

## Electronic structure of schwarzite

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We examine the electronic structure and total energies of schwarzites (negative-curvature analogs of the fullerenes). These structures have curvature induced via the presence of seven- or eight-membered rings. *Ab initio* dynamical relaxations reveal that these structures are closer in energy to graphite than are the fullerenes. Analysis of the electronic structure of these curved nets shows that they have a substantial gap of approximately 1.3 eV, which results from the curvature of the underlying structure.

The discovery of solid  $C_{60}$  has raised the possibility that carbon may adopt a variety of exotic structures in the solid state. Indeed, recent reports on the existence of carbon tubules<sup>1</sup> indicate that carbon's structural variants have not been exhausted. The fullerenes, like graphite, are formed of sheets of atoms, but with positive Gaussian curvature induced by the presence of five-membered rings. We consider the energetics and electronic structure of negative-curvature analogs of the fullerenes (schwarzite); structures whose curvature is introduced by seven- and eight-membered rings.

Work on the structure of periodic minimal surfaces<sup>2</sup> suggests that the fullerenes are but one of the ways in which curvature can be introduced into graphitelike nets. An alternative set of structures has been dubbed the schwarzites.<sup>2-4</sup> (See Fig. 1 for an example of such a structure.) These structures have negative Gaussian curvature introduced by the presence of seven- or eight-

membered rings, in contrast to the fullerenes which have positive Gaussian curvature as a consequence of their five-membered rings. As in  $C_{60}$ , all atoms in the schwarzites are threefold coordinated.

As yet there have been no systematic studies of the electronic structure of the schwarzites. Earlier work using phenomenological energy functions based upon bond-bending forces found that the schwarzites are closer in energy to graphite than is solid  $C_{60}$ .<sup>3,4</sup> However, many issues remain unclear. It is important to determine the structural energies for these various carbon nets using more reliable methods since the earlier phenomenological results differ substantially. In addition, the roles of both curvature and the odd-membered ring topology in determining the nature of the electronic structure have not been established. An electronic-structure-based method is essential to infer the electronic density of states and related information such as the existence of a band gap.

We have carried out *ab initio* dynamical relaxations of four proposed schwarzite structures.  $P216$  is a simple cubic structure with 216 atoms per cell, with only six- and seven-membered ring topologies (c.f. Fig. 1).<sup>3</sup>  $P192$  is based upon the bcc lattice and has only 192 atoms per cell and contains eight-membered rings.<sup>2</sup> We have also considered two structures based on the diamond lattice.  $D216$  is a structure with 216 atoms per primitive cell<sup>3</sup> and  $D168$  is a similar structure proposed by Vanderbilt and Tersoff<sup>4</sup> with 168 atoms per primitive cell.

Our *ab initio* dynamical relaxations were carried out using a non-self-consistent Harris functional implementation of the local-density approximation.<sup>5</sup> Nonlocal, norm-conserving pseudopotentials, and a basis set of four local orbitals per site (one  $s$  and three  $p$ 's) with confinement radius  $r_c = 3.3a_B$  were used. This set of approximations has been applied to C microclusters<sup>6</sup> and to a calculation of the vibrational spectrum of  $C_{60}$ .<sup>7</sup> The results are in excellent agreement with state of the art quantum

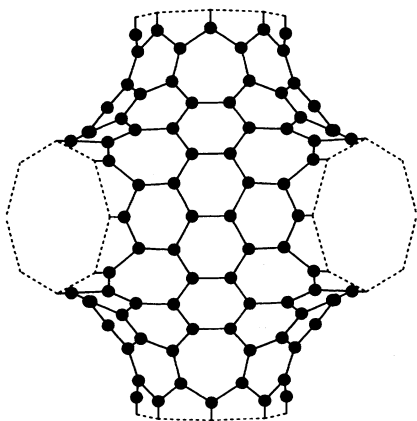


FIG. 1. The  $P216$  structure.

chemistry calculations with much larger basis sets. This *real-space* method is ideal for the present problem because of the rather large cutoffs required for self-consistent Car-Parrinello simulations of carbon.

