either absent or present in small amounts only. This is not surprising since the maximum overall N content in the films produced by Ronning *et al.* correspond to a stoichiometry of C_2N.

The values of $C_{11}N_4$ in Table III are in accordance with experimental data. The N1 energy, when shifted by 2 eV, is 400.8 eV. This is the same value as Ronning *et al.* assigned to nitrogen atoms in a similar configuration in CN_x films grown at a high substrate temperature. The low value of N2 correlate well with that suggested for two coordinated nitrogen atoms. The C values are all within the experimental range. However, as mentioned in the introduction the experimental assignments include tetrahedrally coordinated carbon atoms bonded to one and two nitrogen atoms. Such species are not investigated here. In any case the carbon atoms in graphitic $C_{11}N_4$ can be divided into three groups yielding energies close to the three experimental peaks. The peak at the lowest energy would then be interpreted as arising from carbon atoms without any nitrogen neighbors. The next peak would be due to carbon atoms connected to one N and the peak above 286 eV would belong to C linked to two and three N atoms. Experimentally there was a trend that when the nitrogen concentration increased the low energy C 1*s* peak shifted to somewhat lower values. This shift was assumed to originate from carbon atoms sp^2 bonded to C or N

TABLE IV. Approximate 1*s* core-level XPS energies (eV) suggested for graphite, diamond, and graphitic $C_{11}N_4$.

Compund	C 1*s*	N 1*s*
Graphite	C 284.6	
Diamond	C 284.7	
Graph-C_3N_4	C 287.5	N1 401.3
		N2 398.9
α-C_3N_4	C1 288.9	N1 400.5
	C2 289.3	N2 399.7
		N3 400.4
		N4 400.4
β-C_3N_4	C 289.5	N1 400.0
		N2 400.6
cubic-C_3N_4	C 289.1	N 400.0
pscub-C_3N_4	C 288.6	N 399.7
$C_{11}N_4$	C 286.7−286.8 [a]	N 400.8–401.3 [d]
	C 285.6−286.0 [b]	N 398.2–398.8 [e]
	C 284.4−285.0 [c]	

[a] Coordinated to two and three N.
[b] Coordinated to one N.
[c] Coordinated to C only.
[d] Three coordinated.
[e] Two coordinated.

atoms. The results in Table III support C-C bonding configurations only, and that C atoms with the lowest XPS energies are those which were previously assigned to be in N-like positions.

IV. CONCLUDING REMARKS

The energy shifts in Table II and the Fermi level corrected values in Table III together with a 2 eV correction suggest the XPS energies in Table IV. It is important to note that the correction term is adjusted in such a way that the 1*s* core-ionization energy of C atoms in a pure carbon environment is the same as in Ref. 13 (≈284.7 eV). In order to suit a different reference energy, all values in Table IV can be shifted appropriately.

From the C 1*s* values it is clear that tetrahedral carbon C_3N_4 phases should be distinguishable by high C 1*s* ionization energies. The C 1*s* values of $C_{11}N_4$ are all lower and close to the experimental XPS peak positions of carbon atoms in CN_x films with nitrogen concentrations less the 50%. However, tetrahedral C connected to one and two nitrogen atoms may have similar energies. Such species was not investigated, but attempts to address such bonding configurations will be conducted.

The N 1*s* ionization energies of α- and pseudocubic-C_3N_4 may serve as a measure of XPS energies of pyramidal nitrogen atoms in C sp^3 environments with low nitrogen concentration. The reason is that in these systems the distance between N atoms in the direction of the nitrogen lone pair is rather long.

The values of β-C_3N_4 show that this phase can be detected by C 1*s* ionization energies above 289 eV and two N 1*s* XPS peaks at approximately 400.0 and 400.6 eV, that correlate in intensity with the high C peak. No such correlation could be obtained in the experimental works referred to here.

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[1] M.L. Cohen, Phys. Rev. B **32**, 7988 (1985).
[2] A.Y. Liu and M.L. Cohen Science **245**, 841 (1994).
[3] A.Y. Liu and R.M. Wentzcovitch, Phys. Rev. B **50**, 10 362 (1994).
[4] Y. Guo and W.A. Goddard, Chem. Phys. Lett. **237**, 72 (1995).
[5] D.M. Teter and R.J. Hemley, Science **271**, 53 (1996).
[6] D. Marton K.J. Boyd, A.H. Al-Bayati, S.S. Todorov, and J.W. Rabalais, Phys. Rev. Lett. **73**, 118 (1994).
[7] R. Zhong-Min, D. Yang-Cheng, Y. Zhi-Feng, L. Fu-Ming, L. Jing, R. Yun-Zhu, and Z. Xiang-FU, Nucl. Instrum. Methods Phys. Res. B **117**, 249 (1996).
[8] 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).
[9] S. Kumar, K.S.A. Butcher, and T.L. Tansley, J. Vac. Sci. Technol. A **14**, 2687 (1996).
[10] H. Sjöström, L. Hultman, J.-E. Sundgren, S.V. Hainsworth, T.F. Page, and G.S.A.M. Theunissen, J. Vac. Sci. Technol. A **14**, 56 (1996).
[11] B.C. Holway, D.K. Shuh, M.A. Kelly, W. Tong, J.A. Carlisle, I. Jimenez, D.L.J. Sutherland, L.J. Terminello, P. Pianetta, and S. Hagstrom, Thin Solid Films **200**, 94 (1996).
[12] S. Lopez, H.M. Dunlop, M. Benmalek, G. Tourillon, M.-S. Wong, and W.D. Sproul, Surf. Interface Anal. **25**, 315 (1997).
[13] C. Ronning, H. Feldermann, R. Merk, H. Hofsäss, P. Reinke, and J.-U. Thiele, Phys. Rev. B **58**, 2207 (1998).
[14] J.E. Klemberg-Sapieha, O.M. Kuttel, L. Martinu, and M.R. Wertheimer, J. Vac. Sci. Technol. A **9**, 2975 (1991).
[15] D.A. Zhogolev, O.P. Bugaets, and I.A. Marushko, Zh. Strukt. Khim. **22**, 46 (1981).
[16] P. Blaha, K. Schwarz, and J. Luitz, WIEN97, Vienna University of Technology, 1997. [Improved and updated Unix version of the original copyrighted WIEN-code, which was published by P. Blaha, K. Schwarz, P. Sorantin, and S.B. Trickey, Comput. Phys. Commun. **59**, 399 (1990)].
[17] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[18] C. Kittel, *Introduction to Solid State Physics*, 6th ed. (John Wiley & Sons, Inc., New York, 1986).

[19] J.P. Boutique, J.J. Verbist, J.G. Fripiat, J. Delhalle, G. Pfister-Guillouzo, and G.J. Ashwell, J. Am. Chem. Soc. **106**, 4374 (1984).

[20] A. Reyes-Serrato, D.H. Galván, and I.L. Garzón, Phys. Rev. B **52**, 6293 (1995).

[21] J. C. Philips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).

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