

Structural properties and electronic structure of low-compressibility materials: β - Si_3N_4 and hypothetical β - C_3N_4

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We present a first-principles pseudopotential study of the structural and electronic properties of β - Si_3N_4 and the hypothetical compound β - C_3N_4 . β - C_3N_4 , which is C_3N_4 in the β - Si_3N_4 structure, with C substituted for Si, is used as a prototype for investigating the properties of possible covalent C—N solids. The calculated lattice constant, bulk modulus, and electronic band structure of β - Si_3N_4 are in good agreement with experimental results. This gives support for the predicted properties of β - C_3N_4 . The bulk modulus of β - C_3N_4 is found to be comparable to diamond, and its moderately large cohesive energy suggests that the prototype structure may be metastable. Although the crystal structure and the valencies of the constituent atoms are similar in β - Si_3N_4 and β - C_3N_4 , the electronic bonding properties in these two solids are found to differ. The large core size and repulsive p pseudopotential of the second-row element, Si, results in a more ionic Si—N bond compared with a covalent C—N bond.

I. INTRODUCTION

There is considerable interest in the use of silicon nitride (Si_3N_4) as a high-performance engineering material.^{1,2} Because of its strength and hardness, high decomposition temperature, and good resistance to corrosion and wear, Si_3N_4 is finding application as a high-temperature structural material for use in engine components and cutting tools. Since it has a low mass density, it can be made into lightweight, low-inertia components which have excellent strength-to-weight ratios compared to those composed of metals which have traditionally been used in these applications.

Although the useful structural, thermal, and chemical properties of Si_3N_4 are sensitive to impurities, grain size, porosity, and other effects related to sample processing, in an ideal crystal these properties depend ultimately on electronic structure and microscopic bonding characteristics. Despite the possible usefulness of detailed studies of the electronic structure of this material, the number of studies to date has been limited. This is due at least in part to the complexity of the Si_3N_4 crystal structures. Hence previous studies have concentrated on empirical or semiempirical tight-binding schemes,^{3,4} mostly based on idealized structural models. The only realistic first-principles calculation for crystalline Si_3N_4 that we are aware of employs the orthogonalized linear combination of atomic orbitals (OLCAO) approach.⁵ Although the results of the OLCAO calculation are in general agreement with experiment, some discrepancies exist, and this provides some of the motivation to study this system using a different calculational approach.

Further motivation to study Si_3N_4 comes from the recent suggestion that the hypothetical compound C_3N_4 could have improved structural properties compared to

Si_3N_4 .⁶ A comparative study of the structural and bonding properties of Si_3N_4 and C_3N_4 is therefore of interest. The original study of C_3N_4 was motivated by an empirical model⁷ for the bulk modulus of tetrahedral solids which indicates that short bond lengths and low ionicity are favorable for achieving large bulk moduli. Since the C—N bond satisfies these conditions, tetrahedral C—N solids were suggested as candidates for new low compressibility solids. The most obvious candidate structure to be used as a prototype for a first-principles investigation of the properties of a covalent solid formed between C and N is the simple zinc-blende structure. However, this was ruled out⁶ because in a hypothetical zinc-blende C—N compound the first antibonding band would be occupied and hence it is doubtful that such a structure would be stable. Instead, a more complex structure, based on the known β - Si_3N_4 structure with C substituted for Si, was considered. Although the β - Si_3N_4 structure lacks complete tetrahedral bonding, it is expected to obey the trends contained in the empirical model. This was verified by the results of the first-principles calculation which were consistent with the empirical model and showed that materials like the prototype can have bulk moduli comparable to that of diamond, which has the largest known bulk modulus.

In this work, we use the first-principles pseudopotential total-energy approach within a localized-orbital formalism to calculate the ground-state structural and electronic properties of β - Si_3N_4 and β - C_3N_4 , which is C_3N_4 in the β - Si_3N_4 structure. As in the original study of β - C_3N_4 , the β - Si_3N_4 structure is considered a prototype. The calculated properties of β - C_3N_4 are expected to be representative of other possible partially tetrahedral C—N solids. In addition to the technological interest in β - Si_3N_4 and β - C_3N_4 or similar materials, the bonding and electronic

structure of these systems are also of interest. Despite the similarities in valency of the constituent elements and the crystal structures, the small core size and the lack of p states in the core of the first-row elements lead to interesting differences between the C—N and Si—N bonds.

The remainder of this paper is organized as follows. In Sec. II we briefly describe the method of calculation. This is followed by a presentation of the calculated structural properties of β -Si₃N₄ and β -C₃N₄ in Sec. III. In Sec. IV, we present and discuss the electronic and bonding properties of β -Si₃N₄ and β -C₃N₄. When possible, comparisons to previous theoretical and experimental results are made. In addition, comparisons are made to the bonding properties in some diamond and zinc-blende structure solids such as diamond and SiC. Concluding remarks are given in Sec. V.

