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Possible Hard Materials Based on Interpenetrating Diamond-like Networks

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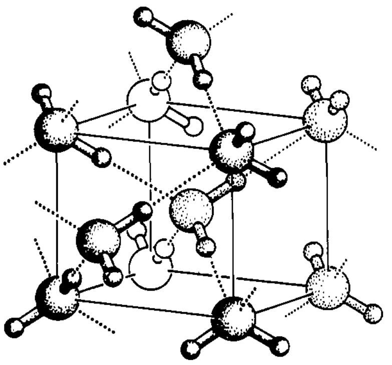
Abstract: Interpenetrating diamondoid nets, where one diamond-type framework is formed by BeF_2 and the other by SiO_2 or GeO_2, are constructed, and their electronic structure has been studied. It is suggested that these will be very hard materials.

One of the authors (P.P.) was writing a science-fiction novel in which a superhard material was used to drill to the center of the earth.[1] He wrote to another of the authors (R.H.) inquiring if the latter might suggest an apposite molecular structure, if possible containing the element beryllium, which already figured prominently in the novel. As it happens, R.H. was at the time admiring again the structure of ice-VII, a high-pressure form of ice shown in 1.[2]



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The beautiful extended structure of ice-VII consists of two interpenetrating diamond lattices, an H_2O sitting on each lattice point. This is also the structure of cuprite, Cu_2O, and the network occurs in a number of remarkable compounds made recently and to which we will return. BeF_2 crystallizes in the diamond lattice, and so we came up with the idea of a BeF_2 net interpenetrating another diamond-type structure as a possible superhard material.

Before we outline the suggested models and their electronic structures, let us review briefly the literature discussion of hardness, and the quest for very hard materials.

Hardness

The two common definitions of hardness are empirical: the indentation (Brinell or Vickers) hardness and the scratch (Mohs) hardness.[3] Hardness can be gauged more quantitatively than on the venerable Mohs scale with the bulk modulus, B_0, which measures the proportion by which a material shrinks under isotropic pressure. At zero temperature

$$B_0 = -V\,dp/dV = V\,d^2u/dV^2 \qquad (1)$$

where V, p, and u are the volume, pressure, and energy, respectively.

Cohen and co-workers have developed an empirical model to estimate the bulk moduli of covalent solids with diamond and zinc-blende structures.[4,5] The general formula they propose (bulk moduli in GPa, 100 GPa = 1 Mbar) is

$$B_0 = (1971 - 220\lambda)d^{-3.5} \qquad (2)$$

where d is the nearest-neighbor distance between the two types of atoms and λ is an empirical parameter that accounts for the effect of ionicity; $\lambda = 0, 1, 2$ for group IV (diamond, SiC), III–V (BN), and II–VI (ZnS), respectively.

Relationship 2 was used to predict the hardness for a hypothetical β-C_3N_4 material.[4] To estimate B_0 for unknown compounds or alloys, ionic or covalent radii may be used to estimate the nearest-neighbor distance. For example, if a tetrahedral compound could be formed between C and N, an estimate of d would be 1.47–1.49 Å, depending on which reported values of the radii are taken. The corresponding estimate of the bulk modulus would be 461–483 GPa, which is significantly larger than that of diamond (443 GPa).

Later Cohen *et al.*[6–8] proposed a structure for the hypothetical β-C_3N_4, starting from the known structure of β-Si_3N_4.[9,10] Using pseudopotential total-energy calculations,[11,12] static properties such as the equilibrium volume (V_0) and isothermal bulk modulus (B_0) were estimated by calculating the total energies of the compound at different volumes (usually ranging from $0.8V_0$ to $1.2V_0$). The Birch–Murnaghan equation of state[13,14] (see a worked example in Jorgensen[15]) is then used to fit the calculated total-energy versus volume curve. With this approach, Cohen *et al.* indicated that β-C_3N_4 should be a superhard material.[16] A general audience account of the quest for such materials may be found in a recent article.[17] Films of β-C_3N_4 have been synthesized; their hardness remains to be determined.[18,19] The electronic and geometrical structure of this material has been studied by Hughbanks and Tian.[19]

A different chapter in the quest involves the real and hypothetical allotropes of carbon. Ruoff *et al.* have suggested

