
Electronic Structure of Ge₃N₄ Possible Structures

B. MOLINA, L. E. SANSORES

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70-360, México DF 04510, México*

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ABSTRACT: Experiments have shown that Ge₃N₄ is a promising material for application in photodiodes, amplifiers, optic fibers, protective coatings, etc., and several experimental studies have been carried out on this material, however, only one theoretical study has been reported in the literature about β -Ge₃N₄. In this work we present a systematic study of the structural properties and electronic structure of five possible structures of Ge₃N₄. The phases under study are the α , β , cubic, pseudocubic, and graphitic. The analysis shows that the hardest is the cubic with a bulk modulus $\mathbf{B} = 232.5$ GPa, while the α and β have the same bulk modulus ($\mathbf{B} = 219.8$ GPa). The pseudocubic and graphitic phases are the softest with $\mathbf{B} = 147.0$ and 61.7 GPa, respectively. The band structure shows that the α , β , cubic, and pseudocubic have an indirect band gap while the graphitic has a direct band gap. Total energy considerations indicate that the β phase is the most stable while the graphitic is the less stable one. Charge density analysis is also included. © 2000 John Wiley & Sons, Inc. *Int J Quantum Chem* 80: 249–257, 2000

Key words: semiconductors; hardness; germanium nitride; electronic structure

Introduction

During the last 70 years a great amount of research has been devoted to Si, Ge, and C due to their important technological applications; more recently the nitrides of these elements have attracted the attention of the research community, of them β -Si₃N₄ has been the most studied one because of its various applications in microelectronic, protective coatings, cutting tools, etc. To

date C₃N₄ is more a hypothetical material; its existence was predicted in an unpublished patent in 1984 by Chien-Ming Sung [1] on qualitative arguments and later by Liu and Cohen on the basis of first-principles pseudopotential total energy calculations [2]. Theoretical calculations show that there should be at least six metastable phases [3–5]. Several attempts have been made to synthesize experimentally [6–17] some of C₃N₄ phases, but they have not been successful and only nanocrystals, difficult to characterize, have been obtained.

Ge₃N₄ has been known since 1930, when the β phase was first synthesized [18, 19] exposing a powder sample of Ge to an ammonia atmosphere at high

Correspondence to: L. E. Sansores.
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temperatures ($\sim 700^\circ\text{C}$). This material was later on identified to have the phenacite hexagonal structure ($\beta\text{-Ge}_3\text{N}_4$) [20, 21] with the following lattice parameters [21]: $a = 8.032 \text{ \AA}$ and $c = 8.078 \text{ \AA}$. Much experimental work has been devoted to synthesize Ge_3N_4 by different techniques [22–33]. Most of the samples obtained are amorphous but both the β and α phases have been identified [26, 27, 29]. $\alpha\text{-Ge}_3\text{N}_4$ has the following lattice parameters: $a = 8.202 \text{ \AA}$ and $c = 5.941 \text{ \AA}$ [26] with a density of 5.254 g/cm^3 . There is also a rhombic structure attributed to Ge_3N_4 with the following lattice parameters: $a = 13.84 \text{ \AA}$, $b = 9.06 \text{ \AA}$, and $c = 8.18 \text{ \AA}$ [34]. $\beta\text{-Ge}_3\text{N}_4$ has a density of 5.287 g/cm^3 [21] and refractive index of 2.1 [23, 24]. It has been experimentally shown that Ge_3N_4 is a good candidate for applications in photodiodes, optic fibers, protective coatings, etc. [22–24, 29–33], and thus there is interest from a technological point of view.

