Phys. **72**, 283 (1988).
5. D. Dimos *et al.*, *Phys. Rev. Lett.* **61**, 219 (1988).
6. J. Mannhart *et al.*, *Appl. Phys. Lett.* **52**, 1271 (1988).
7. R. Gross *et al.*, *IEEE Trans. Magn.* **25**, 2250 (1989).
8. A. Barone and G. Paterno, *Physics and Applications of the Josephson Effect* (Wiley, New York, 1982).
9. A. T. Fiory *et al.*, *Phys. Rev. Lett.* **61**, 1419 (1988).

10. H. Gränicher, *Helv. Phys. Acta* **29**, 211 (1956).
11. We thank J. Berosh, D. R. Clarke, J. Hagerhorst, J. Lacey, M. M. Oprysko, and T. M. Shaw for support. Part of this work was supported by a grant of the Bundesministerium für Forschung und Technology (Projekt 13N5482).

3 May 1989; accepted 20 June 1989

Fig. 2. Valence charge density of β-C_3N_4 in the [0001] plane. The contours are in units of electrons per cell. The contour interval is 20 electrons per cell.

Prediction of New Low Compressibility Solids

AMY Y. LIU AND MARVIN L. COHEN

An empirical model and an ab initio calculation of the bulk moduli for covalent solids are used to suggest possible new hard materials. The empirical model indicates that hypothetical covalent solids formed between carbon and nitrogen are good candidates for extreme hardness. A prototype system is chosen and a first principles pseudopotential total energy calculation on the system is performed. The results are consistent with the empirical model and show that materials like the prototype can have bulk moduli comparable to or greater than diamond. It may be possible to synthesize such materials in the laboratory.

HARDNESS (*1*) IS A COMPLEX PROPerty related to the extent to which solids resist both elastic and plastic deformation. For materials with defects, hardness can be limited by many factors including point defects, dislocations, and macroscopic defects. On the microscopic level, for ideal systems, hardness is determined by the bulk modulus, which in turn depends on the nature of the chemical bonding. It is the strength and compressibility of the bond that plays the primary role in a solid's ability to resist deformation. The largest bulk moduli are found in covalently bonded materials. Diamond, which has the largest bulk modulus (4.43 Mbar), is also the hardest known solid. A theory of the bulk moduli of covalent solids is therefore useful for suggesting schemes to increase hardness.

An empirical model for the bulk moduli of covalent solids was developed (*2*) with scaling arguments based on the Phillips–Van Vechten scheme (*3*) for characterizing the covalent and ionic nature of tetrahedral solids by means of their spectral properties. For purely covalent solids such as C and Si, the bulk modulus scales as the average homopolar energy gap in the reflectivity spectrum divided by the volume of the bond charge. This leads to the bulk modulus varying as $d^{-3.5}$, where d is the bond length. For the zinc blendes, an additional empirical term is added to account for the depletion of bond charge with increasing ionicity. The resulting scaling relation is

$$B = \frac{(19.71 - 2.20\lambda)}{d^{3.5}} \quad (1)$$

where B is the bulk modulus in megabars, d is in angstroms, and λ is a measure of the

ionicity of the compound. For the homopolar semiconductors (group IV), $\lambda = 0$, while for the heteropolar III-V and II-VI zinc blende solids, $\lambda = 1$ and 2, respectively. Similar analytic relations between the bulk modulus and lattice constant have been obtained for the group IV and III-V semiconductors by means of first principles methods based on a pseudopotential scheme (*4*).

The scaling law given by Eq. 1 successfully describes the diamond and zinc blende semiconductors, giving results for the bulk moduli within a few percent. This is comparable in accuracy to first principles calculations (*5*) that require extensive supercomputer time. Equation 1 is also useful for illustrating trends in these materials. For example, to achieve a large bulk modulus, two properties are needed: low ionicity and short bond length. In the past, there was speculation that cubic BN might be harder than diamond. Interpolation of empirical relations for the elastic constants (*6*) led to an estimate of the bulk modulus of BN in
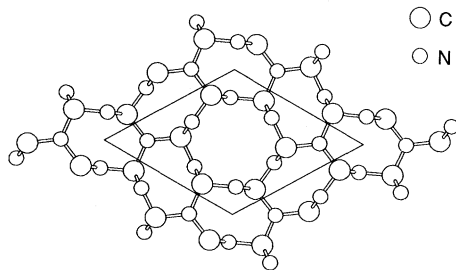