II. CALCULATION

The calculations are based on the pseudopotential total-energy approach.⁸ The local-density approximation (LDA), with the Wigner interpolation formula⁹ for the exchange and correlation functional, is used. The nonlocal pseudopotentials are generated¹⁰ using the same approach as in previous studies of the electronic and structural properties of diamond,¹¹ Si,¹² and BN.¹³ Because there are no p states in the core of C and N, the $2p$ pseudopotentials of these atoms are strongly attractive. Hence a localized-orbital formalism¹⁴ is employed. The electronic wave functions are expanded in linear combinations of Bloch sums of Gaussian orbitals of the form

$$f_{\alpha,l,m}(\mathbf{r}) = e^{-\alpha r^2} r^l Y_{lm}(\theta, \phi). \quad (1)$$

Orbitals of s , p , and d character are used for Si, while only s and p states are included in the basis for C and N. In past studies of diamond¹¹ and BN,¹³ it was found that for C and N, a basis of s and p states gives a good representation of the valence-band states which determine the structural properties. Three, four, and five even tempered Gaussian decay constants, α , are used for C, Si, and N, respectively.

The charge density and crystal potential are iterated to self-consistency with an energy cutoff of 64 Ry. Brillouin-zone averages are sampled using three special \mathbf{k} points¹⁵ in the hexagonal Brillouin zone. Increasing the number to six special \mathbf{k} points results in differences of less than 5 meV in the energy eigenvalues and only slight changes in the calculated structural properties. A further increase in the number of \mathbf{k} points was not possible because of computer limitations.

III. STRUCTURE AND STRUCTURAL PROPERTIES

Silicon nitride exists in two crystalline structures, α and β , as well as in an amorphous form.¹ In all forms, the local order is such that Si atoms occupy slightly distorted tetrahedral sites while N atoms sit in nearly planar triply coordinated sites. The β structure, containing two formula units (14 atoms) per unit cell, is the simpler of the two crystalline structures and is the one considered in this work. Belonging to the hexagonal space group C_{6h}^2 ,

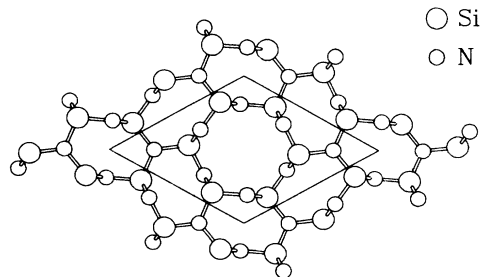


FIG. 1. Structure of β -Si₃N₄ in the a - b plane. The c axis is normal to the page. Half the atoms illustrated are located in the $z = -c/4$ plane and the other half are in the $z = c/4$ plane. The structure consists of these buckled plane stacked in $AAA \dots$ sequence. The parallelogram indicates the unit cell.

the structure of β -Si₃N₄ consists of buckled layers like the one shown in Fig. 1 stacked in $AAA \dots$ sequence.¹⁶ The local geometric configurations suggest sp^3 and sp^2 hybrid orbitals on the Si and N atoms, respectively. The structure can alternatively be thought of as a complex network of SiN₄ tetrahedra which are linked at the corners.

Structural properties are determined from calculations of the ground-state energy as a function of volume. In principle, at each volume, the total energy should be minimized with respect to all the independent structural parameters. For the β -Si₃N₄ structure this process would allow for distortions and tilting of the SiN₄ tetrahedra as the volume is changed. However, because of the complexity of the β -Si₃N₄ structure, a full relaxation of the structure is not practical. Instead, the present calculation considers only uniform compression and expansion of the lattice, with the atomic positions within the unit cell held constant.

The calculated total crystal energies for β -Si₃N₄ and β -C₃N₄ are plotted as a function of volume in Figs. 2 and

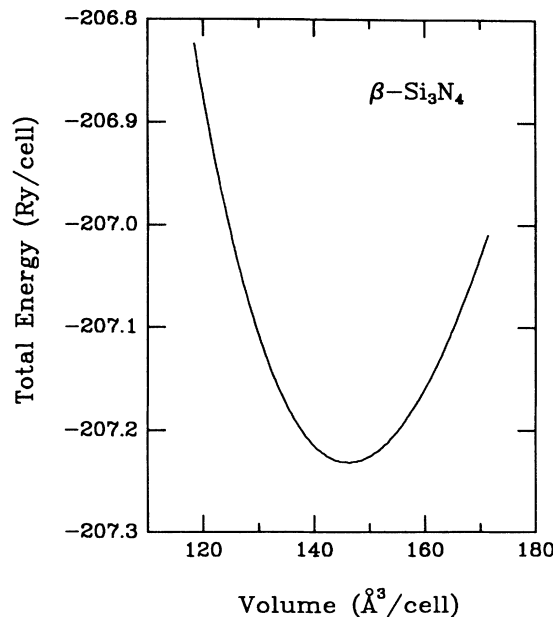


FIG. 2. Calculated total energy as a function of unit cell volume in β -Si₃N₄. The experimental equilibrium volume is 145.9 \AA^3 .