From the theoretical side the only study of the electronic structure was done by Duan et al. [35] in 1997 on $\beta\text{-Ge}_3\text{N}_4$ using the LMTO-ASA method. They found that $\beta\text{-Ge}_3\text{N}_4$ has an indirect gap of 4.03 eV; the upper valence band edge is in the $\Gamma\text{-A}$ direction and the lower conduction band edge at the Γ point. They also show that there is a charge transfer from the Ge atoms to the N atoms. There have been some studies on amorphous GeN [36] and amorphous $\text{Ge}_{1-x}\text{N}_x\text{:H}$ [37]. In the first one, N is considered as an impurity in a Ge cluster, and in the second the effect of the N concentration versus the widening of the gap is studied.

In this work we start from the six structures that have been proposed as possible for C_3N_4 , and

after optimizing the structures we look into the electronic structure, charge density, and bulk modulus. Of the six structures only five are stable; one of the graphitic phases, when relaxed, converges to the pseudocubic, and thus reducing the problem to five possible phases. We also analyze the structure of each phase. The calculations were carried out using the CASTEP code developed at Cambridge University [38]. The program uses a density functional framework [39] within the local density approximation to exchange and correlation [40, 41], and norm-conserving, nonlocal, Kleinman–Bylander soft pseudopotentials [42] generated by the Kerker method [43]. The electronic wave functions are expanded in a plane wave basis set with periodic boundary conditions, and a plane wave energy cutoff of 850 eV was used for all structures. In all cases the Monkhorst–Pack method [44] was used to select the k points set. Parameters of the calculations are given in Table I. To calculate the bulk modulus, we used the Murnaghan equation [45].

Results

In Table I the lattice parameters, total energy per unit formula, cell volume, and density for the optimized fully relaxed structures at zero pressure are given. Figure 1 shows the variation of the total energy per unit formula as a function of the volume for the five stable structures. Our optimized structures have a higher density than those measured experimentally; for the β phase the experimental lattice parameters are bigger than those reported here, the same is true for the α phase; nevertheless,

TABLE I
Structural parameters and calculation details for the five phases under study.

	$\beta\text{-Ge}_3\text{N}_4$	$\alpha\text{-Ge}_3\text{N}_4$	c- Ge_3N_4	p- Ge_3N_4	g- Ge_3N_4
Space group	P6 ₃ /m	P3 ₁ c	I $\bar{4}$ 3d	P $\bar{4}$ 3m	P $\bar{6}$ m2
Lattice	Hexagonal	Trigonal	fcc	Cubic	Hexagonal
a (Å)	7.899	8.060	5.783	4.251	6.026
c (Å)	3.014	5.830	5.783	4.251	5.310
α (°)	90	90	109.47	90	90
γ (°)	120	120	109.47	90	120
Z	2	4	2	1	2
Num. atoms	14	28	14	7	14
FT grid	45 × 45 × 18	48 × 48 × 36	36 × 36 × 36	24 × 24 × 24	36 × 36 × 30
k points	4 × 4 × 4	4 × 4 × 4	4 × 4 × 4	4 × 4 × 4	4 × 4 × 4
ρ (g/cm ³)	5.583	5.545	6.109	5.919	5.446
V/Z (Å ³)	81.436	81.996	74.430	76.816	83.481
E_0/Z (eV)	−1415.4284	−1415.3836	−1415.0385	−1413.9813	−1409.8523

