Predicting Useful Materials

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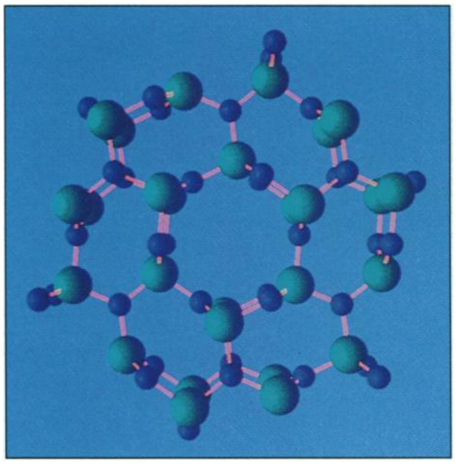
Can useful materials be predicted from first-principles theory? An encouraging answer is provided by the experiments of Niu *et al.* (*1*), reported on page 334 of this issue, in which the theoretically predicted (*2, 3*) material β-C_3N_4 has been synthesized. Although more needs to be done to ascertain the physical properties of this compound, its synthesis shows that theory (*2*) can point the way toward the creation of materials with hardnesses comparable with or larger than that of diamond and that such a material has been correctly predicted (*3*).

Niu *et al.* (*1*) prepared films of carbon nitride and demonstrated that the compositional, structural, and electronic properties are consistent with the predicted compound β-C_3N_4, which is carbon nitride in the β-Si_3N_4 structure. Additional compositional and structural evidence is provided by earlier attempts (*4, 5*) to synthesize and characterize crystalline carbon nitride.

Niu *et al.* (*1*) used a synthesis approach in which fragments from pulsed laser ablation of high-purity graphite and a beam of atomic nitrogen were used to form C-N films on Si(100). The substrate temperature and nitrogen flux were varied to optimize the process. Characterization of the films included electron diffraction, Rutherford backscattering, and photoelectron spectroscopy. The diffraction data strongly support the existence of β-C_3N_4 crystallites in the films.

To predict new materials and explain solid-state properties, we need good quantum models. However, the application of quantum theory to solids has progressed more slowly than application to atoms and molecules. Spectral tests of atomic theories came early, but solid-state optical spectra are broad and more difficult to interpret than the sharp lines seen in atomic and molecular spectra. Also, for solids, there are many structural possibilities, complex many-body and collective effects, and of order 10^{23} particles per cubic centimeter to deal with. Despite these obstacles, new physical models and the availability of more powerful computers have recently resulted in successful theoretical descriptions of real materials and in some cases successful predictions. The modern theoretical approach (*6*) is sometimes referred to as the "standard model" for solids.



The hard stuff. Computer model of β-C_3N_4, which was theoretically predicted to have a bulk modulus comparable to diamond (*3*) and has now been synthesized (*1*). [Courtesy of J. Greenberg, San Diego Supercomputer Center]

The most popular form (*6*) of the standard model assumes that the atomic core electrons are unchanged when the solid is formed. Although this is not a necessary restriction, it reduces the problem to a description of the properties of a model solid in which a sea of valence electrons interacts with a periodic array of positive cores. Each core consists of a nucleus and the atomic core electrons. The valence electrons are attracted to the cores by the Coulomb interaction; however, part of the attraction is "canceled" (*7*) by a repulsive Pauli force, which prevents double occupancy of the core levels. The combined potential is called a pseudopotential (*8*). There are several schemes for generating pseudopotentials from calculations of atomic wavefunctions.

Hence, in principle, the problem of predicting the existence of a solid can be reduced to testing the total energy of a system of valence electrons interacting with different structural arrays of cores and with each other. The latter contribution can be estimated in a variety of ways. For structural properties, it is usually sufficient to assume that each valence electron moves in the average potential generated by the other valence electrons and this potential depends only on the position-dependent electron density. This "local density approximation" (*9*) together with the pseudopotential approximation are the practical techniques that demonstrate that the "standard model" works. Applications to dozens of crystals have yielded structural and electronic information. In some cases, new high-pressure structures and even superconductivity have been predicted (*6*) successfully. The only inputs to these calculations are the atomic numbers and atomic masses of the constituent atoms.