3. By fitting the calculated total energies to the Murnaghan¹⁷ and Birch¹⁸ equations of state, the equilibrium lattice constant and bulk modulus are found. The variation in these properties obtained from fits using different samplings of points along the volume axis and from fits to equations of state with different functional forms is used to estimate the uncertainties in the results. For both β -Si₃N₄ and β -C₃N₄, the numerical uncertainties in the lattice constant and bulk modulus are estimated to be ± 0.01 Å and ± 0.15 Mbar, respectively. Cohesive energies are obtained by taking the difference between the ground-state energies of the isolated spin-polarized atoms and the total energy of the solid at its equilibrium volume. Estimates of the zero point energy of the solids have not been included in the cohesive energies.

The calculated structural properties are summarized in Table I. For β -Si₃N₄, the calculated equilibrium lattice constant is in excellent agreement with the measured value.¹⁶ In addition, the calculated bulk modulus differs from the experimental value¹⁹ by less than 4%, which is within the calculational and experimental uncertainties. This good agreement for the bulk modulus indicates that, to a good approximation, the β -Si₃N₄ lattice undergoes uniform compression with the application of hydrostatic pressure. This is in contrast to the behavior of another partially tetrahedral solid, α -SiO₂, in which pressure leads to a tilting and distortion of the SiO₄ tetrahedral units.¹⁹ Since, in general, less energy is required to change bond angles than to change bond lengths, the difference in behavior of β -Si₃N₄ and α -SiO₄ is consistent with the significantly lower compressibility of β -Si₃N₄.

The good agreement of the calculated structural properties of β -Si₃N₄ with experiment gives support to the predicted properties of β -C₃N₄. Since the β -Si₃N₄ structure is used as a prototype structure for investigating the properties of a covalent solid formed between C and N, there is no reason *a priori* to expect it to be a stable structure in the C—N system. Nevertheless, the cohesive energy of β -C₃N₄ is found to be moderately large, suggesting that it may be a metastable structural phase. As reported earlier,⁶ the bulk modulus β -C₃N₄ is calculated to be 4.27 Mbars, which is comparable to the measured value of 4.43 Mbars in diamond. For comparison, the bulk modulus of diamond calculated with the same scheme and the same basis for the C wave function used in this work is 4.44 Mbar.¹¹ The average bulk velocity of sound in β -C₃N₄ can be estimated from the square root of

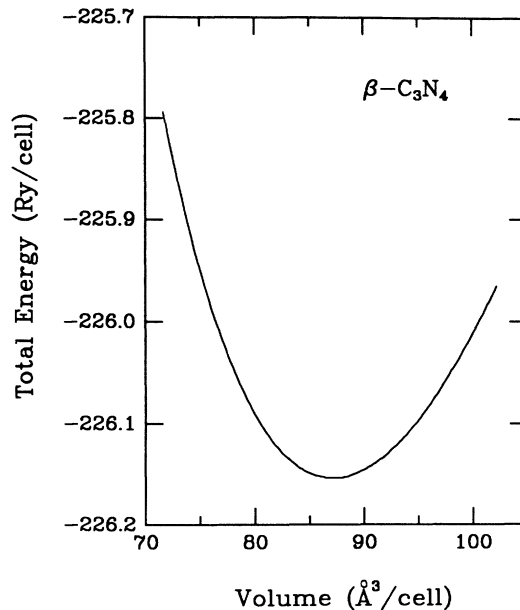


FIG. 3. Calculated total energy as a function of unit-cell volume in β -C₃N₄.

the ratio of the bulk modulus to the mass density. In β -C₃N₄, the low mass density and large bulk modulus combine to yield a large sound velocity of about 1.1×10^6 cm/s.

The calculated bond lengths in β -C₃N₄ and β -Si₃N₄ can be compared to the empirical covalent radii^{20,21} of the constituent atoms. The average C—N bond length in β -C₃N₄ is found to be 1.47 Å, which is intermediate between the sum of the C tetrahedral and N *sp*² radii and the sum of the C and N tetrahedral radii. In contrast, the average Si—N bond length of 1.74 Å in β -Si₃N₄ is significantly shorter than the sum of the N *sp*² and Si *sp*³ radii. This reduction of the bond length in β -Si₃N₄ is similar to what is observed in other compounds such as SiC and AlN, which have elements from both the first and second row of the Periodic Table, with the first-row element having valency equal to or greater than the second-row element. Lacking *p* states in the core, the first-row element in such compounds has a strongly attractive *p* pseudopotential. We believe that the reduction

TABLE I. Lattice constant, bulk modulus, and cohesive energy of β -Si₃N₄ and β -C₃N₄.

		<i>a</i> (Å)	<i>B</i> (Mbar)	<i>E</i> _{coh} (eV/cell)
β -Si ₃ N ₄	Calc.	7.61 ^a	2.65 ^a	74.3 ^a
		7.586 ^b	2.82 ^b	74.8 ^b
	Expt.	7.608 ^c	2.56 ^d	
β -C ₃ N ₄	Calc.	6.44 ^a	4.27 ^a	81.5 ^a

^aPresent work.

^bReference 5.

^cReference 13.

^dReference 16.

in bond length results from the charge transfer from the second-row atom to the first-row atom arising from the strong first-row p potential.

