

Theory of diamondlike amorphous carbon

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First-principles methods are used to study diamondlike amorphous carbon. Several structural models are introduced, and the topological, electronic, and vibrational properties are discussed. We explore the nature of defects in the amorphous network, and particularly the atomistic origin of the virtually defect-free optical gap. We observe that threefold-coordinated defects *pair*, and that this is important for obtaining a gap free of localized defect states as seen in experiments.

I. INTRODUCTION

One of the principal efforts of contemporary research in semiconductors is the quest for new materials with better electronic, thermal, and other properties. A particularly noteworthy effort has been devoted to diamond. Crystalline diamond is widely believed to have unique potential as an electronic device if two difficult problems can be overcome: (1) the lack of a shallow donor impurity and (2) the difficulty of establishing good Ohmic contacts. If these obstacles could be eliminated, it could revolutionize microelectronics [for example, the standard rf amplifier " $\omega^2 L$ " figure of merit is 8200 times larger for diamond than Si Ref. 1]. Recently, McKenzie *et al.*² and subsequently others³ have grown an *amorphous* form of carbon "tetrahedral amorphous carbon" (ta-C), which does not suffer from the difficulties (1) and (2). Like diamond, it has high mechanical hardness and chemical inertness.⁴ It is stable to about 700 °C.⁵ This material has been shown to be largely fourfold coordinated,^{2,6} and has been doped *n* type with both phosphorous⁷ and nitrogen.⁴ Moreover, these donors are shallow (the activation energy for P is about 0.12 eV⁷), and simple devices (a heterojunction diode⁷ and bipolar transistor⁸) have already been fabricated and characterized.

It is important to emphasize how unexpected and unusual these results are. In *a*-Si, it is apparently impossible to make devices from the *unhydrogenated* material. Qualitatively, it is clear that H passivates defects in the *a*-Si network. The *a*-Si:H network can then be doped *n* or *p* type, and useful devices can be fabricated since the carrier mobility is reasonably large. While the resulting *a*-Si:H devices are quite useful, there are limitations which are connected with hydrogenation: particularly with respect to the stability of the material. ta-C on

the other hand possesses an essentially defect-free gap of about 2.0 eV *without hydrogenation*, and generally resembles the other wide gap semiconductors. Moreover, measurements of the ta-C radial distribution function show that the material is topologically very similar to low defect *a*-Si. Clearly the explanation of the difference in the electronic density of states (DOS) lies in the chemical differences between Si and C.

In this paper, we will take a major step toward understanding the physics of ta-C. We will concentrate here on (1) producing structural models consistent with experiments on the material, (2) how a disordered column IV material can have a gap free of defect states, and (3) the geometrical and electronic nature of defects in ta-C. In future publications, we will report theoretical studies of doping. This paper will emphasize a cell we have created at a density near that of ta-C that has a gap containing no defects. We will also briefly comment on several other cells which have been proposed, or seem to be suitable structures to investigate. In this connection we emphasize that it is important that small (up to several hundred atom) supercells should have *no* localized midgap defects to faithfully model the real material. We note that a gap containing only two defect states in a supercell containing 64 or even 216 atoms, corresponds to electronically unacceptable material with a very high density of states in the gap. For example, if only 1% of the atoms constitute defects (about 2 out of 216 atoms), this corresponds to a defect density of about 7.8×10^{21} defects/cm³. If these were spread uniformly over a gap of 2.5 eV, the density of states would be about 7.1×10^{19} /cm³ eV. These are unphysically high numbers. In Ref. 7 a density of states of 10^{18} /cm³ eV is reported at the Fermi surface, which is 0.2 eV above the valence band and the DOS is decreasing exponentially into the gap.

II. PREVIOUS WORK

As the density of *a*-C increases, one expects a higher fraction of sp^3 C atoms at the expense of sp^2 C atoms. This has been observed experimentally and was first obtained in molecular dynamics (MD) simulations by Frauenheim and co-workers. Frauenheim *et al.*⁹ were primarily concerned with trends in sp^3 concentration as a function of density and H concentration. Their computational scheme, a hybrid density functional—nonorthogonal tight-binding method, seems able to correctly describe C bonding in the challenging amorphous environment. These workers noted that for a density of $\rho = 3.3 \text{ gm/cm}^3$, an sp^3 concentration of over 80% was obtained, in reasonable agreement with experiments.

