New sheet structures may be the basis for boron nanotubes

The triangular boron lattice has too many electrons, and the hexagonal lattice has too few. But a hybrid of the two is just right.

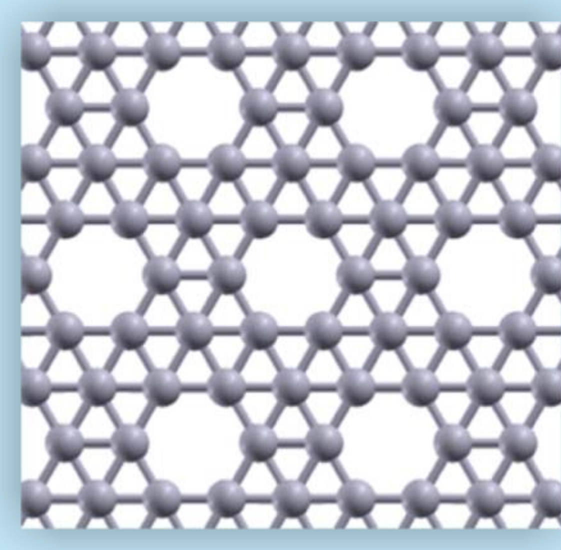

Figure 1. Many new boron-sheet structures can be formed by removing atoms from a triangular lattice to make hexagonal holes. In the pictured lattice, found to be the lowest in energy of that class of structures, $1/9$ of the atoms have been removed and the holes are as evenly spaced as possible. (Adapted from ref. 1.)

Carbon nanotubes are interesting to materials scientists for a variety of reasons, one of which is the nanotubes' electronic behavior. Depending on their structure, they can be either conductors or semiconductors, so they have the potential to perform many different functions in miniaturized electronic technology. The problem is that the structure can't readily be controlled: Known methods of synthesis always yield a mixture of conducting and semiconducting nanotubes, which need to be separated before their electronic properties can be exploited in devices.

That challenge, along with the quest for an even more diverse range of nanotube properties, has led some researchers to turn their attention to nanotubes of other materials whose electronic properties may be both desirable and uniform. Nanotubes have been synthesized of many inorganic materials, including molybdenum disulfide, titanium dioxide, boron nitride (pictured in the article by Marvin Cohen, PHYSICS TODAY, June 2006, page 48), and pure boron.

Carbon's neighbor to the left in the periodic table, boron poses theoretical challenges as a nanotube material that carbon doesn't. Carbon's natural ground-state structure is graphite, a layered material whose sheets (called graphene, and described by Andrey Geim and Allan MacDonald in PHYSICS TODAY, August 2007, page 35) form the basis for carbon-nanotube structures. But elemental boron tends to form networks of icosahedral clusters, not planar sheets that might be rolled up to form nanotubes. Since the energetically preferred boron-sheet structure doesn't occur naturally, scientists have had to look for it. Now, Yale University's Sohrab Ismail-Beigi and his student Hui Tang have made some progress toward that goal.[1] They performed theoretical calculations on a new class of two-dimensional boron sheets and found a sheet that is lower in energy than any structure previously considered.

The graphene-like hexagonal lattice is far from the ideal structure for a boron sheet. It's the ideal structure for carbon, which has four valence electrons per atom: exactly enough to fill all of the bonding (or stabilizing) electronic orbitals but none of the antibonding (destabilizing) orbitals. But when the carbon atoms are replaced by boron atoms, which have only three valence electrons, there aren't enough electrons to fill all the bonding orbitals, and the structure is not stable.

At first glance, the triangular boron lattice may look even worse. After all, if a boron atom doesn't have enough electrons to form stable bonds with its three nearest neighbors in the hexagonal lattice, how can it possibly bond to six nearest neighbors in a triangular lattice? The answer is that the triangular lattice allows the kind of chemical bonds that boron forms best: bonds among three atoms rather than between two. Such three-center, two-electron bonds have been recognized for decades as an important part of boron's complex and diverse chemistry.

The ground state of the triangular boron lattice is electronically degenerate. The degeneracy is lifted, and the energy thus lowered, when the sheet buckles slightly. Before Tang and Ismail-Beigi's work, the buckled triangular lattice was the 2D boron-sheet structure with the lowest known energy. Researchers figured that boron nanotubes would be made of rolled-up pieces of the buckled triangular lattice, with the buckles running either parallel to the length of the tube or in helices around it. Calculations showed such structures to be stable.[2]

Tang and Ismail-Beigi considered a new class of sheet structures, derived from the triangular lattice but with some atoms removed to form hexagonal holes. They found that both the number and the arrangement of the hexagonal holes affect the sheet's energy. The optimal density is one hole for every nine atoms in the original triangular lattice, and the optimal hole arrangement tends to be as evenly spaced and far apart as possible. Of all of Tang and Ismail-Beigi's structures, the lowest in energy is thus the one shown in figure 1. But they found many other structures that were lower in energy than the buckled triangular lattice. The researchers considered buckled versions of their structures too, but found the flat versions to be lowest in energy.