The calculated bulk moduli can be compared to an empirical model for the bulk modulus of tetrahedral semiconductors.⁷ Scaling arguments based on the Phillips and Van Vechten scheme²⁰ for characterizing tetrahedral semiconductors suggest that the bulk modulus in these solids is proportional to $d^{-3.5}$, where d is the bond length. An additional empirical term can be added to account for the effect of ionicity, which tends to deplete charge from the bond. The resulting scaling relation is $B = (19.71 - 2.20\lambda)d^{-3.5}$, where B is the bulk modulus in Mbar, d is the bond length in Å, and λ is chosen to be 0, 1, or 2 for group-IV-IV, -III-V, or -II-VI compounds, respectively. For the diamond and zinc-blende solids, the empirical relation generally gives agreement with experiment to within a few percent. However, with an ionicity factor λ in the range of 0 to $\frac{1}{2}$ (discussed below), the scaling law overestimates the bulk moduli of the IV-V compounds, β - C_3N_4 and β - Si_3N_4 , by an amount on the order of 10%. These overestimates are due to the lack of complete tetrahedral bonding in the β - Si_3N_4 structure. In particular, with the trigonal symmetry of the N sites, only three electrons per N site can participate in the bonding. The lower density of bonds in this structure compared to a tetrahedral structure results in a softer lattice.

IV. ELECTRONIC AND BONDING PROPERTIES

Many of the experimental studies of the electronic structure of Si_3N_4 have used amorphous Si_3N_4 . Because the amorphous and crystalline forms of Si_3N_4 have essentially the same short-range order, some aspects of their electronic structures are expected to be similar. In a recent study of Si_3N_4 , the soft-x-ray emission spectra of α , β , and amorphous Si_3N_4 were found to be quite similar.²² Hence to increase our database, results from the amorphous Si_3N_4 experiments are included in the set of experimental results with which the calculated electronic structure of β - Si_3N_4 is compared.

Techniques used to probe the electronic structure of Si_3N_4 include x-ray photoemission^{23–25} and soft-x-ray emission²² for the valence band, and bremsstrahlung isochromat spectroscopy²⁵ for the conduction band. In these studies, the valence-band spectrum is found to be split into two regimes by an energy gap of about 3 to 4 eV. The upper portion of the valence band, which displays some structure, is 10–12 eV wide, while the lower portion, consisting of a single peak, has width 4–5 eV. Measurements of the gap between valence and conduction states gives values ranging from 4.6 to 5.5 eV. The reason for the discrepancy between measured values of the gap is not clear.

The calculated band structure of β - Si_3N_4 at the equilibrium volume is shown in Fig. 4. With two formula units of Si_3N_4 in the unit cell, there are 32 occupied valence bands. Since a group-theoretical assignment has not been performed on the bands, we will label the bands in ascending order. The gross features of the band structure

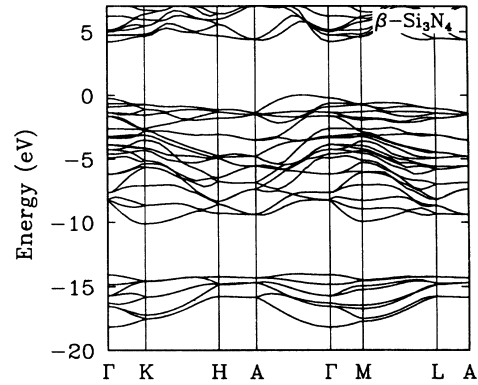


FIG. 4. Electronic band structure of β - Si_3N_4 at the calculated equilibrium volume. Energies are measured from the top of the valence band.

are in good agreement with experiment. For example, the valence band, which has a full width of 18.2 eV, is split by a gap of 3.9 eV. The lower portion of the valence band, consisting of bands 1 through 8, has width 4.2 eV, while the upper portion extends over an energy range of 10.1 eV. The top of the valence band occurs along the Γ to A line and is separated from the bottom of the conduction band at Γ by a calculated LDA band gap of 4.2 eV. Since we are using the LDA, which is known to underestimate gaps by as much 50%, the calculated value is in the expected range. While the band structure in Fig. 3 is similar to the results of the previous calculation⁵ using the OLCAO approach, some differences exist, such as the wider valence and a smaller LDA band gap.

The electronic structure and bonding nature of β - Si_3N_4 can be studied by analyzing plots of the valence charge density corresponding to different energy regimes of the band structure. These are displayed in Fig. 5. For the N on the left of this figure, the bonding plane lies perpendicular to the plane shown, while for the N on the right, the bonding plane lies in the plane of the figure. The states which lie between the valence-band maximum and about -3.2 eV, corresponding approximately to bands 25 to 32, are seen to be composed predominantly of N p orbitals. Since these p orbitals are oriented perpendicular to the bonding planes, they correspond to nonbonding states. In the region from about -3.2 to -10.1 eV are Si–N bonding orbitals. Further analysis reveals that these states consist of N p and Si p bonding orbitals at the higher energies, and N p band Si s bonding orbitals at the lower energies. The lowest eight bands form the split-off lower portion of the valence band and correspond to N $2s$ states. The deviation of these s -like states from spherical symmetry is due to a small amount of mixing with Si $3s$ orbitals.