Orthogonal empirical tight binding has been used to simulate sp^3 amorphous C.¹⁰ In such empirical electronic structure calculations, using an imagined orthogonal basis, researchers fit their Hamiltonian to experimental data and/or more sophisticated calculations. It is claimed that this amounts to a Löwdin orthogonalization of the basis. This is true however, *only* for the local environment originally fit to. There is no reason to suppose that the same Löwdin transformation would apply in a different bonding environment. Thus there is no *a priori* reason to believe that an orthogonal empirical tight-binding Hamiltonian is highly transferable. Menon and Subbaswamy¹¹ has demonstrated that such an assumption of orthogonality reduces transferability for C microclusters. Finally, the reported electronic density of states does not agree with experiments;⁷ there are many localized states midgap. We show later in this paper that a clean gap does *not* require pure fourfold coordination as conjectured by Wang and Ho.¹⁰

Tersoff¹² has performed calculations with an empirical potential which suggest that an sp^3 -bonded network would be badly strained and he suggested that the reported sp^3 fraction might be too large and that alternative form of *a*-C with nearly equal sp^2 and sp^3 content could be more plausible. It now seems clear that his structure is not representative of *ta*-C: there is unambiguous experimental evidence of an sp^3 content approaching 90%.^{6,5}

Pailthorpe and co-workers^{2,13} have performed interesting classical simulations of 1–100 eV neutral C atoms incident on a diamond (111) surface. The C-C interactions were based on a reparametrized Stillinger-Weber potential. These workers show that for energies of ≈ 20 –60 eV, there is ion penetration of the surface and an increase in stress that favors quaternary coordination. This work is reasonable for the early stages of atom-surface interaction, when the incident atom energy is greater than typical bond energies at the surface. The details of how the system equilibrates after some of the initial energy is dissipated into the slab is very hard to handle with empirical potentials, however. For the equilibration study the Stillinger-Weber¹⁴ form is somewhat doubtful, since its three body term is incapable of properly differentiating between sp^2 and sp^3 bonding: the energy functional is a simple function of angle with a minimum at 109.47° — the tetrahedral angle. To reliably describe relaxation

effects and equilibration requires first-principles methods capable of *properly* differentiating between sp^2 , sp^3 and more general forms of hybridization. First-principles methods are also required if dopant impurities are present in the beam, since no empirical potentials have been devised to handle such an alloy system. Very similar work was also carried out by Kaukonen and Nieminen,¹⁵ with the empirical Tersoff potential and fairly similar conclusions were drawn. The basic contention of these authors that compressive stress induces fourfold coordination is very important, but needs more work to be completely accepted. While the present paper does not directly repeat the interesting simulations described here, we will provide information about the atomistic microstructure of the *ta*-C material. A comparison between the structures obtained with empirical potentials directly simulating the growth process, and the models we propose, should reflect upon the reliability of the annealing process using the empirical potentials.

III. METHOD

The calculations reported here used *ab initio*, local orbital molecular dynamics as introduced by Sankey and co-workers.¹⁶ This method properly includes several ingredients missing from previous calculations on *ta*-C. First, it has a theoretical foundation: density functional theory within the local density approximation (LDA) and Harris-Foulkes-Haydock functional approximations. The former is very successful for carbon systems, and the latter is a rigorous stationary principle which has been extensively studied^{17,18} and applied to carbon. A local basis set of four compact pseudoatomic orbitals per site with an interaction range of $8.2a_B$ is used to expand the one electron eigenstates. Three center matrix elements are included in the Hamiltonian, the overlap matrix is computed, and the generalized eigenvalue problem is solved. It is important to note that the eigenvalues of the overlap matrix typically range from ≈ 0.1 to 5; the overlap matrix is far from diagonal. The transferability limitations of an orthogonal basis set discussed above are therefore avoided. The total energy expression is precisely the Harris form,¹⁶ and no empirical fits are used in the short range part of the interaction as in Ref. 9.