The prediction of microscopic properties related to hardness is a good testing ground for the theory. However, hardness is a complex property that depends on both microscopic and macroscopic structural properties, such as large defects and dislocations. Even choosing a scale of hardness can be complex and depend on the method used for measurement. Mohs' empirical scale, which ranges from talc (1) to calcite (3) to quartz (7) up to diamond (10), implies that the hardness of diamond, like the speed of light, will not be exceeded. Ultimately, hardness depends on microscopic properties such as bond strengths. For perfect crystals, hardness generally scales with bulk modulus, *B*. Therefore, the challenge to theory in this area is to compute *B* accurately and to predict materials with large *B* with the use of microscopic information.

The bulk modulus, $B = -V(\partial P/\partial V)$, where V and P are volume and pressure, is measured in the pressure unit gigapascal (1 GPa = 10,000 bar). Approximate values of *B*: rare gas solids (1 to 2 GPa), ionic solids (10 to 60 GPa), simple metals (2 to 100 GPa), transition metals (100 to 300 GPa), and covalent solids (100 to 443 GPa). Because of the large values for the latter group, the current focus has been on the covalent bond and systems similar to diamond. Application of the standard model yields bulk moduli to within about 5% of the experimental value by calculation of the total energy as a function of the volume of a solid. This requires about an hour of supercomputer time for relatively simple solids. However, a semiempirical approach (*2*) requiring the measured bond length as input takes only a second on a hand calculator.

The semiempirical approach (*2*) was first applied to group IV, III-V, and II-VI tetrahedrally bonded materials composed of atoms from the center of the periodic table. For bond lengths *d* expressed in angstroms, *B* is given (*2*) in gigapascals by

$$B = \frac{N_c}{4}\,\frac{(1972 - 220I)}{d^{3.5}} \qquad (1)$$

where N_c is the coordination number. An empirical ionicity parameter $I = 0$, 1, and 2 for groups IV, III-V, and II-VI solids, respectively, accounts for the reduction in *B* arising from increased charge transfer. For tetrahedral systems, $N_c = 4$, otherwise N_c is the average coordination number.

Equation 1 yields values of *B* that are in

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excellent agreement with experiment and rival the costly first-principles calculations for accuracy. In addition, the conditions for which large values of B are obtained are apparent from Eq. 1; that is, minimized d and I. Because small atomic radii imply small d, the first-row atoms of the periodic table are good candidates for building blocks of large B solids. For example, the radii of B, C, and N are 0.88 Å, 0.77 Å, and 0.70 Å respectively. These yield bulk moduli for diamond and BN in agreement with experiment. Because these radii yield d = 1.47 Å for C-N bonds and $I < 1$, Eq. 1 suggests (*2*) that carbon nitride compounds have high bulk moduli.

A prototype crystal structure for C_3N_4 can be chosen with knowledge of the known structure of β-Si_3N_4. The average coordination number for this structure is $N_c = 3.43$. Using estimates of I and d, we see that Eq. 1 yields $B \sim 410$ to 440 GPa which brackets the calculated value for diamond. A first-principles calculation (*3*, *10*) predicts a similar result, $B = 427 \pm 15$ GPa. In contrast, a first-principles calculation (*11*) for β-Si_3N_4 yields $B = 265$ GPa. This smaller value for B results from the larger bond length and larger charge transfer from Si to N.

Niu *et al.* (*1*) examined the question of charge transfer in β-C_3N_4 by measuring the 1*s* binding energy for C and N. They conclude that the C-N bond in β-C_3N_4 is covalent with relatively little charge transfer, which is in agreement with the theoretical predictions. As stated before, according to pseudopotential theory, there is a repulsive Pauli potential keeping the valence electrons away from the core region. For β-Si_3N_4, the *p* electrons in the Si cores repel the valence *p* electrons, whereas the N cores, which are only *s*-like, do not contribute a strong *p* repulsion. The result is considerable charge transfer from Si to N and a much more ionic bond in β-Si_3N_4 than in β-C_3N_4, where both C and N have the same core structure. The resulting C-N covalent bond is strong and somewhat similar to the C-C bond in diamond.

