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# *Ab initio* Hartree-Fock study of structural and electronic properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds

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Structural and electronic properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds are studied using the *ab initio* Hartree-Fock method. The crystalline orbital program CRYSTAL-92 has been used to evaluate the equilibrium binding energy, lattice parameters, bulk modulus, band structure, density of states, and charge-density data of these materials. The calculated structural properties show good agreement with previous density functional calculations and with available experimental information. As expected, the Hartree-Fock cohesive energy is underestimated with respect to the values obtained with other methods that include electron correlation. On the other hand, the band energy gaps are overestimated. The calculated value of the bulk modulus for $\beta$-$C_3N_4$ of 4.50 Mbar is slightly smaller than the value of 4.66 Mbar obtained for diamond with the same method. The charge-density analysis shows a small amount of charge transference between carbon and nitrogen indicating the prevalence of a covalent bond in $\beta$-$C_3N_4$. A mixture of ionic and covalent behavior was found from the charge distribution of $\beta$-$Si_3N_4$. The charge-density maps and a Mulliken population analysis emphasize the existence of two nitrogen sites with different bonding properties, for the two compounds studied.

## I. INTRODUCTION

In 1989, Liu and Cohen[1] predicted the existence of a low compressibility material formed of carbon and nitrogen. An empirical model and a first-principles pseudopotential total-energy calculation, based in the local-density approximation (LDA) of the density-functional theory (DFT), were used to show that the bulk modulus of the hypothetical $\beta$-$C_3N_4$ solid can have a value comparable to that of diamond. The structural and electronic properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ were studied by the same authors[2] obtaining good agreement between calculated and experimental data for the former compound. This result gave support to the predicted properties of $\beta$-$C_3N_4$: an insulating material with a very large bulk modulus and nearly equal to that of diamond in which the velocity of sound was estimated to be about $1.1 \times 10^6$ cm/s, suggesting a high thermal conductivity. In addition, the cohesive energy was calculated to be moderately large indicating that this compound might be an energetically favorable phase.

These results motivated several experimental groups to attempt the synthesis of the hard C-N solid using a variety of methods. Amorphous carbon nitride films were synthesized and indentation tests found the N-rich films to be extremely hard.[3] Niu *et al.*,[4] using pulsed-laser ablation of graphite targets combined with intense atomic nitrogen sources, obtained small crystallites embedded in amorphous C-N films. Electron-diffraction data suggest that $\beta$-$C_3N_4$ is a viable structure for these crystallites. However, adequate samples for measurement of the bulk modulus have not yet been produced. In the past year, several deposition methods have been used to grow carbon nitride thin films,[5–7] in which the $\beta$-$C_3N_4$ phase has been detected together with other stoichiometric forms. More recently, a C-N hard material with oxygen traces on its surface was also synthesized in a low-density web structure.[8]

Theoretical studies of carbon nitride solids have been increased in the past year. A calculation of the electronic band structure of $\beta$-$C_3N_4$, in which an indirect band gap of 6.4 eV and a minimum direct gap at the $\Gamma$ point of 6.75 eV, has been reported.[9] In addition, an *ab initio* variable-shape molecular-dynamics study of $C_3N_4$ solid in three different crystalline structures was reported.[10] The $\beta$ and graphitic phases were found to lie very close in energy and are slightly more stable than the cubic phase. Recently, the optical properties of $\beta$-$C_3N_4$, and their pressure dependence, have been studied showing a linear increment of the band gap with pressure.[11]

In the present work, we report the results of an *ab initio* Hartree-Fock (HF) study of the $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds. HF method is commonly used in the study of the electronic structure of molecules. Standard programs have been developed and are widely used in this field of research.[12] In solid-state physics, most *ab initio*

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calculations are based on density-functional theory[13] in conjunction with plane-wave basis and pseudopotential schemes.[14] There are several reasons for this choice as was discussed by Orlando *et al.*[15] In spite of this situation, *ab initio* Hartree-Fock method has been developed and applied to study crystalline systems.[16] This approach has been implemented in a general computer program, called CRYSTAL,[17] systematically improved over the past fifteen years. Recently, a formulation of the HF method for crystals with possible extensions to treat *ab initio* dynamics simulations has been reported.[18]