The local orbital LDA method has been applied to a wide variety of systems involving carbon with success. Carbon microclusters,¹⁹ fullerenes,²⁰ the diamond (100) surface,²¹ and schwartzites²² have been investigated, and produce results close to self-consistent plane wave methods²³ and quantum chemistry calculations.

To provide additional support for the suitability of the present approach for disordered C, we reproduce the energy as a function of volume for a variety of hypothetical phases of C in Fig. 1. We compare the results to the carbon phase diagram computed with self-consistent LDA methods.²⁴ The results are in impressive agreement, particularly for the cubic phases. This is an improvement over the orthogonal tight-binding Hamiltonian used in Ref. 10. We study the consequences of these differences by relaxing the coordinates of Ref. 10 with *ab initio*

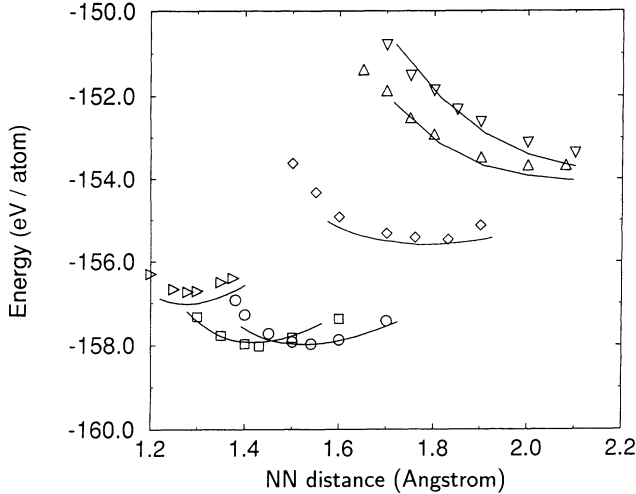


FIG. 1. Cohesive energy vs nearest neighbor distance. Symbols depict self-consistent LDA (SCLDA) calculations (Ref. 24), solid lines depict present method (Ref. 16). Squares: graphite; circles: diamond; diamonds: SC; triangles: bcc; inverted triangles: fcc; triangles to right: linear chain. A single constant was added to all the SCLDA data to make the diamond energies identical at the minimum.

forces, and found that there were major topological rearrangements. This is very strong, albeit circumstantial, evidence that a proper description of the cubic phases is important to properly describing the sp^3 a -C topology. While it is clear that the cubic phases have an energy significantly higher than graphite or diamond it is likely that they carry important information about strongly distorted (amorphous) systems. The cubic phases are important because the amorphous network is clearly *not* just a simple combination of graphite and diamond mixed together. It is not obvious that such a claim is valid even for an entirely fourfold network with distortions characteristic of ta -C. There is a wide range of bond angle and bond length distortions that occur with the defects which are *unrelated* to graphite or diamond. The cubic phases have information about strong *bond angle* distortions relevant to defects that are unrelated to the graphite and diamond structures. We identify a specific kind of defect (π bonded pairs of threefold atoms) later in the paper which involves a more general form of hybridization than just sp^2 or sp^3 .

Our model of ta -C was easily obtained by slowly cooling partly equilibrated liquid carbon in a 64 atom simple cubic supercell, with a density of 3.0 gm/cm³, near the experimental density of ta -C (2.9 g/cm³). The liquid was cooled at constant volume using the velocity rescaling method of Berendsen *et al.*,²⁶ which is very convenient for efficiently changing state, and equilibrating to a new temperature. The liquid was partly equilibrated to ≈ 6000 K, and was then cooled to a target temperature of 600 K using a relaxation time²⁶ of 0.2 ps. After 1.5 ps the structure was suitably annealed and equilibrated. A steepest descent quench was then applied to the equilibrated 600 K structure to obtain the $T = 0$ structure we describe in the rest of this paper. For all of these computations a time step of 1.0 fs was used. For

reasons which will become apparent later, we designate this model structure the “paired defect” cell. All calculations on the 64 atom model used four special points²⁷ for Brillouin zone (BZ) integrals. In both Refs. 10 and 9 it was suggested that a density significantly higher than the experimental density was required to obtain an sp^3 concentration similar to experiment. We found that *ab initio* methods do not require this, and that less dense materials close to the macroscopic experimental density produce sp^3 dominated networks.

