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Theoretical study of a three-dimensional all-sp^2 structure

Michel Côté, Jeffrey C. Grossman, Marvin L. Cohen, and Steven G. Louie
Department of Physics, University of California at Berkeley and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

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We present a study of a highly symmetric crystal made of exclusively sp^2 bonded atoms. Calculations of the structural and electronic properties are performed within the pseudopotential-density-functional approach for two different compositions made of (i) pure carbon and (ii) carbon and nitrogen compound. In both solids, one of the carbon-carbon bond lengths is found to be 1.35 Å, which is considerably smaller than any carbon-carbon bond length found in other carbon solids. The bulk moduli are calculated to be 241 and 286 GPa for the pure carbon and the carbon-nitride compounds, respectively. We demonstrate that the relatively low bulk moduli, considering the short bond lengths found in the structure, is due to the disruption of the carbon π bonding states. This is probably unavoidable when trying to form a three-dimensional structure out of a planar configuration like the sp^2 bonds. The calculated density of states and band structures show that the pure carbon form is metallic whereas the carbon nitride is semiconducting. When carbon atoms are added to the interstitial regions, the carbon solid becomes insulating and the bulk modulus increases to 282 GPa. [S0163-1829(98)01726-3]

In the search for new hard or low compressibility materials, there have been many attempts to make three-dimensional network structures out of sp^2 bonds. The motivation for these attempts lies in the belief that the compressibility of a structure is related to the bond length found in the system; e.g., the shorter the bonds, the harder the solid. The sp^2 bonded carbon systems have bond lengths smaller than those found in diamond, the hardest material known. On the other hand, graphite is intrinsically soft because of its planar nature. Hence, structures have been proposed[1] where carbon atoms form a three-dimensional network of sp^2 bonding configuration. Some of these attempts, like the H-6 (Ref. 2) and bct-4 (Ref. 3) structures, revealed bulk moduli around 370 GPa that are among the highest known but still lower than the value for diamond.

In this paper, we propose a highly symmetric three-dimensional sp^2 bonded structure. Each atom of this structure is threefold coordinated and forms a planar bonding configuration with its nearest neighbors. The results of the structural and electronic properties of this structure are reported for the two cases where (i) carbon atoms are used in the basis, referred to as C20, and (ii) a combination of carbon and nitrogen atoms is employed, labeled as CN. In both cases, one of the carbon-carbon bond lengths is found to be 1.35 Å, which is much smaller than that found in graphite. Despite this reduction in bond length, the bulk moduli are calculated to be 241 GPa for the C20 solid and 286 GPa for the CN compound. The relative softness of these structures can be attributed to a different bond in the structure that is significantly weaker and easily compressible. This weaker bond has a length of 1.47 Å in the C20 solid and a length of 1.42 Å in the CN compound. In the case of the all carbon structure that is metallic, we found that by interstitially adding extra carbon atoms the solid becomes insulating and its bulk modulus increased to 282 GPa. These findings possibly cast doubts on the hope for a material harder than diamond that is made of a sp^2 network.

Throughout this study, a plane-wave basis pseudopotential total-energy scheme[4,5] is used with an energy cutoff of 60 Ry. We employ the local-density approximation (LDA) (Ref. 6) and used the Ceperley-Alder functional[7] parametrized by Perdew and Zunger[8] for the exchange-correlation energy. *Ab initio* pseudopotentials are generated following the method of Troullier and Martins.[9] The Brillouin zone is sampled at six irreducible k points that have been generated according to the Monkhorst-Pack scheme.[10] The structural parameters were relaxed using a Broyden scheme for the forces and stresses.[11]

The structure that we propose here is shown in Fig. 1. Its unit cell contains 20 atoms but only two are inequivalent; the remaining atoms are obtained by the symmetry of the crystal.