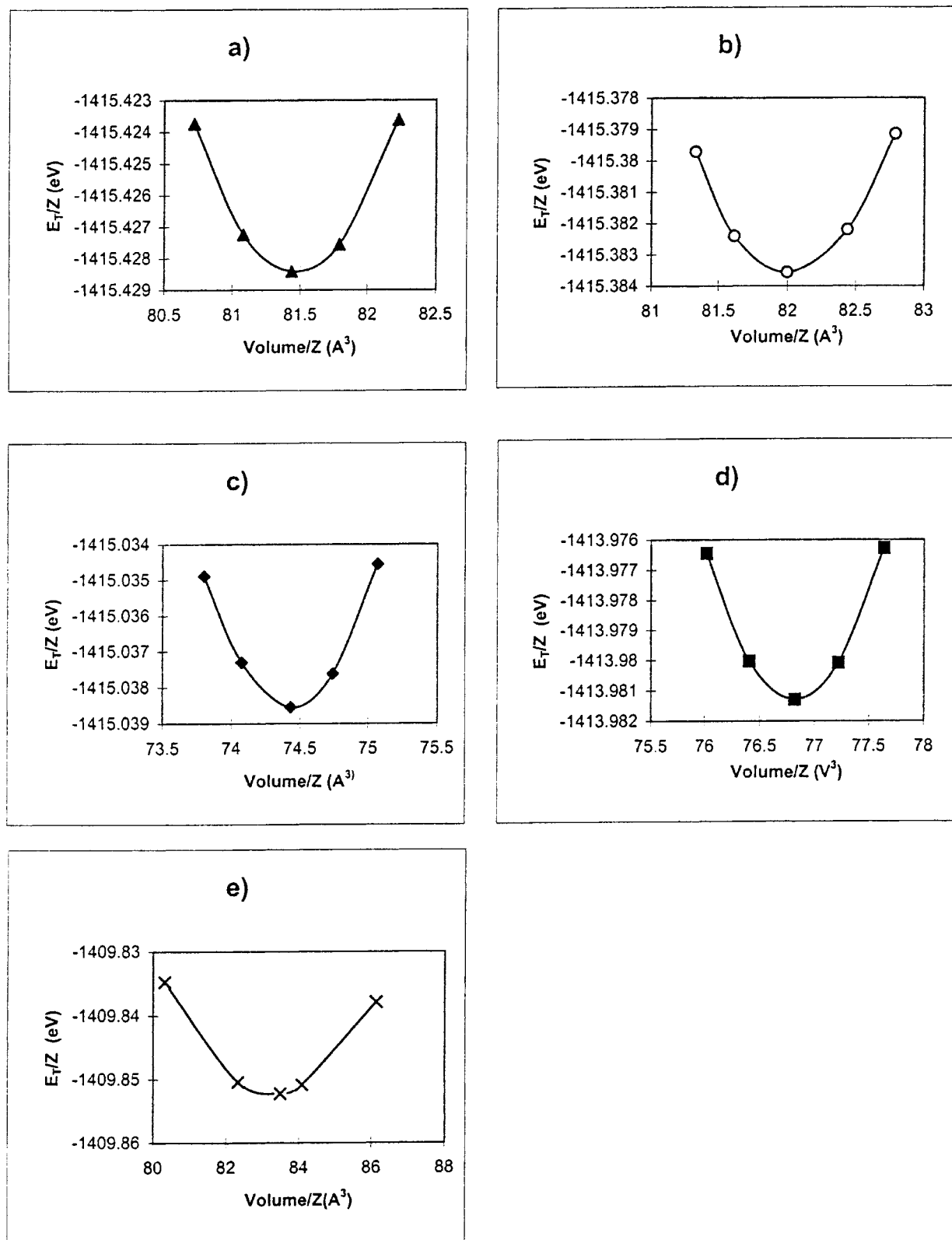


FIGURE 1. Total energy as a function of volume as hydrostatic pressure is applied for the five phases under study: (a) $\beta\text{-Ge}_3\text{N}_4$, (b) $\alpha\text{-Ge}_3\text{N}_4$, (c) cubic- Ge_3N_4 , (d) pseudocubic- Ge_3N_4 , and (e) graphitic- Ge_3N_4 .

the density of the β is bigger than that of the α , as reported experimentally. The phase with highest density is the cubic and that with lowest density is the graphitic. The behavior of the density is similar to that predicted for the C_3N_4 [5] except that in that case the α and β have the same density. From the total energies the β phase is the most stable, the α is only about 1 kcal/mol above; the other phases are much higher in energy. The cubic is about 9 kcal/mol, the pseudocubic is 33 kcal/mol, and the graphitic is 128 kcal/mol higher with respect to the β phase. This means that β and α phases that have been synthesized experimentally should be more easily obtain than the other ones. On the other hand the pseudocubic and the graphitic are so high in energy that they should be almost absent of any synthesis. Results for each of the phases studied follow.