It has been suggested^{4,26} that the p - $d\pi$ interaction between Si and N stabilizes the 120° Si–N–S bond angle in β - Si_3N_4 compared to the smaller bond angles found in other trivalent group-V systems such as elemental As. However, the present calculation indicates that Si d orbitals do not play an important role in the valence-band states. Instead we believe that an explanation for the pla-

nar triply coordinated N site lies in the fact that N is a first-row element. The first-row elements, with localized $2p$ states, behave differently from the elements lying below them in that sp^2 hybridization is energetically favorable for some first-row solids. For example, the lowest-energy structure for both C and BN is a hexagonal layered structure, while tetrahedral structures are preferred by the corresponding second-row solids. Hence the sp^2 hybridization of N in β -Si₃N₄ is not surprising, even though it differs from the behavior of other trivalent group-V elements in solids.

The calculated band structure of β -C₃N₄ is shown in Fig. 6. The total valence-band width is 24.8 eV and the calculated LDA band gap is 3.2 eV. In the upper portion

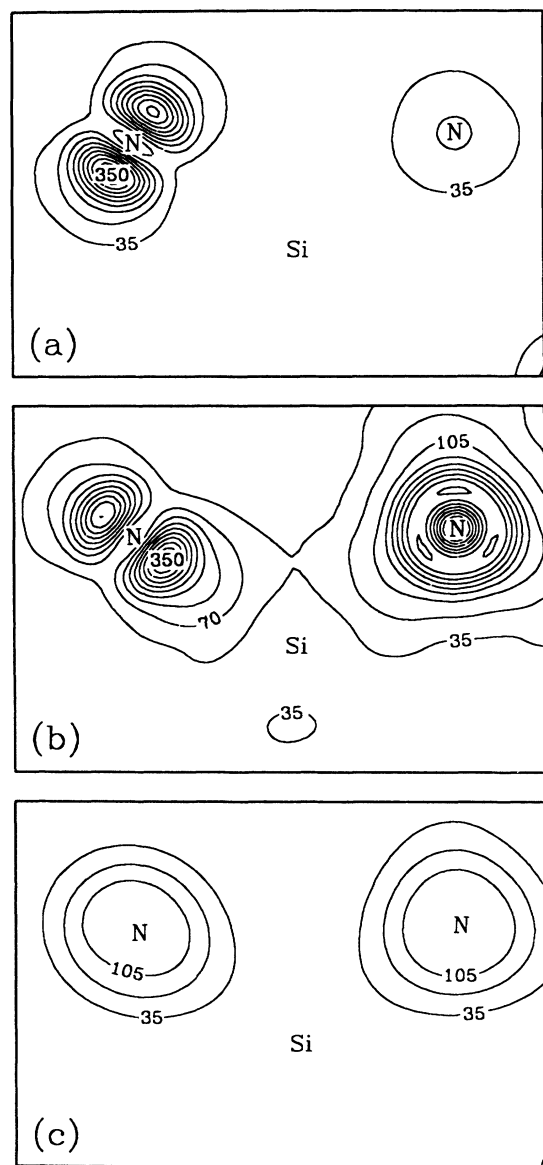


FIG. 5. Contributions to the valence charge density of β -Si₃N₄ from different energy regimes of the electronic band structure. The plots show the charge density in a N—Si—N bonding plane. The step size between contours is 35 electrons/cell and the energy regimes are (a) $-3.2 < E < 0.0$ eV; (b) $-10.1 < E < -3.2$ eV; (c) $-18.2 < E < -14.1$ eV.

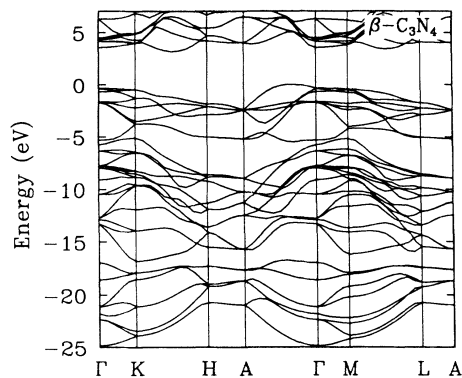


FIG. 6. Electronic band structure of β -C₃N₄ at the calculated equilibrium volume. Energies are measured from the top of the valence band.

of the valence band, the composition of the states is similar to what is found in β -Si₃N₄. For example, the charge density plots shown in Fig. 7 reveal that the states which lie between the valence-band maximum and about -5.3 eV correspond to nonbonding N p orbitals. Below these are bonding bands involving N p and C p orbitals and N p and C s orbitals. However, unlike the case in β -Si₃N₄, bands 1 through 8 in β -C₃N₄ do not split off and form a separate valence band. This reflects the smaller asymmetric part of the potential in β -C₃N₄, which allows stronger mixing between the low-lying N and C states. As can be seen from Fig. 7, the lowest-lying bands in β -C₃N₄ consist primarily of C s and N s and p bonding states. With this mixing, the N $2s$ states do not split off from the rest of the valence band as they do in β -Si₃N₄, and the gap separating bands 8 and 9 closes. This is similar to the behavior in zinc-blende and rocksalt compounds in which the valence-band gap at the X point in the Brillouin zone is found to scale roughly as the Phillips–Van Vechten ionic gap, which in turn is a measure of the asymmetric potential.²⁷