This paper shows the results of a HF study of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ obtained with the CRYSTAL-92 program.[19] The aim of this calculation is to gain an additional insight of the electronic and structural properties, as well as of the bond formation mechanism of these hard materials, through the use of the all-electron HF method. A comparison of these results with previous pseudopotential DFT-LDA calculations,[2] despite the lack of correlation effects in the present study, will be useful to calibrate the performance of the HF approach. This information is necessary, for example, to interpret more complex HF calculations[20] in which other elements, like oxygen, can be intercalated in the carbon nitride solid as suggested by recent experimental results on C-N thin films.[21,22] In addition, useful information can be expected when core electrons are treated explicitly, even at the HF level, instead of using pseudopotentials. As a matter of fact, DFT-LDA pseudopotential calculations for materials containing first row elements, are particularly cumbersome and therefore computationally expensive.[23]

The organization of the paper is as follows: in Sec. II we present the computational details of the calculation. The results and discussion of the calculated structural and electronic properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ are presented in Sec. III. Finally, in Sec. IV, we give the conclusions of this work.

## II. COMPUTATIONAL DETAILS

We used the all-electron *ab initio* self-consistent-field (SCF) Hartree-Fock linear combination of atomic orbitals (HF-LCAO) computational scheme, implemented for crystalline systems in the CRYSTAL-92 program,[19] and described in previous papers.[16] CRYSTAL-92 is a general program designed to treat crystalline compounds of any space group. It has been applied to the study of semiconductors,[15] ionic crystals,[24] and other materials.[16] In general, the information obtained with this approach shows trends similar to those expected from molecular calculations. The lattice parameter and bulk modulus errors with respect to experimental data, obtained with an optimized basis set are typically about 1% and 10%, respectively.

The structure of the $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds used in the present calculation is illustrated in Fig. 1(a), which is a simple hexagonal phenocetelike structure formed by 14 atoms: 8 N and 6 Si or C. One half of the atoms in the cell are in the plane $z = c/4$ and the other half in the plane $z = -c/4$. The atom projection on the basal plane of the unit cell is shown in the Fig. 1(b). The hexagonal structure for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ [space group $P6_3/m(C^2_{6h})$] is shown in Fig. 2(a) whereas the first Brillouin zone of this cell is presented in Fig. 2(b). Initial values of the lattice parameters for $\beta$-$Si_3N_4$ were taken from Ref. 25. For $\beta$-$C_3N_4$, the initial structural data were obtained from the experimental values

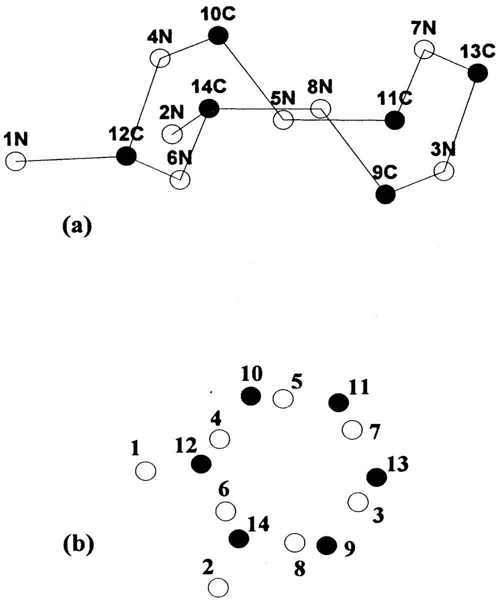

FIG. 1. (a) Unit cell of $\beta$-$C_3N_4$ and $\beta$-$Si_3N_4$ when C are substituted by Si atoms. (b) Atom projection on the basal plane of the unit cell. Open circles are N atoms and full circles are C or Si atoms.

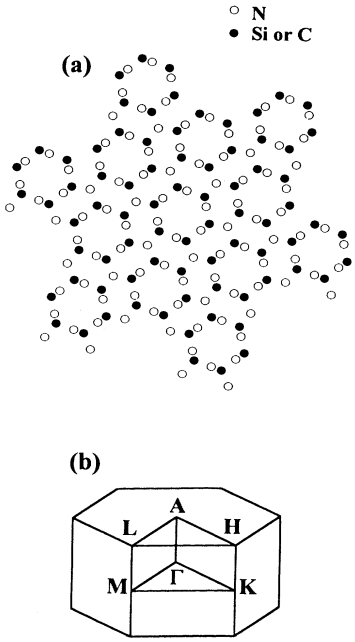

FIG. 2. (a) Hexagonal structure for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$. (b) Brillouin zone for the hexagonal lattice with the high symmetry points labeled.

given by Yu *et al.*[5] We used the 3-21G basis set shown in Tables 6.73.1, 7.74.1, and 14.19.1 for C, N, and Si atoms, respectively, given in Ref. 26. The last exponents in these basis sets were modified according to Table 4 of Ref. 15. The choice of the basis set was done after making a compromise between accuracy and computational resources available.