β -Ge₃N₄ (P6₃/m) PHASE

The structural analysis of the optimized unit cell shows that there are two types of nitrogen atoms. The first one, denoted as N1, has all carbon nearest neighbors at the same distance (1.799 Å), all Ge–N1–Ge angles are 120°, and all bonds are in a plane (torsion angle Ge–Ge–Ge–N1 of 180°, Ge nearest neighbor to N). The other one, called N2, has two Ge nearest neighbors at a distance of 1.810 Å and one at 1.802 Å. There are two Ge–N2–Ge angles of 123.0° and one of 113.5°, and the torsion angle Ge–Ge–Ge–N2 is 3.9°. This difference in the N neighborhood give raise to different charge distribution. There is a higher charge density around N1 than around N2, as can be seen in Figure 2(a). Also from Figure 2(a) the bonding is mainly covalent with some degree of ionic character.

Figure 3(a) shows the band structure for this phase. The upper valence band edge is in the Γ -A direction and the lower conduction band edge is at Γ , it has an indirect band gap of 3.10 eV, while the band gap at the Γ point is 3.11 eV. Our results are in general agreement with those of Duan [35] although our gaps are smaller. This small difference between the indirect and direct band gaps must have important consequences in the optical absorption. The energy gaps and valence bandwidth are given in Table II.

α -Ge₃N₄ (P3₁c) PHASE

From the structural point of view this is the most complicated phase of those analyzed here. There

are four different types of N atoms. The first one, N1, has all three Ge nearest neighbors at 1.799 Å distance with Ge–N1–Ge angles of 120.0° and in almost flat configuration (torsion angle Ge–Ge–Ge–N1 of 0.6°). The second one, N2, has its three Ge nearest neighbors at different distances (1.806, 1.803, and 1.814 Å) with three different Ge–N2–Ge angles (120.1°, 113.7°, and 125.7°) and the nitrogen is slightly out of plane (Ge–Ge–Ge–N2 of 4.5°). N3 has three nearest neighbors Ge at the same distance 1.801 Å with bond angles Ge–N3–Ge of 116.5° and angle Ge–Ge–Ge–N3 of 21.2°. Finally, N4 has its three Ge nearest neighbors at distances of 1.790, 1.808, and 1.812 Å, with Ge–N4–Ge bond angles of 122.2°, 117.0°, and 98.2° and torsion angle 10.6°. This distribution in bond lengths and bond angles indicate a disordered structure and thus a higher dispersion is expected. Also the reduction in the density with respect to the β phase indicates that this structure is more stressed and thus has a higher total energy than the β phase.

Figure 2(b) shows the charge density contours around the N1 and N2 atoms. The different environments of the nitrogen atoms give rise to different charge distribution around them; N1 has the smallest charge density while N4 has the highest. The differences are small but have an effect on the degree of ionic character of the bond.

Figure 3(b) shows the band structure for this phase. The upper valence band edge is at K point, while the lower conduction band edge is at Γ , it is also an indirect band gap. The difference between the indirect band gap and the band gap at Γ (0.06 eV) is bigger than for the β phase, but it is small. As expected, the disorder in the structure gives raise to flatter bands than for the β phase.

CUBIC-Ge₃N₄ (I43d) PHASE

The structure optimization gives a much simpler cell than those of the two previous phases. The optimized parameters are given in Table I. In this case all nitrogen atoms have the same behavior. All Ge–N bonds have the same bond length, 1.810 Å, all bond angles Ge–N–Ge are 119.3° and the Ge–Ge–Ge–N torsion angle is 9.9°. This indicates that in this phase the nitrogen tend to an sp^3 hybridization and thus it has a higher density.