The general agreement between values of B calculated with Eq. 1, first-principles calculations, and experiments lends support to the usefulness of Eq. 1 for the calculation of trends and specific values for covalent systems. In addition, Eq. 1 suggests that the bulk modulus of diamond, unlike the speed of light, can be exceeded. Specifically, C-N compounds may break the diamond barrier. At present, the bulk modulus and hardness of β-C_3N_4 are yet to be measured. However, Niu *et al.* (*1*) state, on the basis of qualitative observations, that their C-N films are "thermally robust and hard." Because of the high Debye temperature of carbon nitride compounds, these materials should also be excellent heat conductors.

More generally, the study of hardness or bulk modulus is a good touchstone for theory. When the general prediction (*2*) of how short, nonionic covalent bonds increase bulk moduli and specific predictions for prototype materials are tested, there will be feedback to the theory. Subsequent modifications of the theory or suggestions for new classes of materials to be tested can broaden the domain of the models. In any case, at this point, the confirmation of theory implied by the measurements of Niu *et al.* (*1*) indicate that we have entered an era in which it is possible to use theory to design materials with predictable properties.

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Vancomycin Resistance: Decoding the Molecular Logic

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The 1990s may come to be remembered as a decade in which infectious diseases made a dramatic worldwide resurgence, largely because of the appearance of antibiotic-resistant microbes (*1*). In the United States alone, the unrecognized yearly cost of antibiotic resistance is estimated to be $100 million (*2*). The deciphering of drug resistance mechanisms will not only allow a better understanding of incipient clinical crises but may also suggest strategies for reversing resistance and preventing the appearance of new resistant microbes. Recent work has shed light on the development of resistance to vancomycin, a glycopeptide antibiotic that for 25 years has been an effective treatment for Gram-positive bacterial infections.

Vancomycin is the drug of choice for infections caused by streptococcal or staphylococcal strains that are resistant to β-lactam antibiotics (such as penicillin) and for patients who are allergic to the latter drugs. β-Lactam antibiotics and vancomycin interfere with separate but contiguous steps in the biosynthesis of bacterial cell walls—β-lactams by blocking crosslinking steps that strengthen the wall and vancomycin by forming a complex with the substrate for the penicillin-sensitive reaction. Because about 95% of *Staphylococcus aureus* isolates are resistant to the β-lactam methicillin (*3*), vancomycin has found expanded usage in situations where *S. aureus* is particularly problematic, such as in long-term care facilities, burn centers, among narcotics abusers, in infective endocarditis, and in patients with indwelling intravenous lines (*4*). A major advantage of vancomycin treatment had been the virtual absence of resistant strains; thus, the recent emergence of vancomycin resistance in the clinic, observed first in Europe and now globally (*5*), has been met with great apprehension.

Vancomycin is a modified heptapeptide with a cup-shaped architecture. The "cavity" of the drug, which is created by posttranslational crosslinks of tyrosine residues, binds tightly to peptidoglycan (PG) strands in the bacterial cell wall that terminate in D-Ala-D-Ala (*6*). Complex formation between vancomycin and D-Ala-D-Ala termini at the exterior surface of the cell blocks transglycosylation and transpeptidation of nascent PG strands. As a result, the crosslinking of PG strands and the tensile strength of the PG layer are reduced, rendering the bacteria susceptible to osmotic lysis.

The genes responsible for high-level vancomycin resistance in pathogenic enterococci have recently been cloned and sequenced (*7*). Resistance involves the action of nine genes contained within the transposable element Tn 1546, which is carried on a plasmid (*8*). The gene products include a transposase and a resolvase, which, by promoting mobilization of Tn 1546 from one DNA locus to another, allow the rapid spread of vancomycin resis-

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