To test the computational procedure as well as the accuracy of the results, calculation of various physical properties of diamond in the cubic phase was done using the 3-21G basis set, with the last exponent modified according to Ref. 15. The results obtained for diamond will be discussed together with those of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$.

## III. RESULTS AND DISCUSSION

### A. Structural properties

Structural properties were determined from calculations of the ground-state total energy as a function of volume. A uniform compression and expansion of the lattice, with the relative atomic positions within the unit cell held constants, were used to make an isotropical variation of the cell volume. The calculated total energy for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ are displayed as a function of the cell volume in Figs. 3(a) and 3(b). Figure 4(a) shows the corresponding data for diamond. The total-energy values were used to fit the Murnaghan[27] equation of state. The fitted curve is also shown in Figs. 3 and 4(a). Table I shows the optimized parameter values of the total energy per cell and volume at equilibrium as well as the bulk modulus and its first derivative for the three materials studied.

The values obtained for diamond are in very good agreement with those obtained by Orlando *et al.*[15] using the same method and basis set. This comparison gives support to the values obtained for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ and establish a gauge to discuss the accuracy of the method. Cohesive energies can be obtained from the difference between the total energy of the solid cell at the equilibrium volume and the HF ground-state energy of the isolated atoms, calculated with the same basis set. The calculated structural properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ are summarized in Tables II and III, respectively.

For $\beta$-$Si_3N_4$, the calculated equilibrium lattice parameters are in excellent agreement with the experimental results[28] and the LDA values.[2,29] The calculated bulk modulus is overestimated by about 16% with respect to the measured value,[28] and 12% compared to the LDA result.[2] A better agreement can be expected when a larger basis set (6-21G) is used, as was discussed by Orlando *et al.*[15] in the study of other binary semiconductors containing silicon atoms.

The calculated equilibrium lattice parameters for $\beta$-$C_3N_4$ are in good agreement with a recent experimental measurement[5] and with previous LDA values.[2,10] For the bulk modulus, the HF value obtained is 4.50 Mbar which is about 3–5 % higher than the values calculated with the LDA approach.[2,10] Using the same method and basis set, we calculated the bulk modulus of diamond obtaining a value of 4.66 Mbar which is about 5% higher than the experimental result of 4.43 Mbar.[30] This comparison gives an additional support to the prediction that $\beta$-$C_3N_4$ has a hardness comparable to that of diamond, as was originally proposed by Liu and Cohen,[1,2] from a DFT-LDA study of this material.

In a recent work by Liu and Wentzcovitch,[10] a variable-shape molecular dynamics study of $C_3N_4$ was done to optimize the cell shape in the calculation of the structural properties of this material. They concluded that an optimization of the crystal shape does not lead to large changes in the predicted structural properties of $\beta$-$C_3N_4$. In particular, they observed a variation of about 2% in the $c/a$ and bulk modulus values with respect to a previous calculation,[2] in which an isotropic variation of the cell volume was used. A similar behavior was obtained in the present HF study when total-energy calculations were done for different values of the ratio $c/a$ to allow for anisotropic variations in the crystal cell of $\beta$-$C_3N_4$.