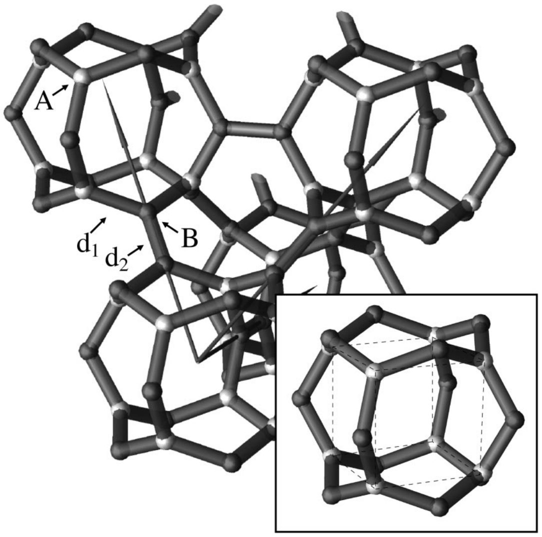

FIG. 1. Ball and stick model of the structure considered in this work. The inset shows a particular choice of the basis atoms. Type A and B atoms as well as the two inequivalent bond lengths d_1 and d_2 are identified.

TABLE I. Calculated structural parameters for the carbon (C20), the carbon-nitride (CN), and the 22 carbon (C22) solids. The positions of the basis atoms are given by the two parameters a and b. Type A atoms are at the corners of a cube, which in Cartesian coordinates correspond to (a,a,a), and all the symmetry related positions. Type B atoms are located on the edges of the cube at $(b,b,0)$ and all the other symmetry related positions. The bond lengths d_1 and d_2 are described in the text. For comparison, the structural parameters for graphite and diamond calculated within this method are also listed.

Solid	Volume/Atom (Å^3)	a,b (Å,Å)	d_1 (Å)	d_2 (Å)	E_{coh} (eV/atom)	B (GPa)
C20	9.34	1.262, 1.792	1.468	1.348	7.907	241
CN	8.65	1.231, 1.731	1.420	1.357	7.131	286
C22	8.62	1.384, 1.805	1.507	1.345	8.490	282
Graphite	8.74		1.42		8.868	30
Diamond	5.57		1.54		8.863	448

A particular choice of the basis atoms is displayed in the inset of Fig. 1. As we can see from the dashed line shown in the inset, one type of atom is located at the corners of a cube and the other type is near the edges. However, this latter type is not directly between two corner atoms but further from the center of the cube. We will refer to the corner atoms as type A atoms and the near edge atoms as type B. There are eight atoms of type A and 12 atoms of type B per unit cell. The crystal is made by repeating this basis in a fcc lattice. From such a construction, one can see that the basis has all the symmetries of the bravais lattice and therefore this structure has the highest symmetry possible for a periodic system. Due to this high symmetry, there are only two unique bond lengths: the bond between the type A and B atoms that we refer to as d_1 and the other inequivalent bond between the type B atoms across different unit cells that is labeled d_2. In the CN compound, type A atoms are nitrogen and type B atoms are carbon. It is unfavorable to assign type B atoms to be nitrogen since the resulting crystal would have nitrogen-nitrogen bonds between the unit cells.

Total-energy calculations have been performed for these two solids, where the structure has been relaxed for every volume considered. From the equation of states, it was possible to extract equilibrium configurations, binding energies, and bulk moduli (Table I). One interesting observation from the table is that the d_2 bond length, which is a carbon-carbon bond in both cases, is significantly smaller than the bond length found in sp^2 systems like graphite or C_{60}. In fact, this kind of bond length is more often associated with the double bond in carbon systems. When considering these shorter bond lengths alone, one might hope for large bulk moduli, however, our calculations indicate that these structures are surprisingly compressible.

Figures 2 and 3 show the percentage change of both bond lengths as a function of the change of the unit-cell length. The dashed line represents the value of the bond if one were to isotropically compress the structure from its equilibrium configuration. We can see that, in both cases, the d_2 bond is stiffer than the d_1 bond. The low bulk moduli of these structures is due in part to the compressibility of the d_1 bond. The remaining effect is in the flexibility of the angle between the d_1 and d_2 bonds; this angle decreases as the structure is compressed, resulting in a decrease of volume.