In Figs. 8 and 9, the total valence charge densities for β -Si₃N₄ and β -C₃N₄ are presented. These plots lie in the (0001) plane and show a central N site surrounded by its three neighboring C or Si sites. Around each C or Si site, two of the four neighboring N atoms are seen in the plane of the figure. The other two neighbors lie above and below the plane shown. In both plots the contour levels are in units of electron per cell and the contour step size is 40 electrons per cell. The charge density for β -C₃N₄ is covalent in nature, with the charge weighted towards the N sites. The asymmetry in the bond charge is intermediate between that for the first-row group-IV and -III-V tetrahedral compounds (diamond and BN).⁶ In contrast, the calculated charge density for β -Si₃N₄ exhibits much more ionic character and resembles more closely that found in III-V systems. However, the bonding in both of these compounds differs from that in zinc-blende structure compounds in that the two constituent atoms both contribute one electron to each covalent bond. Hence the ionicities β -Si₃N₄ and β -C₃N₄ are likely to be lower than those of the corresponding hypothetical zinc-blende compounds.

A comparison of the bonding and ionicity of $\beta\text{-C}_3\text{N}_4$, $\beta\text{-Si}_3\text{N}_4$, and other first- and second-row semiconductors and insulators can be made by examination of the charge densities along the bonds. In Fig. 10, the calculated line charge density along the bond in diamond, SiC, $\beta\text{-Si}_3\text{N}_4$, and $\beta\text{-C}_3\text{N}_4$ is plotted. To facilitate comparison between different structures, the charge densities have been normalized by the total number of valence electrons per cell. Hence if the valence charge density were uniformly distributed throughout the cell, the curve would be a horizontal line of height 1. Since the bonds have all been normalized to the same length, a comparison of the

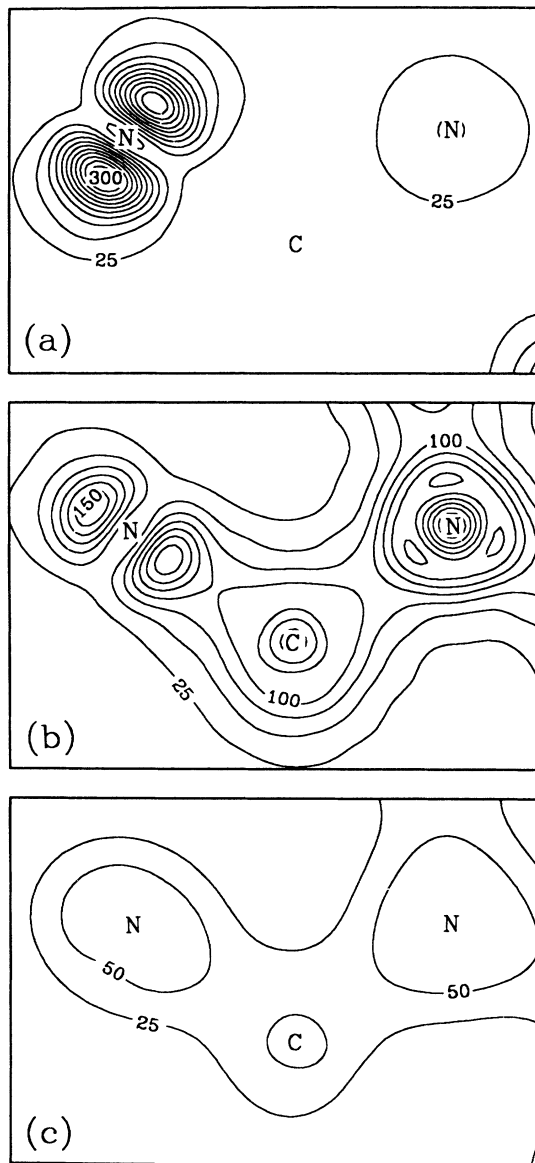


FIG. 7. Contributions to the valence charge density of $\beta\text{-C}_3\text{N}_4$ from different energy regimes of the electronic band structure. The plots show the charge density in a N—C—N bonding plane. The step size between contours is 25 electrons/cell and the energy regimes are (a) $-5.3 < E < 0.0$ eV; (b) $-16.8 < E < -5.3$ eV; (c) $-24.8 < E < -16.8$ eV.