To study the schwarzite polymorphs, we begin with the four structures described above, and relax them at fixed volume. The forces and total energies are calculated using only a single  $k$  point ( $k=0$ ), and the structures are relaxed until the energy change per step is less than 0.002 eV/atom. As a check that the  $k$ -point sampling is adequate, we also used other high-symmetry points within the Brillouin zone and find that the total energies and the electronic density of states (DOS) are essentially unchanged. The proposed structures are remarkably close to a minimum in the total energy, and only minor rearrangements were obtained upon relaxation. In Table I we show the structural energies associated with  $C_{60}$  and the schwarzites measured relative to graphite. The graphite energy is for a single carbon layer, with the *ab initio* lattice constant of 1.416 Å. The energies for both  $C_{60}$  and the schwarzite structures are for the relaxed structures. Typical relaxation energies are of order 0.05 eV/atom. As in the earlier total energy calculations, we find that the schwarzite structures are much closer in energy to graphite than is  $C_{60}$ .

These calculations suggest that the schwarzites are *energetically* feasible. This does not by itself provide sufficient evidence to predict the existence of these structures in nature. In addition to the energy differences separating the schwarzites from graphite, there are significant kinetic factors which determine whether a given structure may be nucleated or not. Unfortunately, the barrier to the nucleation of the schwarzites is unknown. However, similarities between the radial distribution function of random schwarzites and that observed in thin films of amorphous carbon suggest the tantalizing possibility that schwarzites already exist.<sup>8</sup>

By analogy with graphite, it might be expected that the  $\pi$  and  $\sigma$  manifolds would be decoupled, with the resonance of the  $\pi$  orbitals resulting in metallic, or semimetallic, behavior. Surprisingly, we find that in all four schwarzite structures there are significant gaps, indicating semiconducting or insulating behavior. The gaps are shown in Table II. The gaps reported above are the difference in energy between the highest occupied orbital and lowest unoccupied orbital at  $k=0$  for the relaxed structures. To insure that the presence of these gaps is not an artifact of partial Brillouin-zone sampling or an incorrect unit-cell volume, we have examined the behavior of the electronic states as a function of both the atomic volume, as well as

TABLE I. Energies of structures relative to graphite (measured in eV/atom).

Structure	LDA	Ref. 3	Ref. 4
P216	0.212	0.197	...
D216	0.216	0.182	...
P192	0.193	0.186	...
D168	0.249	0.218	0.11
$C_{60}$	0.438	...	...

TABLE II. Band gaps for various schwarzites.

Structure	Gap (eV)
P216	1.35
D216	1.24
P192	1.29
D168	1.34

at different points in the Brillouin zone. We find that for the whole range of volumes from  $0.91\Omega_{\text{ideal}} < \Omega < 1.09\Omega_{\text{ideal}}$ , the gap remains larger than 1.2 eV for the P216 structure. Similarly, calculation of the spectrum at the zone edges in both the (100) and (111) directions reveals the presence of a gap larger than 1 eV. Furthermore, we find that the relaxation of the structures increases the gap.

Two possible origins for the gap in the schwarzites are the curvature of the structures, which modulate the interatomic couplings, or the difference of their topology from that of graphite as manifested through the presence of odd-membered rings.<sup>9</sup> Armed with the knowledge that the  $\pi$  orbitals are the relevant orbitals near  $\epsilon_f$ , we have used a simple Hückel model to investigate the dependence of the electronic structure on both of these effects. The Hamiltonian is

$$H = - \sum_{(ij)} t_{ij} c_i^\dagger c_j, \quad (1)$$

where the sum is over near neighbors, and spin indices have been suppressed. This Hamiltonian describes the contribution of the  $\pi$  orbitals to the electronic states, with  $t_{ij}$  the hopping strength from site  $i$  to site  $j$ .