The reason why the d_2 bond is significantly shorter and stiffer than bond lengths found in graphite can be understood by considering the local environment of this bond; namely, the ability of the atoms to form π bonds with their neighbors. Since each atom is in a planar environment with its neigh-

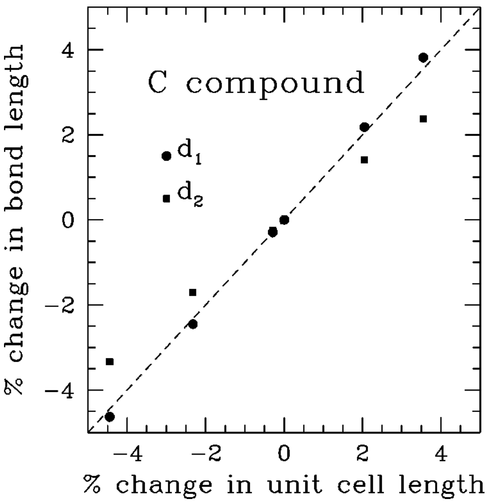

FIG. 2. Graph of the percentage changes of the two bond lengths for the C20 solid with respect to the percentage change in the unit-cell length.

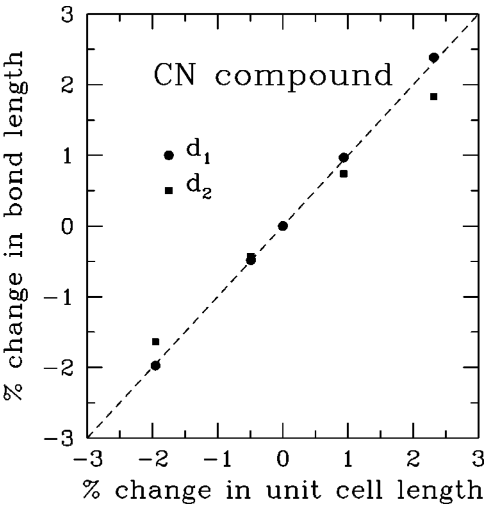

FIG. 3. Graph of the percentage changes of the two bond lengths for the CN compound with respect to the percentage change in the unit-cell length.

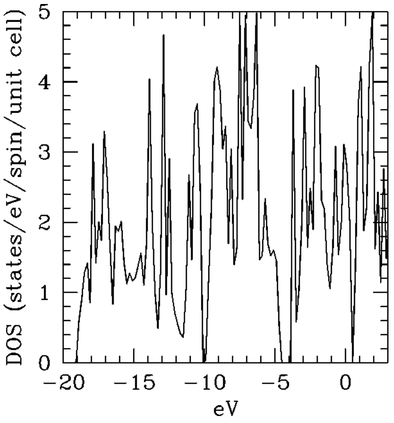

FIG. 4. Density of states per eV per spin per unit cell for the C20 solid.

bors, we can define a normal to this plane for each atom. This normal is the direction of the π state on that atom. Type A atoms have all their nearest neighbors of type B, which, however, have all their π states perpendicular to the type A atoms. The fact that these π states on neighboring atoms are perpendicular reduces the possibility of π bonding between these atoms. This is the reason why the d_1 bond length is longer than in graphite for the C20 solid and softer upon pressure. We can see that when type A atoms are replaced by nitrogen, the bond length decreases, making this weak bond slightly stiffer, which is expressed in the larger bulk modulus of this compound versus that of the pure carbon compound.

On the other hand, one of the neighbors of type B atoms is another type B atom and they both have their π states in the same direction. Therefore the π states of these atoms can bond. Moreover, their π states cannot be shared with the other two neighbors of type A, resulting in a very strong bond between the two type B atoms. In fact, the d_2 bonds are so strong that if the volume change were governed by just those bonds, these structures would have bulk moduli of 486 and 434 GPa for the carbon and carbon nitride compounds, respectively. This effect of disrupting the π bonding state was already observed in fullerenes[12] and in other three-dimensional sp^2 structures such as the bct-4 and H-6;[3] however, in those cases the bond lengths were larger than in graphite.

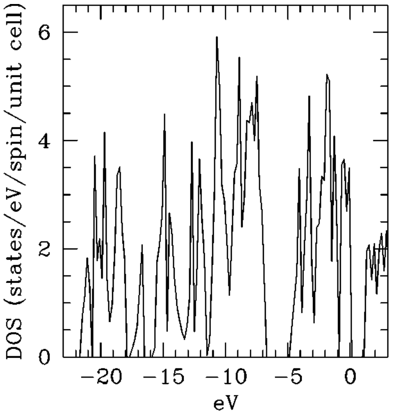

FIG. 5. Density of states per eV per spin per unit cell for the CN compound.