Fig. 1. Structure of β-C_3N_4 in the *a-b* plane. The *c*-axis is normal to the page. Half the atoms illustrated are located in the $z = -c/4$ plane, the other half are in the $z = c/4$ plane. The structure consists of these buckled planes stacked in AAA. . . sequence. The parallelogram shows the unit cell.
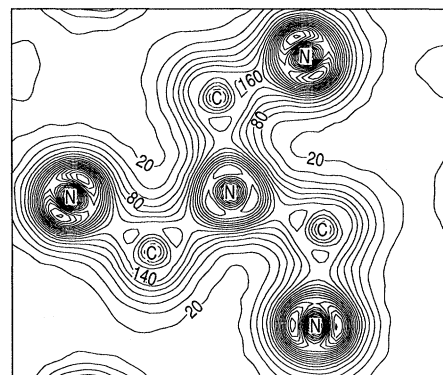
the range of 4.65 Mbar. In contrast, because both the bond length and ionicity are larger in BN than in diamond, Eq. 1 predicts that BN should have a smaller bulk modulus than diamond. With $\lambda = 1$ and $d = 1.56$ Å, the scaling law yields $B = 3.67$ Mbar for BN. A recent measurement (*7*) of the bulk modulus of BN yields 3.69 Mbar. The good quantitative agreement of the results of the empirical model and experiment demonstrates the predictive power of the model.

Based on this model, it was suggested (*2*) that a covalent solid formed between C and N could have a larger bulk modulus than diamond. In this work, we investigate the structural and electronic properties of a solid of this type using first principles pseudopotential calculations (*5*). In choosing a candidate structure that can be used as a prototype for a covalent C-N solid, the simple zinc blende structure is ruled out because in a hypothetical zinc blende compound the first antibonding band would be occupied. This would distribute charge in antibonding regions and it is doubtful that such a structure would be stable. Instead, a more complex structure for a C-N solid, based on the known β-Si_3N_4 structure with C substituted for Si, is considered. The octet rule for covalent bonding is satisfied in this structure, and no antibonding states are occupied. In Fig. 1, the structure is shown to consist of buckled layers stacked in an AAA. . . sequence (*8*). The unit cell is hexagonal and contains two formula units (14 atoms) with local order such that C atoms occupy slightly distorted tetrahedral sites while N atoms sit in nearly planar triply coordinated sites. This structure can be thought of as a complex network of CN_4 tetrahedra that are linked at the corners. The atomic coordination suggests sp^3 hybrids on

Department of Physics, University of California, Berkeley, CA 94720, and Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

the C atoms and sp^2 hybrids on the N atoms.

The hexagonal unit cell and the planar coordination of the N sites raise the possibility that this structure may exhibit anisotropic elastic properties. However, on a local scale, the CN_4 tetrahedra are linked in such a way that the in-plane and out-of-plane bonding are similar. The network is three dimensional and is not obviously weak in any direction. This is supported by measurements (9) of the elastic constants of β-Si_3N_4 which show nearly equal in-plane and out-of-plane linear compressibilities. Hence the β-Si_3N_4 structure is a good prototype for this study even though the bonding is not exclusively sp^3. The lack of complete tetrahedral coordination suggests that Eq. 1 may not be as precise as in the diamond and zinc blende cases, but it is expected that the trends contained in the scaling law will be followed. Our ab initio study described below is intended to test this assumption.

The structural and electronic properties of the hypothetical compound β-C_3N_4 (C_3N_4 in the β-Si_3N_4 structure) are calculated by means of the first principles pseudopotential total energy approach (5). The local density approximation, with the Wigner interpolation formula (10) for the exchange and correlation functional, is used. Because there are no p states in the core of C and N, the $2p$ pseudopotentials for these atoms are strongly attractive. Hence a localized orbital formalism (11), in which the electronic wave functions are expanded in linear combinations of Bloch sums of Gaussian orbitals localized on the atomic sites, is employed. Orbitals of s and p character are included in

Fig. 3. Normalized valence charge density along the bond in diamond, β-C_3N_4, and BN. The normalization factor, ρ_o, is the number of valence electrons per cell.

the basis. The charge density and crystal potential are calculated self-consistently with an energy cutoff of 64 Ryd.

The structural properties of β-C_3N_4 are determined by calculating the total crystal energy as a function of volume. Since β-C_3N_4 is used only as a prototypical structure, there is no reason a priori to believe that it is the lowest energy structure for the C-N system. However, at the equilibrium volume, the cohesive energy of β-C_3N_4 is calculated to be 81 eV per cell or an average value of 5.8 eV per atom. This moderately large cohesive energy suggests that there is a good chance that β-C_3N_4 is at least a metastable structure.

At the calculated equilibrium volume, the average C-N bond length is found to be 1.47 Å. This is in good agreement with the sum of the tetrahedral covalent radii (3, 12) of C and N. The bulk modulus of β-C_3N_4 is determined by fitting the total energy as a function of volume to Murnaghan's equation of state (13) which yields a value of 4.27 (± 0.15) Mbar. For the calculated bond length and an estimated ionicity factor of $\lambda = 1/2$ (discussed below), the scaling law (Eq. 1) overestimates the bulk modulus of β-C_3N_4 by about 10%. A similar overestimate is found for the bulk modulus of β-Si_3N_4 which has a measured (9) value of 2.5 Mbar. These overestimates are most likely caused by the structural difference between these materials and the zinc-blende systems on which Eq. 1 was based. In particular, the trigonal coordination of N in β-C_3N_4 and β-Si_3N_4 allows only three electrons per N site to participate in the bonding. The remaining N electrons occupy nonbonding p orbitals perpendicular to the bonding plane. This reduction in the number of bonds compared to a tetrahedral system results in elastic constants that are slightly lower than those predicted by Eq. 1.