Figure 2(c) shows the charge density contours for the plane defined by one nitrogen and two nearest neighbor germanium atoms. Charge density around the N is smaller than for the β and α phases so the ionic character of the bond is decreased. In Fig-

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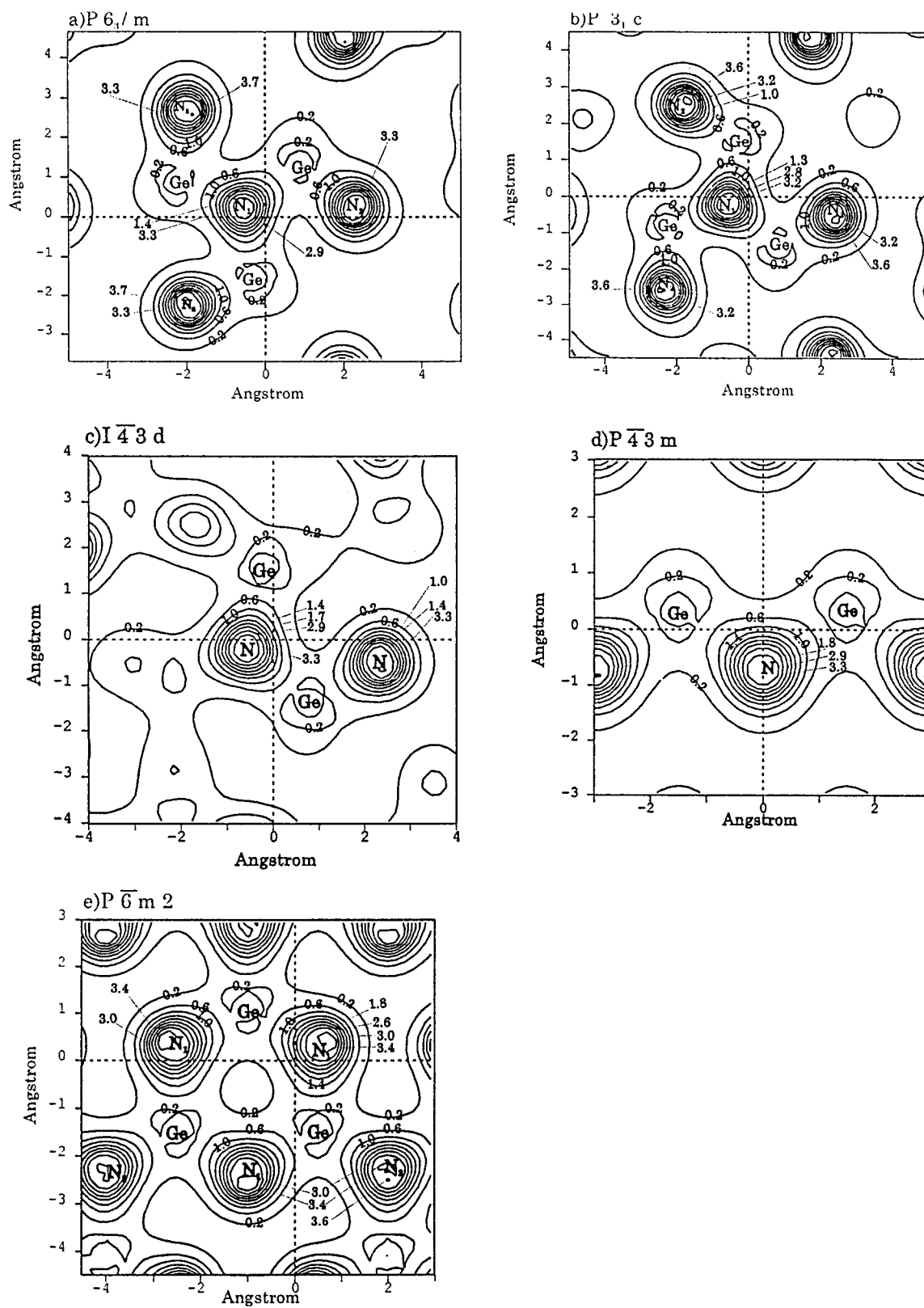