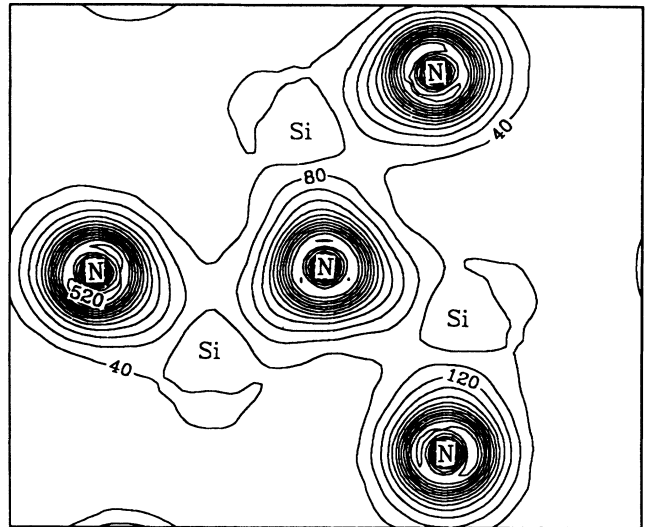


FIG. 8. Total valence charge density of $\beta\text{-Si}_3\text{N}_4$ in the (0001) plane. The contour interval is 40 electrons/cell.

widths and positions of peaks in different curves is not appropriate. Instead we are concerned only with the overall shape of the curves, i.e., double or single peak, and the relative peak heights.

Two factors can contribute to the ionicity of these compounds: a difference in valence of the constituent atoms and a difference in core size and core states of the constituent atoms. Consider first the purely covalent bond in diamond. The homopolar C—C bond exhibits two local maxima. Lacking p states in the core, the C atoms have highly localized p orbitals, which splits the bond charge into two peaks. Next, in order of increasing ionic character, is $\beta\text{-C}_3\text{N}_4$. In $\beta\text{-C}_3\text{N}_4$, the difference in valence between C and N leads to a charge density in

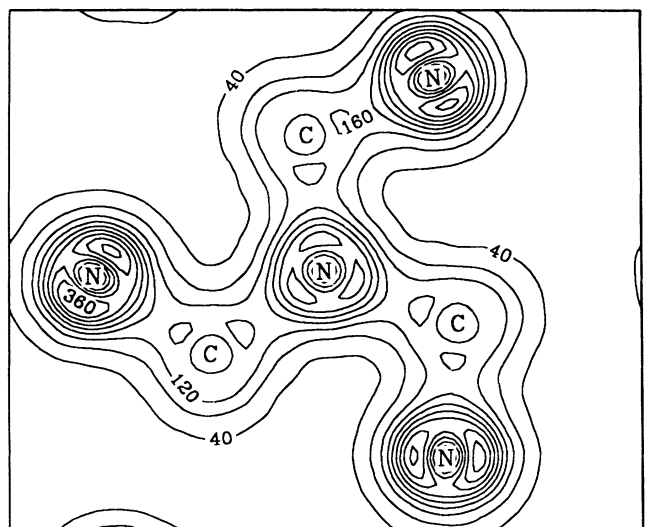


FIG. 9. Total valence charge density of $\beta\text{-C}_3\text{N}_4$ in the (0001) plane. The contour interval is 40 electrons/cell.

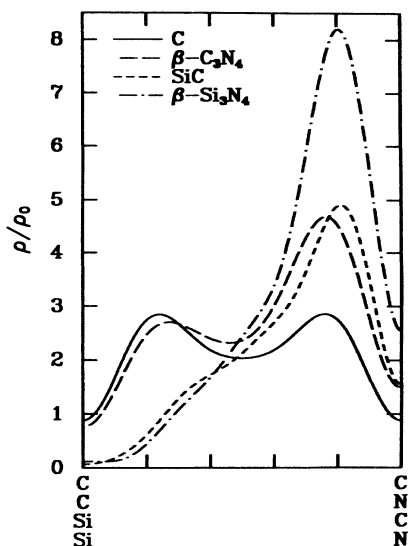


FIG. 10. Total valence charge density along the bond in diamond, β - C_3N_4 , SiC, and β - Si_3N_4 , normalized by the number of valence electrons per unit cell, ρ_0 . All the bond lengths have been normalized to the same length.

which there are still two local maxima along the bond, but the charge is weighted towards the N site. The fact that the height of the local maximum near the C site is close to the value in diamond indicates that there is not a lot of charge transfer in the C—N bond. Hence the asymmetry of the charge density along the bond in β - C_3N_4 is due primarily to the extra nonbonding electrons on the N sites. On the other hand, in SiC, the constituent atoms have the same valency, and it is the difference in core size and core states which is responsible for the ionic character of the bond. The large Si core size and the repulsive component of the Si p pseudopotential lead to transfer of charge from the Si to the C sites. The charge density along the bond is highly asymmetric, exhibiting a single peak near the C site. Finally, in β - Si_3N_4 , both valency and core effects come into play. Since both effects tend to localized charge near the N sites, the β - Si_3N_4 bond exhibits the most asymmetric character of the four compounds considered here. It should be pointed out that in some III-V systems such as BP and BAs, the two effects of differences in valence and differences in core size and core states work in opposite directions and a reversal of the usual direction of charge transfer from the group-III to the group-V element is possible.²⁸

V. CONCLUSION

We have calculated the structural and electronic properties of β - Si_3N_4 and the hypothetical compound β - C_3N_4 .