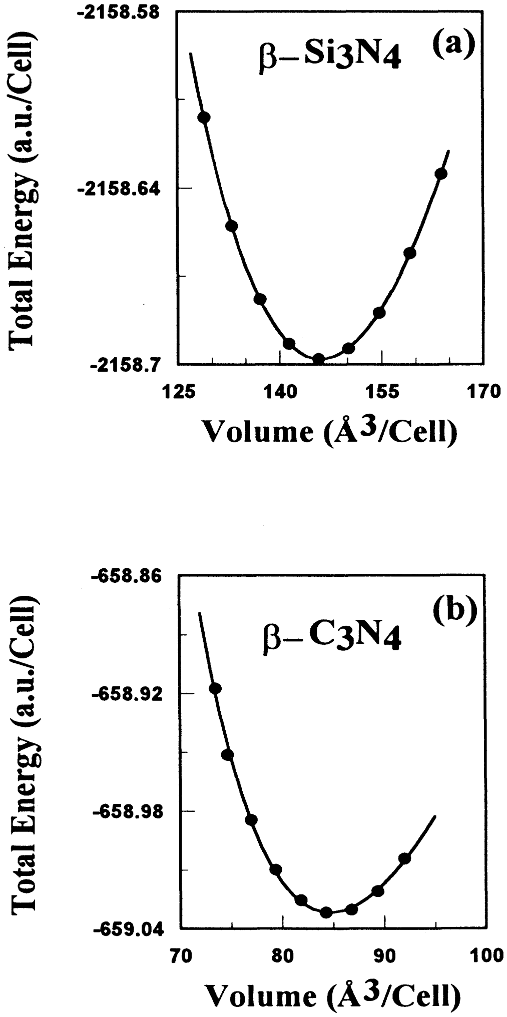

FIG. 3. Calculated total energy per cell vs volume for (a) $\beta$-$Si_3N_4$ and (b) $\beta$-$C_3N_4$. The full line was fitted to the Murnaghan equation of state (see text).

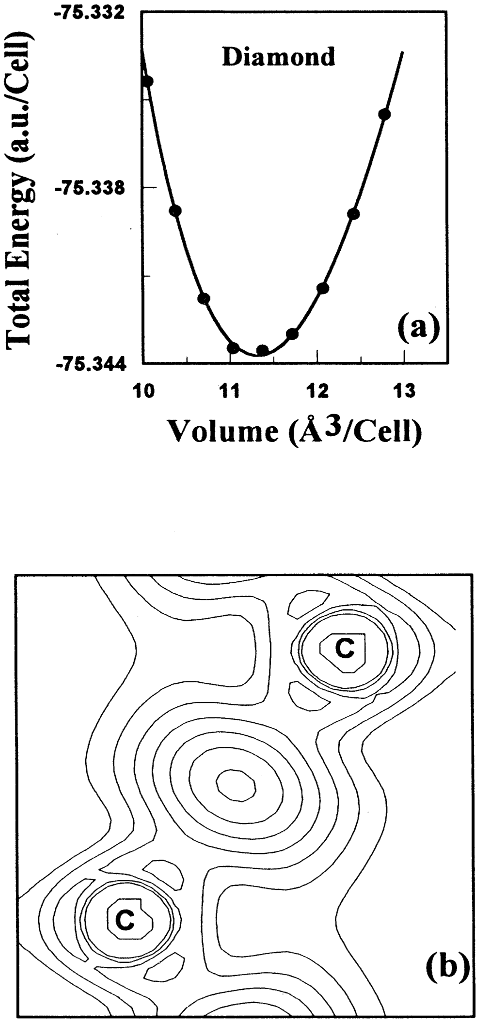

FIG. 4. (a) Calculated total energy per cell vs volume for diamond. The full line was fitted to the Murnaghan equation of state (see text). (b) Charge-density difference in a region of the plane (110) of diamond. Isodensity plots are taken in increments of 0.01 electron/bohr$^3$.

Changes of ±4% in the $a$ and $c$ values with respect to those obtained in the isotropic optimization, were used to generate cell shapes, to perform additional total-energy calculations. These data were used to make a fit of the Murnaghan[27] equation of state and obtain a set of optimized structural parameters. The comparison of these values with those obtained through the isotropic compression and expansion of the cell volume shows small differences (less than 2%), justifying such approximation, in agreement with the results from Liu and Wentzcovitch.[10] The cohesive energies calculated with the HF scheme for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ need to be corrected due to correlation effects before they are compared with experiments or other theoretical approaches. Several methods have been designed to implement such corrections in other materials,[31] and will be applied to the present systems in the future.