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extreme hardness for C_{60}.[20] C_{60} is a discrete molecule, packing in the crystal in an face-centered cubic lattice. For molecular crystals the bulk moduli at atmospheric pressure are always small, because of the weak nonbonding interactions between the molecules in the crystal. However, under pressure it is possible to induce hard-sphere contacts. In the absence of a phase transition, the bulk modulus could be very high. By applying a simple mechanical model, using the icosahedral symmetry and the C–C bond strength, Ruoff estimated the bulk modulus for solid C_{60} at pressures above 20 GPa. The computed moduli are considerably higher (620–670 GPa) than those of both diamond and β-C_3N_4. In reality a phase transition at high pressure takes place in C_{60}, leading to an intriguing collapsed material of still undetermined structure.[21]

Tamor and Hass[22] described a beautiful all-sp^2 carbon lattice (related to a carbon material suggested by one of us to be metallic[23]), claiming that it should be harder than diamond (B_0 of 690 GPa). Their calculations were of the tight-binding type; together with Liu and Cohen[24] they repeated the calculations with a pseudopotential method. Even though the proposed structure was found to be unstable, the computed bulk modulus was 372 GPa, lower than diamond (443 GPa), but still the largest among all other materials.

Julg[25] proposed an empirical relation between the Mohs scale and the bond-ionicity α,

$$H = K(1 - {}^{2}/_{3}\alpha^{4}) \tag{3}$$

where K is a constant determined by the row to which the atoms A and B belong in the periodic table. Unfortunately this formula cannot give values greater than 10 (which is diamond). For example, if it is applied to β-C_3N_4 (here the α value for BN was used), H will be approximately 9.8.

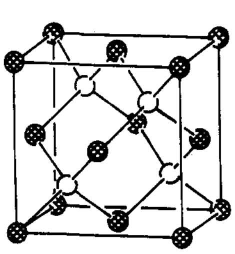
Finally, a relationship between microscopic chemical reactivity, macroscopic hardness, and compressibility has been derived by Yang, Parr, and Uytterhoeven.[26]

Simple and Interpenetrating Diamond Nets

The diamond lattice is very dense in terms of the numbers of atoms per cubic centimeter that it contains. But it is not close packed. There are two ways to look at this.

Consider first the simple diamond net, shown in its cubic form in **2**. One way to think about this structure is that it is a face-centered cubic lattice (cross-hatched spheres) with half of the eight tetrahedral holes (white spheres) and none of the four octahedral holes (center of the cube, midpoint of each edge) filled. In fact, filling these (**3**, black spheres are additional atoms) would generate an entirely equivalent diamond net, displaced by half a unit cell. Actually, the two lattices together form a new body-centered cubic lattice, indicated by the smaller unit cell drawn in at the bottom left in **3**.

An alternative, perhaps a little more "chemical", is to focus on the adamantane type unit which is at the heart of diamond, the light line structure in **4**. The central "hole" of the adamantane could be, in principle, the location of another atom; from that center another tetrahedral network could be strung, through the centers of the four cyclohexane rings. This is drawn with dark lines in **4**.



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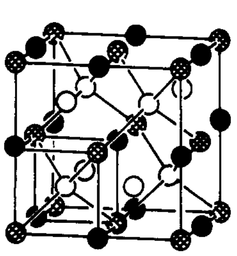

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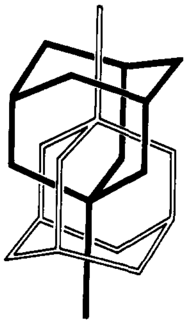

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If the diamond cubic unit cell spacing is a, (3.567 Å), then the shortest contact (bond) in the simple diamond structure is $a(\sqrt{3})/4$ (C–C = 1.54 Å). And in the interpenetrating diamond structure the internet short contact is the same. There are four such short internet contacts per atom, and six other contacts just a bit longer, at $a/2$ (C···C = 1.78 Å).

If carbon were to seek such a lattice, it would be in deep trouble, since each lattice site is eight-coordinate. To put it another way, the center of the adamantane hole in **4** is just as near to the four carbons of the other diamond sublattice as it is to the four carbons of its own lattice.