Since radial distribution function measurements of $n(r)$ bear much resemblance to the other column IV amorphous semiconductors it is reasonable to simply take widely used models of a -Si, rescale them to the appropriate density for ta -C, and anneal them using carbon interactions and *ab initio* MD.^{16,28} Of course there is no guarantee that this idealization is *physical*: the structure may not be an accessible conformation for the ta -C system, as presently experimentally grown. The best known example of a widely used continuous network model is the a -Si cell of Wooten, Weaire, and Winer (WWW). Recently Wooten and Thorpe (WT) Ref. 29 constructed a cell using the WWW method, but suitable for C. We relaxed the cell with first-principles methods, and discuss it below. Only the Γ point was used for computing BZ integrals for the 216 atom cells.

IV. PROPERTIES OF STRUCTURES

A. Energetics

One measure of the credibility of model amorphous structures is the total energy of the structure relative to a reference [in Table I we report the total energies of our annealed and relaxed 64 atom paired defect cell, the fully relaxed 216 atom WT cell and fully relaxed tight binding molecular dynamics (TBMD) cell]. We note that the total energy by itself is a very incomplete measure of the quality of a model: First, none of the amorphous structures are at equilibrium. Further, at finite temperatures the appropriate measure is the free energy $H = U - TS$, for U the configurational (potential) energy, T the temperature and S the entropy. Unfortunately, it is not easy to evaluate the entropy of the disordered network. Also, the properties of a model cell is *path dependent*: to be entirely plausible one needs to indicate a path in phase space starting in one realistic structural state and ending as the desired model of ta -C. In other words, one would prefer to directly simulate laboratory procedures. This is probably the greatest challenge to atomistic simulations because of the *very* short time scale set by the atomic dynamics. No completely realistic simulations satisfying

TABLE I. Energies (in eV/atom) of several t -C structures.

Structure	Energy (eV/atom)
Wooten	-157.533
Paired-defect	-157.332
Wang-Ho (unrelaxed)	-157.259
Wang-Ho (relaxed)	-157.331

this criterion exist and we expect that none will in the foreseeable future. We are inclined to have more confidence in methods of modeling amorphous C which indicate a “path,” even if it involves unphysical quenching and annealing rates, rather than a method using a presumably unphysical path like the “bond switching” algorithm of WWW, even though the WT cell has the most favorable energy of all the structures we have investigated. Also, all carbon atoms are constrained to be fourfold coordinated in the WWW approach, so that one cannot investigate the role of sp^2 bonded C in a largely sp^3 environment: these defects are certainly present in the real material. Nevertheless, the WT structure is an important idealization of an entirely quaternary coordinated network, and may appropriately model local regions of the ta-C network. We note that some care should be taken in interpreting the results of Table I, since they depend on relaxing the cell volume. The paired-defect cell is at zero pressure; the other cells are probably very close, but this has not been checked in detail.

B. Number density function

The radial distribution function for the paired defect cell is shown in Fig. 2, and agrees well with experiment. The fourfold fraction is 91%, though as we will discuss in greater detail below, this represents a very incomplete tally of spectral defects present in the cell. The radial distribution functions for the other cells are rather similar. This is observed despite significant topological differences in the various cells. For example, the WT cell is 100% sp^3 . This is a reminder that $n(r)$ by itself is an inadequate measure of the credibility of a network as a candidate for an amorphous material. It is a necessary, but certainly not a sufficient condition for having confidence in a model structure. The vibrational, and *especially the electronic properties* are much more sensitive measures of a model structure.