TABLE I. Total energy per cell ($E_0$), equilibrium volume ($V_0$), bulk modulus ($B$), and bulk modulus derivative ($B'$) obtained from the fit of the calculated data, for $\beta$-$Si_3N_4$, $\beta$-$C_3N_4$, and diamond.

| | $E_0$ (a.u./cell) | $V_0$ (Å$^3$) | $B$ (Mbar) | $B'$ |
|---|---|---|---|---|
| $\beta$-$Si_3N_4$ | -2158.6982 | 146.03 | 2.97 | 3.36 |
| $\beta$-$C_3N_4$ | -659.0317 | 84.67 | 4.50 | 6.71 |
| Diamond | -75.3437 | 11.32 | 4.66 | 4.47 |

TABLE II. Lattice parameters and volume at equilibrium, bulk modulus, and cohesive energy for the $\beta$-$Si_3N_4$.

| Parameter | Ref. 2 | Ref. 29 | Experiment | This work |
|---|---|---|---|---|
| $a$ (Å) | 7.61 | 7.586 | 7.606[a] | 7.61 |
| $c$ (Å) | | 2.902 | 2.909[a] | 2.91 |
| $V$ (Å$^3$) | | 144.62 | 145.9[b] | 146.03 |
| $B$ (Mbar) | 2.65 | 2.82 | 2.56[b] | 2.97 |
| $E_{coh}$ (a.u./cell) | 2.73 | 2.75 | 3.05[c] | 1.8 |

[a] Reference 25.
[b] Reference 28.
[c] Reference 32.

### B. Electronic properties

To analyze the bonding properties of the $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds, the charge-density difference between the studied systems and the corresponding atomic superposition arrays were calculated. For the isolated atoms the standard atomic 3-21G modified basis set[26,15] has been adopted. Figure 4(b) shows the charge-density difference over a region of the plane (110) of diamond, in which the charge-density steps are taken in increments of 0.01 electron/bohr$^3$. The high concentration of charge midway along the C-C bond confirms the covalent nature of the bonding in diamond. This well-known result[15] is shown here for comparison with the bonding properties of the materials under study.

Figures 5(a) and 5(b) show the charge-density difference of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$, respectively. These plots lie on the plane formed by 4 N and 3 C or Si atoms located at $z = c/4$ in the unit cell. In both plots, the contour step size is of 0.01 electron/bohr$^3$. The Si-N bond shown

TABLE III. Lattice parameters and volume at equilibrium, bulk modulus, and cohesive energy for the $\beta$-$C_3N_4$.

| Parameter | Ref. 10 | Ref. 2 | Experiment[a] | This work |
|---|---|---|---|---|
| $a$ (Å) | 6.41 | 6.44 | 6.3 | 6.37 |
| $c$ (Å) | 2.40 | 2.46 | 2.38 | 2.40 |
| $V$ (Å$^3$) | 85.53 | 88.35 | 81.80 | 84.67 |
| $B$ (Mbar) | 4.37 | 4.27 | | 4.50 |
| $E_{coh}$ (a.u./cell) | 3.5 | 2.99 | | 1.32 |

[a] Reference 5.

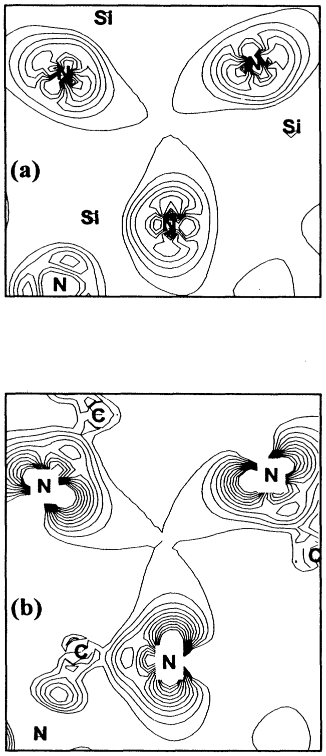

FIG. 5. Charge-density difference in a region of the basal plane formed by (a) 4 N and 3 Si, for the $\beta$-$Si_3N_4$, and (b) 4 N and 3 C, for the $\beta$-$C_3N_4$. Isodensity plots are taken in increments of 0.01 electron/bohr$^3$.