So for a main-group element the interpenetrating diamond lattice is essentially impossible—cubic eight-coordination does not meet the valence and bonding requirements of main-group elements. As a reviewer has pointed out, this is not to say that such a lattice cannot be built from carbon atoms alone—most simply by inserting an acetylenic CC spacer between the diamond net vertices.[27]

But now suppose we stretch the lattice, increasing a, by inserting a "spacer" atom where there was a C–C bond in diamond. Two such simple diamondoid structures (not interpenetrating) are BeF_2 and SiO_2 (β-cristobalite). In BeF_2 a is 6.67 Å (Be–F = 1.44 Å),[28a] and in SiO_2 a is 7.17 Å (Si–O = 1.61 Å). Actually in β-cristobalite the O's do not lie along the Si···Si line; the Si–O–Si angle is 147°.[28a,29] A similar distortion is expected for BeF_2, after simple geometrical consideration giving Be–F = 1.55 Å and F–Be–F = 138°. No recent accurate structural determination of BeF_2 appears to be available.[28a]

Cuprite, Cu_2O, actually crystallizes in the interpenetrating diamondoid structure, in fact lending its name to this structural type.[30] This geometry is shown in **5** (stereopair; two-coordinate Cu in smaller spheres),[31] with a doubled unit cell. The two networks are obtained by translation of the smaller unit cell; a = 4.267(2) Å with Cu–O = 1.85 Å and Cu–O–Cu = 180°.[32] This

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[31] Stereodrawing **5** is reproduced with permission from the following: Müller, U. *Inorganic Structural Chemistry*; Wiley: Chichester, 1993; p 115.

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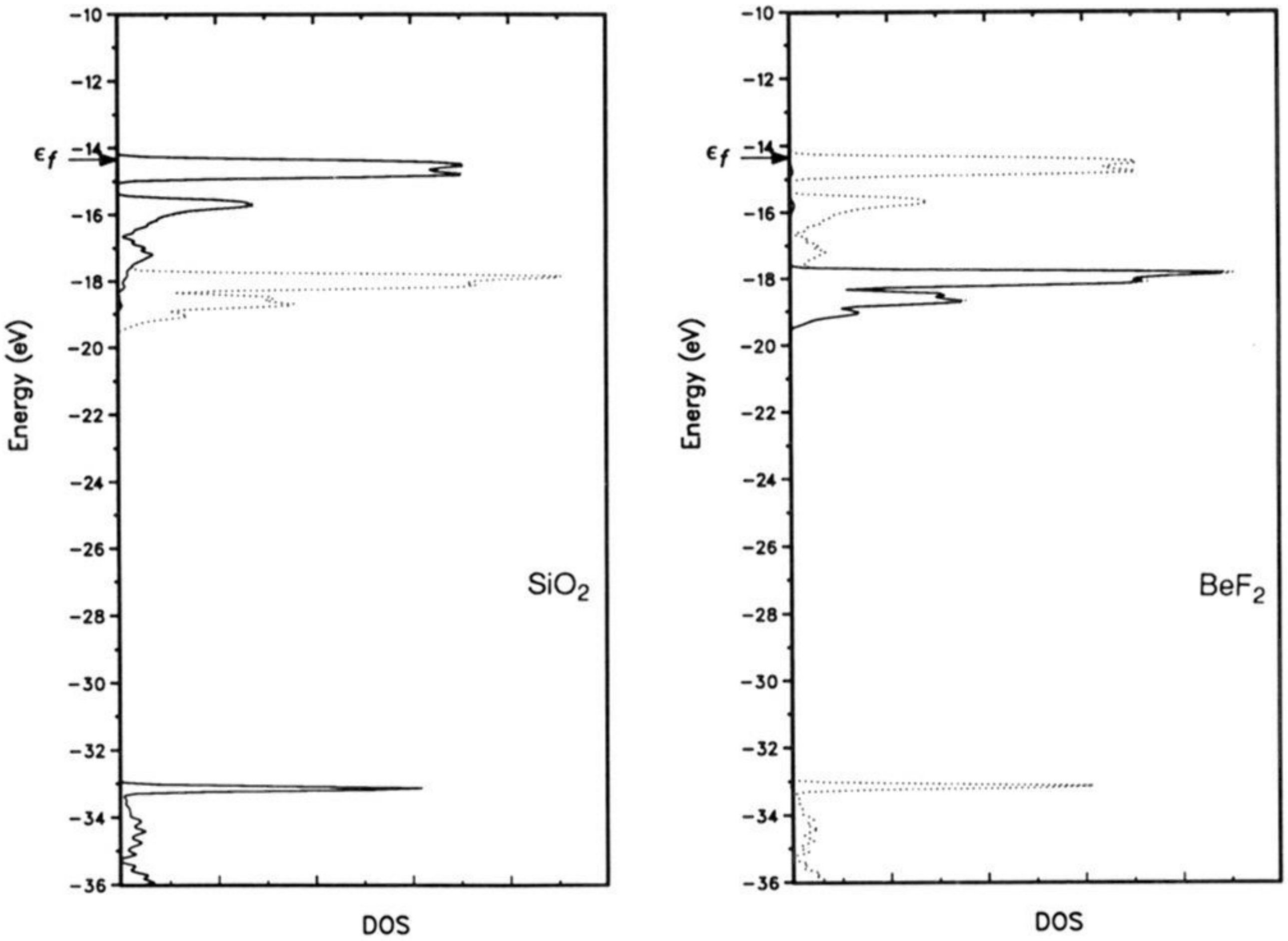
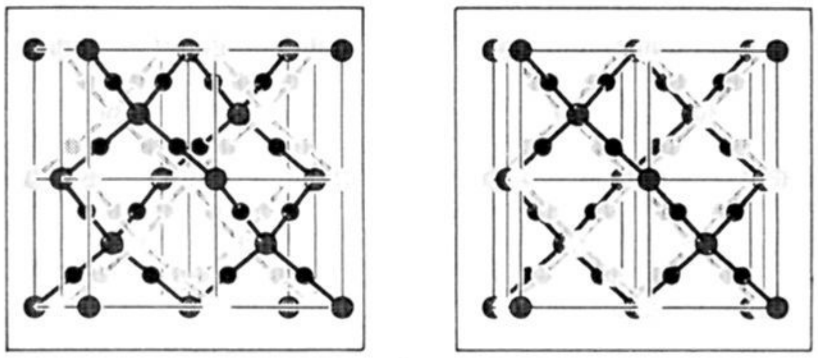