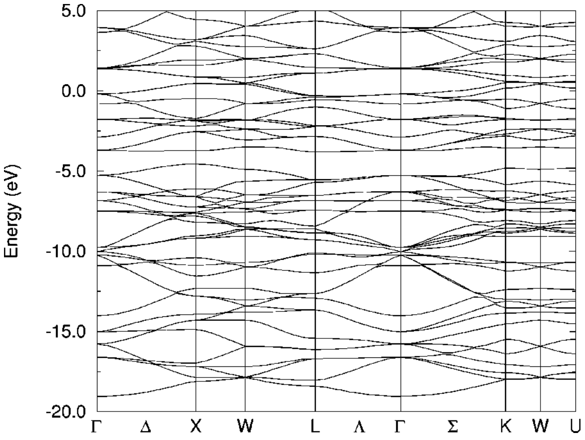

FIG. 6. Band structure for the C20 solid.

Figures 4 and 5 show the density of states per spin per unit cell for the two solids. When the structure is composed of carbon atoms only it is found to be metallic, whereas with the nitrogen, it is semiconducting with a gap of 1 eV. Because LDA has the tendency to underestimate gaps, the real gap is likely to be larger than this value. The band structures for both of these materials are displayed in Figs. 6 and 7.

We have also examined the angular decomposition of the density of states and the energy resolved charge density in order to assess the features in these plots. In the C20 solid, the dip in the density of states at -10 eV corresponds to the separation between the lower energy s orbitals and the higher energy p orbitals of carbon. This kind of separation is also observed in other carbon materials such as diamond and graphite. In the p orbital energy range, the states between energies -10 and -5 eV are those forming the sp^2 bonding network between the atoms. At -4 eV there is an energy gap that separates the sp^2 states and the states between -4 and -1 eV that are located on type B atoms and make up the π double bonds between those atoms. Near the Fermi level, the states correspond to partially occupied π orbitals on type A atoms.

For the CN compound, the energy gap at around -5 eV is larger than in the C20 solid. As in the previous case, the states below this energy gap correspond to sp^2 bonding

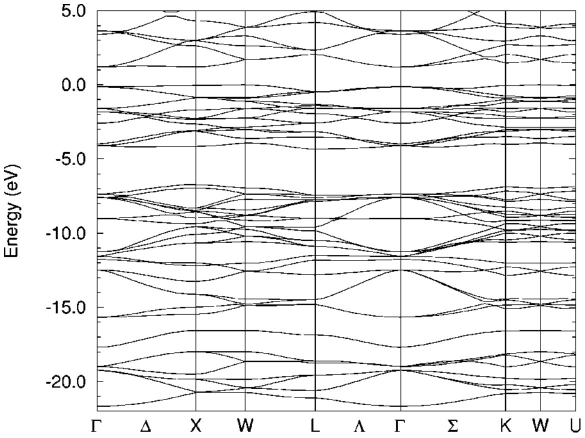

FIG. 7. Band structure for the CN compound.

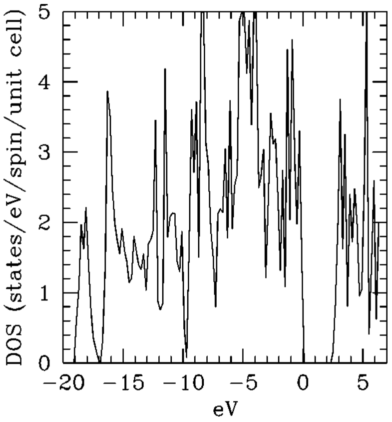

FIG. 8. Density of states per eV per spin per unit cell for the C22 solid.

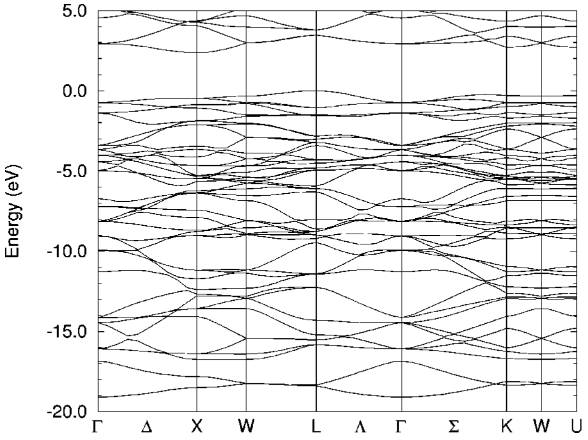

FIG. 9. Band structure for the C22 solid.