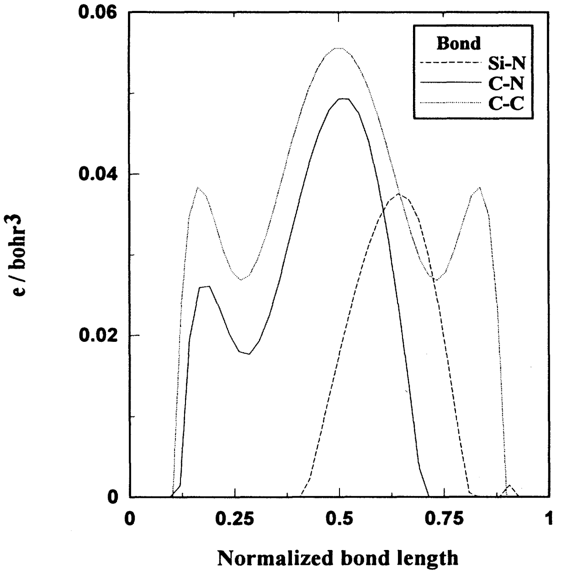

FIG. 6. Charge-density difference along a Si-C, C-N, and C-C bond in $\beta$-$Si_3N_4$, $\beta$-$C_3N_4$, and diamond vs normalized bond length.

TABLE IV. Electronic population in each atom of the cell for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$. Atoms 1 and 2 are located outside the ring of 12 atoms [Fig. 1(b)] for both compounds.

| Atoms | Charge ($e$) | Population per shell ($e$) | | | |
|---|---|---|---|---|---|
| | | $K$ | $L$ | $M$ | $N$ |
| | | $\beta$-$Si_3N_4$ | | | |
| 1–2 N | 8.594 | 1.989 | 2.085 | 4.520 | |
| 3–8 N | 8.577 | 1.989 | 2.069 | 4.519 | |
| 9–14 Si | 11.892 | 1.998 | 7.823 | 1.935 | 0.136 |
| | | $\beta$-$C_3N_4$ | | | |
| 1–2 N | 7.764 | 1.991 | 2.220 | 3.552 | |
| 3–8 N | 7.850 | 1.991 | 2.212 | 3.648 | |
| 9–14 C | 4.895 | 1.990 | 1.871 | 1.034 | |

in Fig. 5(a) is characterized by an asymmetric distribution of electronic charge towards the N atom suggesting a mixture of covalent and ionic behavior. A different picture is found for the C-N bond in Fig. 5(b). The charge density for $\beta$-$C_3N_4$ is showing a covalent bond with a slightly higher concentration towards the N sites.

To explore the degree of charge transference in these materials, the charge-density difference along the C-C, Si-N, and C-N bonds in diamond, $\beta$-$Si_3N_4$, and $\beta$-$C_3N_4$ was calculated and plotted in Fig. 6. Since the different bond lengths have been normalized to the same value, only a qualitative analysis of the shape of these curves is possible. The C-C bond in diamond exhibits a symmetric distribution with respect to the middle point. The central

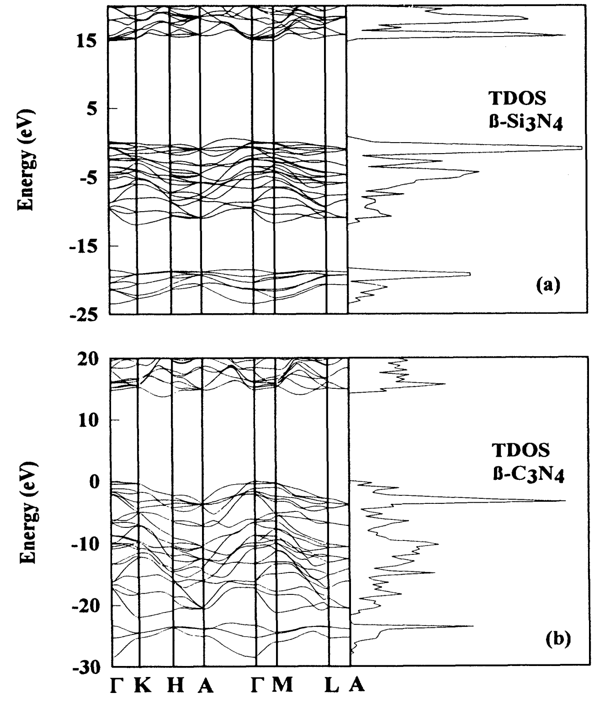

FIG. 7. Band structure calculated along the symmetry lines of the first Brillouin zone shown in Fig. 2(b) for (a) $\beta$-$Si_3N_4$ and (b) $\beta$-$C_3N_4$. The total density of states at the right of each figure is shown.