For β - Si_3N_4 , the calculated lattice constant, bulk modulus, and band structure are all in good agreement with experiment. This lends support to the predicted properties of β - C_3N_4 . While the structure of β - Si_3N_4 is used as a prototype for investigating the properties of a covalent solid formed between C and N, the calculated cohesive energy of β - C_3N_4 indicates that it may be a metastable structural phase. β - C_3N_4 is found to be a good candidate for a new low compressibility material, with bulk modulus comparable to that of diamond. In addition, the velocity of sound in β - C_3N_4 is estimated to be over 20% larger than that in β - Si_3N_4 . This large sound velocity could lead to useful thermal properties in β - C_3N_4 , such as a high thermal conductivity.

The bonding properties of these IV-V compounds have also been investigated and compared to the bonding in other first- and second-row semiconductors and insulators. The asymmetric character of the bonds in these materials has two contributions: the difference in valency between atoms in different columns of the periodic table and the difference in core states between atoms in different rows. Only the first effect is present in β - C_3N_4 , while both effects play a role in β - Si_3N_4 . Hence the Si—N bond exhibits significantly more ionic character than the C—N bond.

In conclusion, we suggest that it may be possible to synthesize a covalent C—N solid such as β - C_3N_4 . One possible approach is the application of high pressures and temperatures to amorphous carbon nitride or other combinations of carbon and nitrogen. This treatment could induce a phase transition to a solid with at least partial tetrahedral bonding. If a low-compressibility C—N solid can be fabricated, not only could it lead to useful new materials for engineering applications, but also, from a more basic point of view, it would add support for the theoretical approach used in this work.

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¹D. R. Messier and W. J. Croft, in *Preparation and Properties of Solid State Materials*, edited by W. R. Wilcox (Dekker, New York, 1982), Vol. 7.

²R. N. Katz, *Science* **208**, 841 (1980).

³R. J. Sokel, *J. Phys. Chem. Solids* **41**, 889 (1980).

⁴J. Robertson, *Philos. Mag. B* **44**, 215 (1981).

⁵Y. Xu and W. Y. Ching, in *Silicon Dioxide and its Interfaces*, edited by S. T. Pantelides and G. Lucovsky (MRS, Pittsburgh, 1988), p. 181; Y. Xu and W. Y. Ching, *Physica B (Amsterdam)* **150**, 32 (1988).

⁶A. Y. Liu and M. L. Cohen, *Science* **245**, 841 (1989).

⁷M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).

- ⁸M. L. Cohen, *Phys. Scr.* **T1**, 5 (1982).
- ⁹E. Wigner, *Phys. Rev.* **46**, 1002 (1934).
- ¹⁰D. R. Hamann, M. Schlüter, and C. Chiang, *Phys. Rev. Lett.* **43**, 1494 (1979).
- ¹¹S. Fahy and S. G. Louie, *Phys. Rev. B* **36**, 3373 (1987).
- ¹²M. T. Yin and M. L. Cohen, *Phys. Rev. B* **26**, 5668 (1982).
- ¹³E. Knittle, R. M. Wentzcovitch, R. Jeanloz, and M. L. Cohen, *Nature (London)* **337**, 349 (1989).
- ¹⁴J. R. Chelikowsky and S. G. Louie, *Phys. Rev. B* **29**, 3470 (1984); C. T. Chan, D. Vanderbilt, and S. G. Louie, *ibid.* **33**, 5747 (1973).
- ¹⁵D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- ¹⁶O. Borgen and H. M. Seip, *Acta Chem. Scand.* **15**, 1789 (1961).
- ¹⁷F. D. Murnaghan, *Proc. Nat. Acad. Sci. USA* **30**, 244 (1944).
- ¹⁸F. Birch, *J. Geophys. Res.* **57**, 227 (1952).
- ¹⁹L. Cartz and J. D. Jorgensen, *J. Appl. Phys.* **52**, 236 (1981).
- ²⁰J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
- ²¹C. Kittel, *Introduction to Solid State Physics*, 6th ed. (Wiley, New York, 1986).
- ²²R. D. Carson and S. E. Schnatterly, *Phys. Rev. B* **33**, 2432 (1986).
- ²³Z. A. Weinberg and R. A. Pollak, *Appl. Phys. Lett.* **27**, 254 (1975).
- ²⁴R. Karcher, L. Ley, and R. L. Johnson, *Phys. Rev. B* **30**, 1896 (1984).
- ²⁵A. Iqbal, W. B. Jackson, C. C. Tsai, J. W. Allen, and C. W. Bates, Jr., *J. Appl. Phys.* **61**, 2947 (1987).
- ²⁶P. Morgan, in *Nitrogen Ceramics*, edited by F. Riley (Nordhoff, Leyden, 1977), p. 23.
- ²⁷D. J. Chadi, M. L. Cohen, and W. D. Grobman, *Phys. Rev. B* **7**, 5587 (1973).
- ²⁸R. M. Wentzcovitch, M. L. Cohen, and P. K. Lam, *Phys. Rev. B* **36**, 6058 (1987).