The straight dope

To understand the greater stability of the new structures, think of them as hexagon-doped triangular lattices. The hexagonal boron lattice doesn't have enough electrons to form all the necessary bonds: Its Fermi energy (shown as a black vertical line in the density-of-states plot in figure 2) lies below the boundary between the bonding and antibonding orbitals (at which the density of in-plane states is zero). The sheet

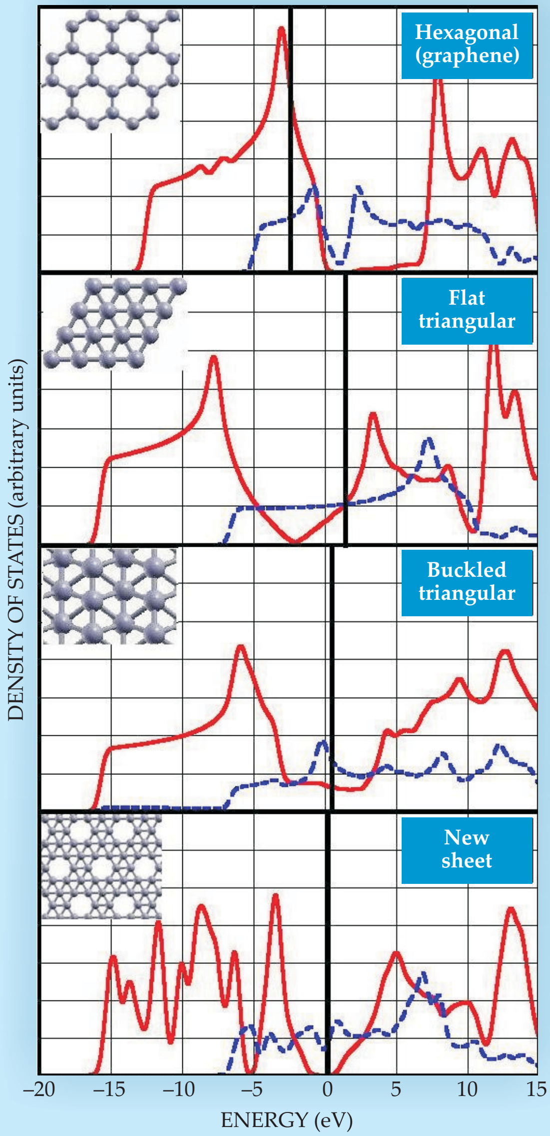

Figure 2. The density of states calculated for several boron-sheet structures. The states are divided into in-plane (solid red line) and out-of-plane (dashed blue line) orbitals. The black vertical lines correspond to the Fermi energies, which mark the boundary between filled states to the left of the line and empty states to the right. In each of the flat structures—the hexagonal lattice, the flat triangular lattice, and the new sheet—the boundary between bonding and antibonding orbitals is marked by a zero in the density of in-plane states. (Adapted from ref. 1.)

thus acts as an electron acceptor. The triangular lattice, on the other hand, has a Fermi energy that's too high: Some electrons are forced to occupy antibonding orbitals that have a destabilizing effect, and the sheet tends to act as an electron donor. By combining the electron-donating triangles with electron-accepting hexagons, Tang and Ismail-Beigi were able to tune the Fermi energy so that all the bonding orbitals are filled and all the antibonding orbitals are empty.

Figure 2 reveals another important fact about the sheets' electronic properties. For the boron hexagonal lattice, zeroes in the in-plane and out-of-plane densities of states coincide. The same is true for graphene: The total density of states at the Fermi energy is zero, but there is no bandgap between the occupied and unoccupied orbitals. The electronic properties of carbon nanotubes derived from graphene are thus very sensitive to the density of states right around the Fermi energy, which in turn depends on the tube's structure. For the lowest-energy boron sheet, however, the in-plane density of states is zero but the out-of-plane density of states is not. That means that the boron sheet, or any nanotube made from it, should be an excellent electrical conductor via the out-of-plane orbitals.

Earlier this year researchers from Rice University, led by Boris Yakobson, did some similar calculations on boron clusters,[3] and their results are consistent with the doping interpretation. Yakobson and colleagues found that boron can form highly stable cage-shaped clusters of 80 atoms each. The clusters have the soccer-ball structure of C_{60} fullerenes, but with an additional boron atom at the center of each hexagonal face. The cages are thus made up of triangles and pentagons, and they are probably stabilized in the same way as Tang and Ismail-Beigi's lattices, made up of triangles and hexagons.

Knowing what structures boron nanotubes are likely to have can be helpful in fabrication and synthesis efforts, according to Lisa Pfefferle, Ismail-Beigi's Yale colleague who heads the only group so far to have synthesized boron nanotubes.[4] A commonly used technique for confirming the presence of nanotubes in a sample is to look in the Raman vibrational spectrum for a characteristic low-frequency mode that corresponds to the radial expansion and contraction, or "breathing," of the nanotube. That frequency depends on both the tube's diameter and its structure.

Pfefferle and her coworkers have some control over their nanotubes' diameters—they grow the tubes inside the parallel pores of a mesoporous catalyst—so it's especially useful for them to know what structure to expect and how that structure influences the breathing-mode frequency. There's also the possibility that knowing what structures to aim for, and how those structures might be stabilized by a catalyst, could help them to refine their synthesis process.

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References

1. H. Tang, S. Ismail-Beigi, *Phys. Rev. Lett.* **99**, 115501 (2007).
2. A. Quandt, I. Boustani, *ChemPhysChem* **6**, 2001 (2005).
3. N. Gonzalez Szwacki, A. Sadrzadeh, B. I. Yakobson, *Phys. Rev. Lett.* **98**, 166804 (2007).
4. D. Ciuparu, R. F. Klie, Y. Zhu, L. Pfefferle, *J. Phys. Chem. B* **108**, 3967 (2004).