FIGURE 2. Charge density contours for the five phases under study: (a) β - Ge_3N_4 , (b) α - Ge_3N_4 , (c) cubic- Ge_3N_4 , (d) pseudocubic- Ge_3N_4 , and (e) graphitic- Ge_3N_4 .

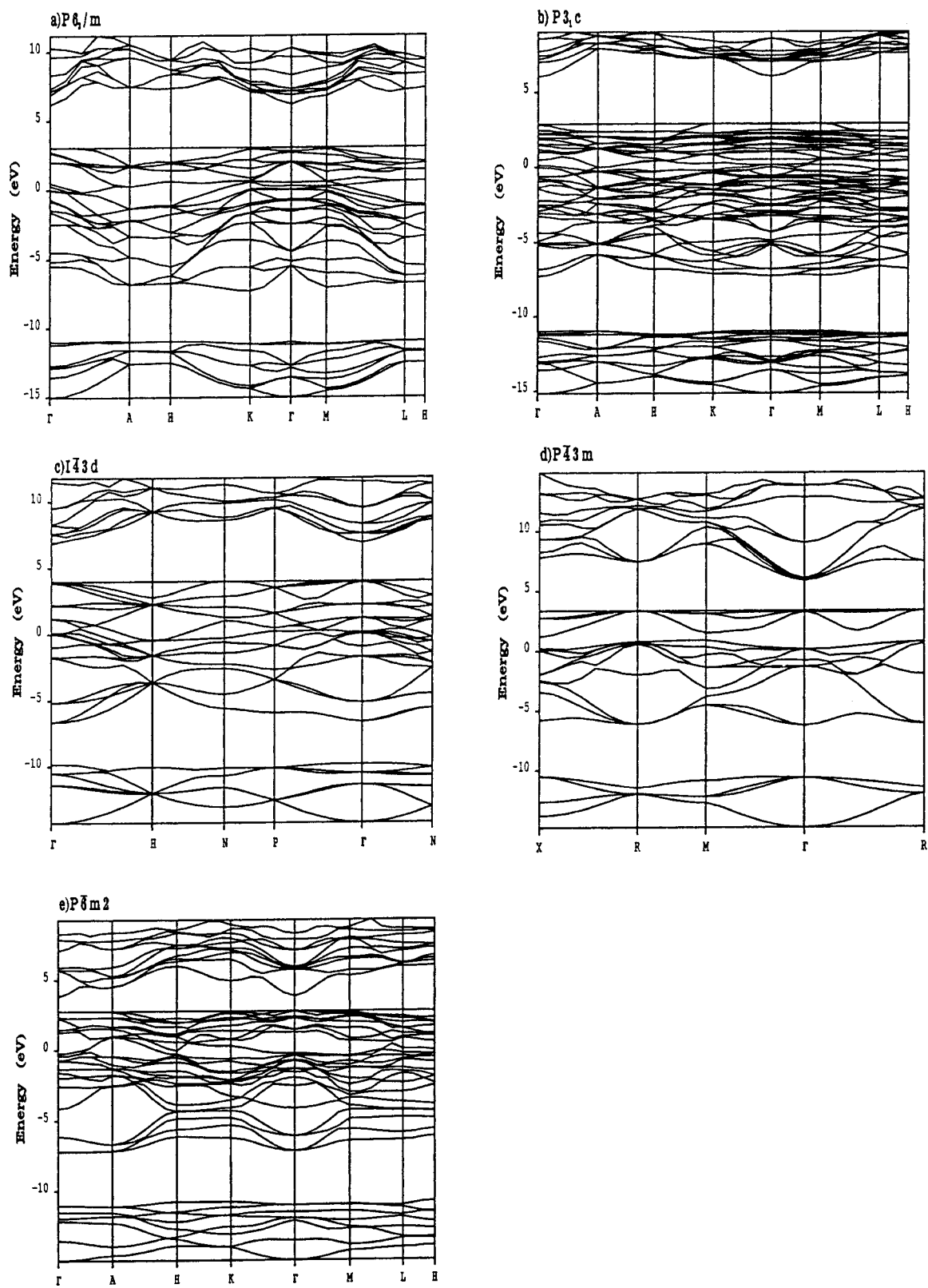


FIGURE 3. Band structure for the five phases under study: (a) β -Ge₃N₄, (b) α -Ge₃N₄, (c) cubic-Ge₃N₄, (d) pseudocubic-Ge₃N₄, and (e) graphitic-Ge₃N₄.

TABLE II
**Band gap (E_g), direct band gap at Γ point (E_Γ),
 valence bandwidth (ΔE_v), and bulk module (B) for
 the five phases under study.**

Phase		This work	Ref. [14]
β -Ge ₃ N ₄	E_g (eV)	3.10	4.03
	E_Γ (eV)	3.11	4.18
	ΔE_v (eV)	18.10	16.22
	B (GPa)	219.78	
α -Ge ₃ N ₄	E_g (eV)	3.18	
	E_Γ (eV)	3.24	
	ΔE_v (eV)	18.05	
	B (GPa)	219.78	
c-Ge ₃ N ₄	E_g (eV)	2.87	
	E_Γ (eV)	2.89	
	ΔE_v (eV)	18.25	
	B (GPa)	233.56	
ρ -Ge ₃ N ₄	E_g (eV)	2.50	
	E_Γ (eV)	2.61	
	ΔE_v (eV)	18.15	
	B (GPa)	147.06	
g-Ge ₃ N ₄	E_g (eV)	1.06	
	ΔE_v (eV)	17.75	
	B (GPa)	61.73	

ure 3(c) the band structure for this phase is shown. The band gap is again indirect, with the upper valence band edge at N and the lower conduction band edge at Γ . Also here the difference between the indirect band gap and the direct band gap at Γ is small, 0.02 eV.

PSEUDOCUBIC-Ge₃N₄ ($P\bar{4}3m$) PHASE