Figure 1. Calculated densities of states for $BeF_2 \cdot SiO_2$, with the contributions of the component subnets (SiO_2 at left and BeF_2 at right) indicated by a solid line. The F 2s orbitals are off-scale at low energy.

leads to the shortest nonbonding contact between the two diamondoid lattices of 3.7 Å (Cu···Cu or O···O).[33]



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Can we compute the bulk moduli for these structures? For SiO_2, formula 2 was applied, using as a nearest-neighbor distance the one between the two Si (3.1 Å).[34] The resulting B_0 of 37.6 GPa is surprisingly close to the value for α-quartz SiO_2 (36.4 GPa).[15,35] For quartz, application of pressure leads to a tilting and distortion of the SiO_4 tetrahedral unit with a dramatic effect on the Si–O–Si linking angle. It is quite possible that a similar effect occurs for β-cristobalite. Both bond stretching and bending are involved in the compressibility of covalent solids. Since bending force constants are generally low, we can expect bending to be an important route for distortion in these structures.

We can apply eq 2 to Cu_2O and obtain a value of 20 GPa, lower than the old experimental one (50 GPa, from Gmelin handbook, Vol. 60B).

Other Interpenetrating Diamondoid Nets

These have become quite popular recently. Hoskins and Robson[36] have redetermined the single-crystal structure for $Zn(CN)_2$ and $Cd(CN)_2$,[37] suggesting that "A theoretical study of these interlocking frameworks and especially of the nature of the interactions between frameworks would be interesting and valuable." Ermer[38] observed fascinating interpenetrating hydrogen-bonded networks in adamantane-1,3,5,7-tetracarboxylic acid. Kim and Kanatzidis[39a] found a complex network in K_2PdSe_{10}, related to the cuprite structure. Recently, interwoven three-dimensional coordination polymers have been obtained through the self-assembly of Cu(I) and Ag(I) cations with linear bidentate ligands.[39b,c,d]