TABLE V. Band-structure analysis for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$. Valence band (VB) are split in two parts by a gap.

| | $\beta$-$Si_3N_4$ | | $\beta$-$C_3N_4$ | |
|---|---|---|---|---|
| | Ref. 2 (eV) | This work (eV) | Ref. 9 (eV) | This work (eV) |
| Direct gap | | 15.32 | 6.75 | 14.84 |
| Indirect gap | 4.2 | 14.67 | 6.4 | 13.75 |
| VB upper | 10.1 | 12.84 | | 21.88 |
| VB gap | 3.9 | 6.77 | | 0.98 |
| VB lower | 4.2 | 5.10 | | 5.63 |
| VB full | 18.2 | 24.71 | 24.5 | 28.49 |

maximum indicates a pure covalent system whereas the two symmetric local maxima closer to the nucleii come from core states. In $\beta$-$C_3N_4$, the charge-density along the C-N bond also shows a central maximum characteristic of a covalent bond. In addition, a lower maximum close to the C site reflects the core electron effects in the bonding and practically no additional charge in the N atom site. In contrast, the strong peak towards the N atom along the Si-N bond observed in $\beta$-$Si_3N_4$, suggest that some ionic behavior is present in the bond.

A Mulliken population analysis is useful to gain some insight into the bonding properties, for example, to study the degree of charge transference in these compounds. Table IV shows the Mulliken population data for $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$. From such numbers, it is found that the N atoms in $\beta$-$Si_3N_4$, that are outside the ring which is part of the unit cell [atoms 1–2 in Fig. 1(b)], have more charge than those forming the ring [atoms 3–8 in Fig. 1(b)]. An opposite behavior is observed in $\beta$-$C_3N_4$, where the N atoms forming the ring are more charged than those that are outside of it. These results emphasize the existence of two N sites with different bonding properties in these compounds. In addition, it is found that each Si atom transfer more than two electrons to the N atoms in $\beta$-$Si_3N_4$, whereas each C atom transfer more than one electron to the N atoms in the bonding formation of $\beta$-$C_3N_4$. This analysis is consistent with the charge-density distributions discussed above. It must be stressed, however, that the Mulliken population data are sensible to the basis set used, and should be taken in a qualitative sense.[15]

The band structure and the total density of states (TDOS) of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ crystals are presented in Figs. 7(a) and 7(b), respectively. The calculations were done along the symmetry lines of the first Brillouin zone shown in Fig. 2(b). The valence band of $\beta$-$Si_3N_4$ is divided in two parts by a gap of 6.77 eV. The upper and lower portions have bandwidths of 12.84 eV and 5.10 eV, respectively, giving a full width of 24.71 eV. The direct band gap is of 15.32 eV whereas the indirect one is of 14.67 eV. In $\beta$-$C_3N_4$, the valence band has a small gap of 0.98 eV separating the upper band of 21.88 eV of width from the lower one with a width of 5.63 eV. The total valence-band width is of 28.49 eV. The direct and indirect band gaps are of 14.84 eV and 13.75 eV, respectively.

Table V summarizes the HF results for the band-structure calculations. In general, the topology of the present HF band structure agree with the LDA calculations of Liu and Cohen[2] and Yao and Ching.[11] However, it is known that the HF band gaps and HF band widths are systematically overestimated by a factor of 2 or more with respect to experimental values, as was observed by Orlando *et al.*[15] in the HF calculation of the band struc-