There is only one type of N in the optimized structure of this phase; all Ge–N bond lengths are 1.810 Å and all Ge–N–Ge bond angles are 110.8°; the torsion angle Ge–Ge–Ge–N is 33.3°. This means that also in this phase the N is in an sp^3 hybridization; it has a high density similar to the cubic phase.

The charge density contours presented in Figure 2(d) show that the charge density around the N and the Ge are very similar to those of the cubic phase, so both phases have the same degree of covalence bonding.

As seen in the band structure shown in Figure 3(d) this phase also has an indirect band gap with the upper valence band edge at R and the lower conduction band edge at Γ . The difference be-

tween the indirect and direct band gaps is bigger than for the other phases (0.11 eV).

GRAPHITIC Ge₃N₄ ($R3m$ AND $P\bar{6}m2$) PHASES

Two graphitic structures were studied, both with rhombohedral lattices but with different space group. Optimization of the structure with $R3m$ space group gave the same structure of the pseudocubic phase, and thus it is concluded that this graphitic structure cannot exist. The graphitic structure with space group $P\bar{6}m2$, shown in Figure 4, has a lamella structure. There are two planes of atoms, the difference is on the bond length and bond angles, the bonding arrangement is the same and the rings are flat in both. In this phase both Ge and N have an sp^2 hybridization that gives a total energy higher than for the other phases and a low density.