The degree of ionicity in β-C_3N_4 can be seen in plots of the charge density. Figure 2 shows the total valence charge density in the [0001] plane of β-C_3N_4. This plane contains a central N atom surrounded by its three C neighbors. The bonds are highly directional, as expected for a covalent system. For comparison, linear plots of the charge density along a bond in diamond and BN, as well as β-C_3N_4, are given in Fig. 3. To facilitate comparison between the different structures, the charge densities have been normalized by the total number of electrons per cell. In diamond, there are two local maxima along the bond. The presence of the double hump rather than a single maximum near the center of the bond is a result of the strongly attractive C $2p$ potential. The two maxima reach a normalized height of 2.9. With increasing ionicity, the local maximum near

the anion grows at the expense of the one near the cation. In β-C_3N_4, the two local maxima remain, but the charge is weighted towards the N site. The height of the peaks are 2.7 and 4.6. In BN, the charge is strongly localized near the N site and the bond exhibits only a single peak of height 6.3. Thus the heteropolarity of the C-N bond in β-C_3N_4 lies intermediate between purely covalent diamond and partially ionic BN.

In conclusion, we suggest that it may be possible to synthesize a covalent C-N solid such as β-C_3N_4 with compressibility comparable to diamond. A possible starting material is amorphous carbon nitride, which has a polymeric structure (14). The application of high pressures and temperatures to α-C:N may induce a phase transition to a structure with more tetrahedral bonding. This transition would be similar to the transition of graphite to diamond. Since other factors such as chemical reactivity and fracture toughness are important for applications, the prediction of hardness does not guarantee usefulness in engineering applications. Nevertheless, the fabrication of a covalent solid formed between C and N could result in an important new high-performance material that may best be used as part of a composite. From the scientific point of view, the fabrication of a low compressibility C-N solid would add support for the theoretical approach used here and provide information for further applications.

REFERENCES AND NOTES

1. See, for example, *Proceedings of the Third International Conference on the Science of Hard Materials*, V. K. Sarin, Ed. (Elsevier, Oxford, 1988).
2. M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).
3. J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic Press, New York, 1973).
4. P. K. Lam *et al.*, *Phys. Rev. B* **35**, 9190 (1987).
5. M. L. Cohen, *Phys. Scr.* **T1**, 5 (1982).
6. J. A. Sanjuro, E. Lopez-Cruz, M. Cardona, *Phys. Rev. B* **28**, 4579 (1983).
7. E. Knittle *et al.*, *Nature* **337**, 349 (1989).
8. O. Borgen and H. M. Seip, *Acta. Chem. Scand.* **15**, 1789 (1961).
9. L. Cartz and J. D. Jorgensen, *J. Appl. Phys.* **52**, 236 (1981).
10. E. Wigner, *Phys. Rev.* **46**, 1002 (1934).
11. J. R. Chelikowsky and S. G. Louie, *Phys. Rev. B* **29**, 3470 (1984); C. T. Chan, D. Vanderbilt, S. G. Louie, *ibid.* **33**, 2455 (1986).
12. C. Kittel, *Introduction of Solid State Physics* (Wiley, New York, ed. 6, 1986).
13. F. D. Murnaghan, *Proc. Nat. Acad. Sci. U.S.A.* **30**, 244 (1944).
14. H.-X. Han and B. J. Feldman, *Solid State Commun.* **65**, 921 (1988).
15. Supported by National Science Foundation (NSF) grant DMR8818404 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under contract DE-AC03-76SF00098. Cray computer time was provided by the U.S. Office of Energy Research of the Department of Energy at the National Magnetic Fusion Energy Computer Center and by the NSF at the San Diego Supercomputer Center.

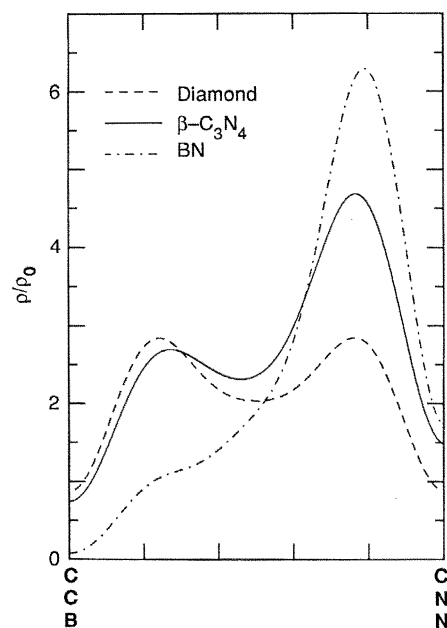17 May 1989; accepted 23 June 1989