The interpenetrating diamondoid net structure is also found in styrene-isoprene star-block copolymers, as well as in linear polystyrene-polydiene diblock copolymers.[40] It also occurs in lipids (glycerol monooleate), where the lipid forms a single three-dimensional bilayer separating two continuous interlinked water networks of diamondoid symmetry.[41]

Some Hypothetical Interpenetrating Diamond Nets

The idea we had was to form a hypothetical net of diamondoid AX_2 interpenetrated by a similar net of BY_2 (see **5** where A and B are the big circles). Candidate structures are the aforementioned β-cristobalite type structures of SiO_2 and BeF_2. We add GeO_2 (Ge–O = 1.73 Å) as a possible alternative, even though we found no evidence of a β-cristobalite form of GeO_2 in the literature.[42] Electronic structure calculations of the extended Hückel type (parameters may be found in the Appendix) were done on $BeF_2 \cdot SiO_2$ (and $BeF_2 \cdot GeO_2$) and compared with the lattices of isolated BeF_2 and SiO_2.[43] We took a lattice parameter of 7.17 Å, which would correspond to Be–F = Si–O = 1.55 Å

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Table 1. Atomic Parameters Used in the Calculations

atom	orbital	H_{ii}(eV)	ζ
Be	2s	−10.0	0.975
	2p	−6.0	0.975
F	2s	−40.0	2.425
	2p	−18.1	2.425
Si	3s	−17.3	1.383
	3p	−9.2	1.383
O	2s	−32.3	2.275
	2p	−14.8	2.275
Ge	4s	−16.0	2.160
	4p	−9.0	1.850

(here the Si–O–Si and Be–F–Be angles were assumed to equal 180°). The shortest internet separation is 3.10 Å for Be···Si and 2.53 Å for O···F. The calculated density of such a material is 3.86 g cm^{-3}.

Figure 1 shows the computed density of states (DOS) for the $BeF_2 \cdot SiO_2$ composite, along with the contributions of the two subnets. The SiO_2 net states range from −17.5 eV up to the Fermi level; the prominent peak just below the Fermi level consists of the oxygen lone pairs. The states of the BeF_2 net are below the Fermi level; the peak around −18 eV is composed of the fluorine 2p lone pairs. The F 2s levels are below the energy window of the figure. Other peaks correspond to Si–O and Be–F bonding orbitals.

A comparison of the DOS of the composite with isolated subnets shows that these two nets are pretty much non-interacting, as would be expected from their relatively large separation. The Si–O and Be–F overlap populations change only slightly from the isolated nets to the composite, 0.538 to 0.562 (SiO) and 0.308 to 0.311 (BeF), respectively. Only very weak repulsive interactions are calculated for the internet contacts: Be···Si (overlap population −0.015) and F···O (−0.003). Very similar results are obtained for a hypothetical $BeF_2 \cdot GeO_2$ with a unit cell spacing of 8.0 Å. In this model Be–F = Ge–O = 1.73 Å, yielding a calculated density of 3.93 g cm^{-3}.

Even though the interpenetrating nets do not interact much, they are almost in contact. A small bending distortion at a two-coordinate bridging atom, the most likely simple deformation of one net, is likely to lead to substantial internet repulsion. A reviewer has also pointed out quite correctly that the stress in these lattices may not be distributed uniformly, and superlattice structures might form.

These new types of compounds may have a high bulk modulus; it will take calculations better than ours to determine just how hard they are. In summary, we suggest the existence of a hard phase of silica and beryllium fluoride, one that should be sought synthetically, perhaps following the lines of the preparation of polymorphs of BeF_2.[44]

Appendix

All the calculations are of the extended Hückel type, implemented for extended structures with a tight-binding approach.[45] The atomic parameters, summarized in Table 1, are from the literature: Be,[46] F,[47] Si,[48] Ge.[49]

Acknowledgment. D.M.P. thanks Edith Chan for helpful discussion and Chong Zheng for providing the Silicon Graphics version of the tight-binding extended Hückel program. We are grateful to Qiang Liu for assistance with the calculations and Jane Jorgensen for the drawings. Our work at Cornell was supported by NSF Research Grant No. CHE 89-12070.

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