Figure 2(e) shows the charge density contours for the central sheet. It can be seen that the three coordinated nitrogen atoms have an sp^2 hybridization, while those connecting the rings have a high density toward the outside of the ring. These are dangling bonds due to their low coordination. The charge distribution on the base sheet is similar, although the charge around the nitrogen atoms is higher in this plane.

This phase has a direct band gap as shown in Figure 3(e), both the upper valence and the lower conduction band edges are at Γ . It has the smaller band gap of all the structures considered (see Table II), which is expected due to the lamella structure and the Ge sp^2 hybridization.

Bulk Modulus

The bulk modulus for each of the five phases was done using the Murnaghan equation [45] and the data of Figure 1; the results are shown in Table II. Cubic phase has the highest bulk module, while the graphitic has the lowest; the α and the β have the same value below that of the cubic but bigger than the pseudocubic. Since the energy considerations show that the α and the β are the more stable structures, it should be a fairly hard material.

Conclusions

We have calculated the electronic structure of five possible phases of Ge₃N₄ and shown that the most

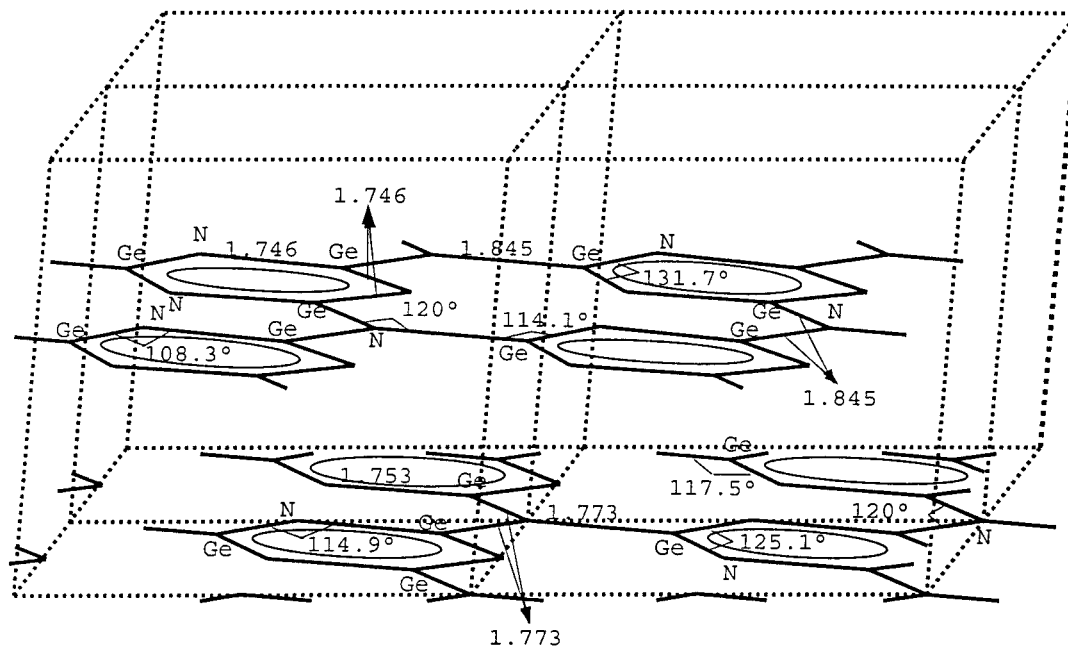


FIGURE 4. Structure of the graphitic- Ge_3N_4 phase. Bond lengths and angles are indicated.

stable is the β . The α phase is very near in energy, so it should also be considered as possible to be synthesized. Both phases have been observed experimentally. The cubic phase is not too high in energy, so it should also be a possibility. All of them, except for the graphitic, have an indirect band gap; the α has the biggest gap while the graphitic has the smallest one. The difference between the direct band gap at Γ and the indirect band gap is small. From the bulk modulus we can conclude that it is a hard material, the cubic phase being the hardest one. The α and β phases have the same hardness.

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