One of the crucial features of the schwarzites is their curvature. A consequence of this curvature is misalignment of the local normals at each site. This misalignment has the effect of reducing the coupling between  $\pi$  orbitals to

$$t_{ij} = t_\pi |\hat{n}_i \cdot \hat{n}_j|, \quad (2)$$

where  $\hat{n}_i$  and  $\hat{n}_j$  are the local normals at sites  $i$  and  $j$ . To examine the role of this misalignment we have calculated the electronic structure both with and without the  $\hat{n}_i \cdot \hat{n}_j$  modulation. In the absence of the  $\hat{n}_i \cdot \hat{n}_j$  factor, the calculation reflects only the topology of these structures, while the modulation described in Eq. (2) incorporates their curvature as well. The local normals at each site may be defined in a variety of ways, and we have chosen one of the simpler schemes.<sup>10</sup> The three near neighbors of a given atom define a plane, and it is the normal to this plane that defines our local  $\pi$ -orbital alignment. Manousakis has performed careful tight-binding calculations on  $C_{60}$  which suggest that  $t_\pi = 2.5$  eV.<sup>11</sup> For our calculation with the angular modulation due to  $\pi$ -orbital misalignment, we have taken  $t_\pi = 2.7216$  eV. This choice insures that when we calculate the electronic structure of undimerized  $C_{60}$  we recover Manousakis' results. The numerical value reflects the fact that in undimerized  $C_{60}$ ,  $|\hat{n}_i \cdot \hat{n}_j| = 0.9186$ , since the angle between local normals is  $23.28^\circ$ .

In the absence of the modulation, with  $t_\pi = 2.5$  eV, we find that although there is a gap of 0.87 eV at the  $\Gamma$  point,

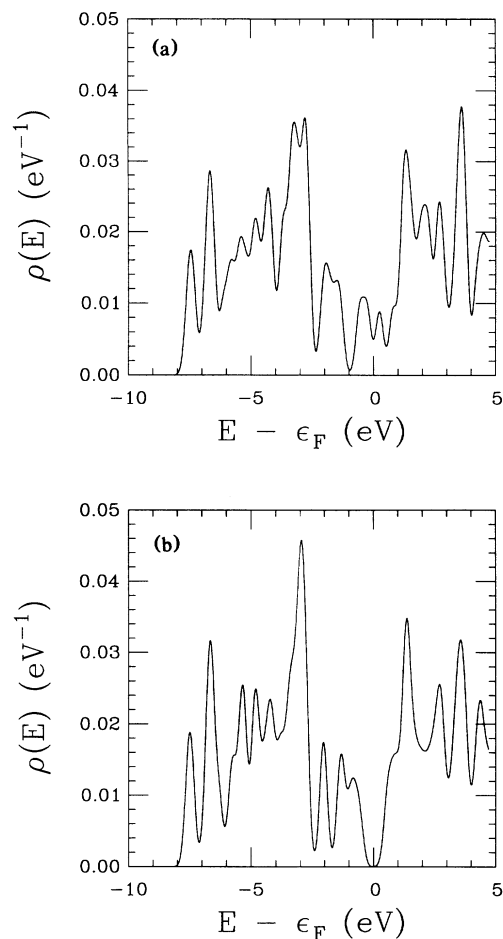


FIG. 2. (a)  $\pi$  electron density of states for *P216* in absence of local normal modulation. (b)  $\pi$  electron density of states for *P216* in presence of local normal modulation.

the gap in *P216* vanishes at the (100) zone edge. On the other hand, when we use the modulation defined in Eq. (2), a gap of 0.9 eV is found in the *P216* spectrum, which remains along both the (100) and (111) directions. The calculations with and without the modulation described by Eq. (2) are contrasted in Fig. 2 where we show the densities of states for the  $\pi$  orbitals. The DOS is calculated by applying a Gaussian broadening to the (111) zone-edge eigenvalues. We attribute the opening of the gap in these structures to the distribution of couplings which result from their curvature. In the absence of the modulation, all the hopping matrix elements between near neighbors are equal. On the other hand, with the modulation present there is a distribution of hopping strengths, with the lowest value coming from local normals which are  $34.21^\circ$  apart. In much the same way that dimerization in linear structures like polyacetylene is known to open a gap, the schwarzites appear to acquire a gap by virtue of their curvature which has the same effect on the couplings as do variations in bond length.

In summary, we have calculated the total energies of hypothetical negative-curvature analogs of the fullerenes, and shown that they are much closer in energy to graphite than in solid  $C_{60}$ . We predict that in the event that the schwarzites can be synthesized, they will exhibit semiconducting or insulating properties as a result of a substantial gap in their spectrum. Gap formation in these structures has been shown to result from their curvature which leads to a misalignment of neighboring  $\pi$  orbitals.

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