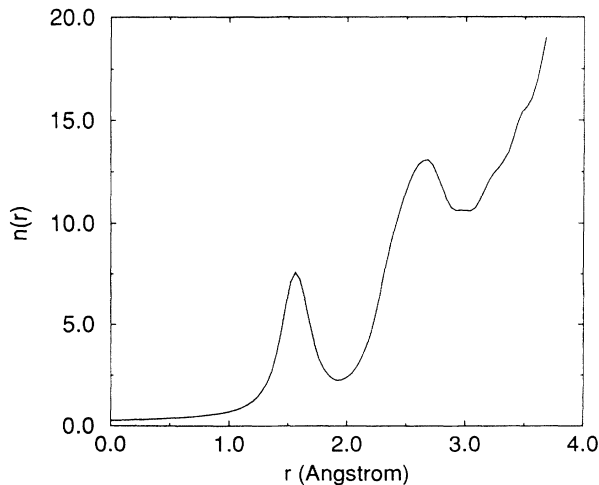


FIG. 2. Radial distribution function for the paired-defect cell. The small- r tail is an artifact of Lorentzian broadening used to construct $n(r)$.

C. Electronic properties and defects

The language needed to discuss defects and states in the gap can be quite confusing. Thus, at this point, we introduce our definitions. As in previous work on α -Si, a geometrical irregularity will be called a geometrical defect. In the present context, this includes C atoms that are not fourfold coordinated as well as fourfold coordinated C atoms that have abnormally stretched or strained bonds. We shall reserve the appellation of a spectral defect for a reasonably well localized state in or near the gap of the material. However, for amorphous C with a substantial content of sp^2 bonding the situation with the gap is somewhat complex. Since crystalline diamond has a gap of about 5.5 eV, one would expect amorphous diamond to have a gap of around 6 eV. However, the sp^2 bonding will fill in some or all of this gap. We will refer to localized states in this pseudogap as spectral defects. One can then further differentiate between cells with a true or clean gap (no spectral defects over a range of 2–3 eV) and samples that do not possess a true or clean gap.

1. Paired-defect cell

This cell with a realistic density of states and $n(r)$ has been extensively investigated. The electronic density of states is shown in Fig. 3. Each bar on the figure represents an energy eigenvalue averaged over the four k points. The quantity $Q_2(E)$ is a measure of the localization of a state, $Q_2(E) = \sum Q(n, E)^2$, where $Q(n, E)$ is the localized charge associated with eigenvalue E at the site n . Use of $Q_2(E)$ amounts to a participation ratio analysis of the electronic states. The key feature is the existence of a 2.5 eV optical gap (the separation of the highest occupied and lowest unoccupied energy levels averaged over four special points in the Brillouin zone), slightly larger than experiment.³⁰ As noted in earlier work on Si (Ref. 31) the states immediately above the gap are more localized than the states just below the

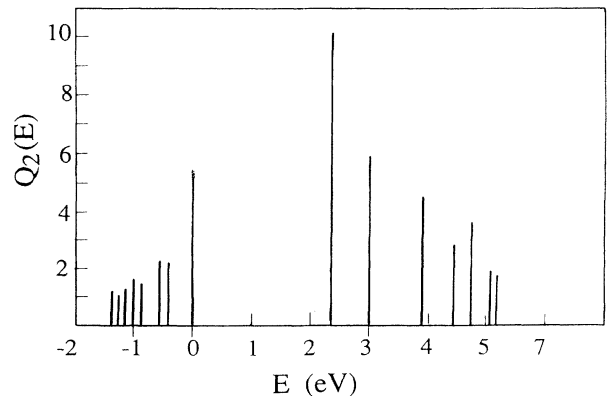


FIG. 3. Localization for the paired-defect cell for states near the gap. The Fermi level is in the middle of the gap and $Q_2(E)$, a measure of localization, is defined in the text. $Q_2(E)$ would equal one for an extended state with equal weight on all C sites.

gap. Note that this is not a region of a density of states reduced from the diamondlike DOS but, in fact, is a clean gap.