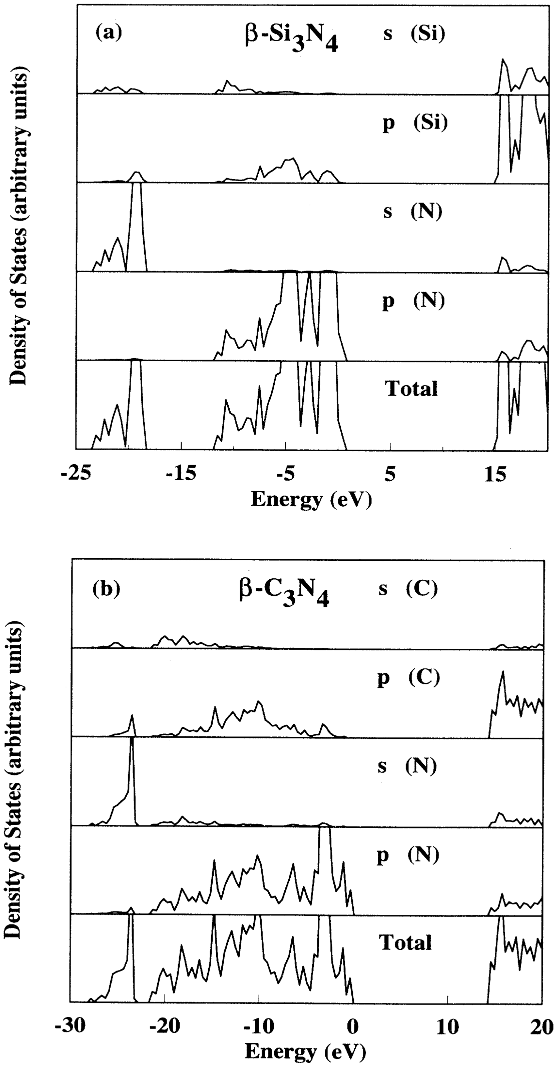

FIG. 8. Projected and total density of states. (a) $\beta$-$Si_3N_4$. (b) $\beta$-$C_3N_4$.

ture of various semiconductors. In fact, the band gap values shown in Table V are about two times larger than the DFT-LDA results obtained by Corkill and Cohen[9] and Yao and Ching[11] after they include self-energy corrections. The results from the present HF calculations are consistent with the trend observed by Orlando *et al.*,[15] for the band structure of other semiconductor materials.

The total density of states was also included in Figs. 7(a) and 7(b) to point out the contribution of each band to the different peaks of the TDOS. The partial components of the TDOS in $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ are shown in Figs. 8(a) and 8(b), respectively. The overall difference between the TDOS's of these compounds is given by the presence of smaller dispersion and larger gaps, typical features of ionic behavior, in $\beta$-$Si_3N_4$ compared with $\beta$-$C_3N_4$. The projected density of states of $\beta$-$Si_3N_4$ shows that the upper part of the valence band is formed of *p* orbitals coming mostly from N plus a small fraction due to Si. At lower energies, the N *p* orbitals mix with the *s* and *p* states of Si to contribute to the bottom the band. The lowest-lying part of the valence band is composed of *s* orbitals coming from Si and N atoms whereas the conduction band of this compound is dominated by Si states with *s* and *p* character. The analysis of the partial components of the TDOS in $\beta$-$C_3N_4$ reveals that the states which lie between the valence-band maximum and about $-5.0$ eV correspond to *p* orbitals of N with a small participation of *p* states from C. Below this portion of the TDOS there is a region with bands involving *p* orbitals, and some *s* states at lower energies, coming from N and C atoms. The lowest-lying bands consist mainly of *s* orbitals corresponding to N and C atoms plus a small contribution of *p* states from N and C. The conduction band for this case is mainly formed by carbon *p* orbitals. This description of the partial components of the TDOS is in good agreement with the analysis previously done from LDA calculations.[2,11]

## IV. CONCLUSIONS

The structural and electronic properties of $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ compounds were calculated from an all-electron *ab initio* Hartree-Fock study. A good agreement with previous LDA (Refs. 2, 10, and 11) results has been found for the equilibrium lattice parameters, bulk modulus and topology of the band structure. Calculated cohesive energies, band gaps, and bandwidths suffer from the lack of electron correlation effects, intrinsic of the HF method. The bulk modulus result gives additional support to the prediction that $\beta$-$C_3N_4$ is a material with a hardness comparable to that of diamond.[1,2] Our study of the electronic properties offer additional information regarding the bonding properties of these materials. A covalent bond in $\beta$-$C_3N_4$ and a mixture of covalent and ionic character in the bonding of $\beta$-$Si_3N_4$ were found from the analysis of the charge-density distribution and the projected density of states of these compounds. In addition, the presence of two N sites with different bonding properties is confirmed from a Mulliken population analysis.

The present study on $\beta$-$Si_3N_4$ and $\beta$-$C_3N_4$ has shown that the accuracy of the HF method is sufficient to give quantitative information on their structural and electronic properties. The relative low computational cost of these calculations open more opportunities in the study of real materials from first-principles methods.

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