states whereas those above form the double bond on the carbon (type B) atoms. The valence states at the Fermi level are essentially made of the π orbitals on the nitrogen (type A) atoms and we observed a contribution of those orbitals down to the energy gap at -5 eV. The fact that this material is insulating can be explained by the occupation of these orbitals, which are filled for CN but only partially filled for C20. The fundamemtal gap in the carbon-nitride compound is indirect from the occupied state at W to the unoccupied state at Γ.

The binding energy of the C20 solid is 7.9 eV per atom (Table I), which is about 1 eV lower than the binding energy of graphite within this method. This difference reflects the unfavorable bonding between type A and B atoms. It is difficult to comment on the binding energy of the CN compound since we do not have other compounds with the same stoichiometry with which to compare.

In the case of the C20 solid, the low binding energy and the fact that it is metallic can be understood by considering the π orbitals of the A atoms at the Fermi level. As discussed above, these orbitals cannot bond with their neighbors and therefore do not contribute to the binding energy of the crystal. It is possible to correct this deficiency by introducing extra atoms that provide the possibility for those orbitals to form bonds. The cavity between the unit cells in which these π orbitals are pointing has tetrahedral symmetry and the distance between the A atoms and the center of the cavity is slightly larger than the bond length in diamond, making it an ideal location for an extra carbon atom. In Fig. 1, this cavity is in the middle of the four basis units depicted. Placing an atom in this cavity corresponds to adding two atoms in the unit cell located at $\pm(0.25,0.25,0.25)$ in terms of the lattice vectors.

We have fully relaxed this structure, which we refer to as C22, and calculated the same properties as for the other structures (see Table I). Although the volume per atom decreases, the volume of the unit cell actually increases by 1.5%. Note that d_1 becomes larger as the A atoms move toward the added carbons. The resulting bond length between the A atoms and the atom in the middle of the cavity is 1.552 Å. The binding energy of the crystal is 8.5 eV/atom, which is significantly increased and roughly the same as for C_{60}.

In this C22 structure, the type A atoms have less freedom to move due to their extra bonding and this is reflected in the larger bulk modulus as compared with the C20 solid. The density of states for the C22 solid is shown in Fig. 8 and its band structure is given in Fig. 9. The additional atoms cause the solid to be insulating with a calculated energy gap of 2.3 eV, indicating that all the orbitals are now satisfied (i.e., the π orbitals of the type A atoms are now able to form bonds with the added atoms). Indeed, contrary to the C20 solid, the valence and conduction states at the Fermi level correspond to the double bond states on type B atoms. The π orbitals on the A atoms have moved down in energy forming bonds with the orbitals of the added atoms. Consequenly, the gap between the sp^2 states and the double bond states (previously at around -5 eV) is now filled because of the presence of sp^3 bonds in the system. As shown in Fig. 9, the gap is indirect from the occupied state at L to the unoccupied state at X.

If one of the pure carbon solids were to form, it would certainly have interesting electron-phonon properties. The strong double bond would have a significantly higher vibrational frequency that could be identified in infrared or Raman spectroscopy. Since the 20 carbon compound is metallic, it might be a superconductor. The C22 solid can be doped to be made metallic. Interestingly, in the case of the carbon-nitride compound it has a stoichiometry that is often observed in the synthesis of carbon-nitride thin films.[13,14] The x-ray signature of this structure should be easily identifiable since it is cubic and the different bonding environments between graphite and these types of double bonds should reveal itself in core-level shift measurements.

In conclusion, we have studied and proposed a highly symmetric three-dimensional sp^2 bonded structure with a composition of carbon or carbon and nitride atoms. The nature of the bonding environment is such that one of the carbon-carbon bond lengths is significantly smaller than that found in any other carbon solid. However, the calculated bulk modulus is in the 250–300 GPa range, which is much lower than an estimate would give based on the bond length alone. These low bulk moduli are caused by the disruption of the π binding states that is probably unavoidable when trying to form a three-dimensional structure out of a planar configuration like the sp^2 bonds.

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