It is of central interest that the gap we observe occurs *despite* the presence of numerous spectral defects in the network. About 12% of the 128 electronic eigenvalues were significantly localized and it is important to note that the localization was rarely on only one defect: rather there was a clear tendency to "defect resonances" in which a given eigenvector connected to a localized state was spread over *several* defects, although there was a tendency for one defect to be somewhat dominant in the participation ratio. Since isolated defects lead to gap states, it is tempting to interpret the extension of the defect wave functions as indicating defect-defect interactions. In this picture, there is "defect band formation" due to a large degree of mixing between the defects. This banding seems to be important to gap formation as we see below.

The first variety of defect observed is a modified sp^2 hybrid. Six out of 64 atoms are threefold coordinated. They all occur in nearest neighbor pairs, and form distorted π -bonded pairs; the "z" axes of the pairs are 26° , 18° , and 10° of being parallel. We call these paired π defects, because the atoms are three coordinated, and there is substantial π bonding. The π defects are the first example of a basic difference between *a*-Si and *a*-C. Because π bonding is energetically unfavorable for Si-Si interactions, there is no tendency, or at best a very weak tendency for neighboring three-coordinated Si atoms to align themselves into a π bonded configuration. In *a*-C, it seems likely that because the sp^2 bond is almost energetically degenerate with sp^3 bonding, that the existence of a single dangling bond *causes* a structural modification in a neighboring C atom producing a π pair defect. In other words, the chemistry of carbon prefers three-coordinated atoms to appear in pairs rather than singly, whereas one has to pay a large energy penalty for the same topology in Si. We found that the π structures did produce spectral defect states which were strongly connected with eigenvectors with one or more states above the gap and also with one or more states below the gap. There was no simple pattern which related the geometry of the π pair defect to the location of a localized eigenvalue in the density of electronic states. Certainly, such defects do *not* necessarily split equally between occupied and unoccupied bandtail states and neither is their a simple one to one correspondence between spectral defects states and the π pairs.

We observed that some care was needed to quench the liquid slowly enough to allow pairing to occur. If a cell is quenched too rapidly the dangling bond could be frozen in without pairing. In that case, we find a localized midgap defect state, as in *a*-Si. These observations suggest that to a large degree dangling bonds are *self healing* for sufficiently slow quench rates of ta-C. So, while it is still possible to obtain an isolated dangling bond, the probability of this is greatly reduced by the π defect pair formation mechanism.

In addition to the π pair defects, there were several "strain" defects which were fourfold coordinated, but

with geometries very different from either ideal sp^3 or sp^2 bonding. Our supercell sample contained two strain geometrical defects which were identified with bond angles of over 150° . Sketches of the defects are included in Fig. 4. Some of the localized states just above and below the gap had a considerable spectral weight on the centers of these geometrical defects. Such strain defects have also been observed in *a*-Si simulations.³² In this case, the supercell samples had a smaller density of defects and a geometrical defect could be associated with a spectral defect. In this case, the strain defect leads to a localized state in the gap of *a*-Si.

In the present supercell, we have also detected another type of geometrical defect. We call this defect a *stretched bond defect* since a bond between two fourfold coordinated atoms was anomalously long; between 1.8 and 1.9 Å. All other bonds were less than 1.73 Å and all but three were less than 1.70 Å. (For our purposes here, a bond exists for atoms separated by less than 2.0 Å.) Two of these stretched bond defects occur in our supercell and, like the strain defects, there is significant localization of some of the localized states at these sites. Thus, besides the three pairs of sp^2 defects, the cell contains two strained bond defects and two stretched bond defects.

We note that all three types of defects, π pairs, strain defects, and stretched bond defects, interact with each other and hybridize and they all have a significant spectral weight in localized states both below and above the gap. All of the localized states above and below the gap have a significant localization on a number of geometrical sites. The sample with a number of interacting defects rearranges itself so that some of the (occupied) defect states are pushed lower in energy and some of the (unoccupied) defect states are pushed higher in energy. The decrease in energy obtained from the lowering of the occupied eigenvalues more than compensates for any additional strain energy. The reason that this can occur in *a*-C but not in *a*-Si is because of the richer chemistry of C.

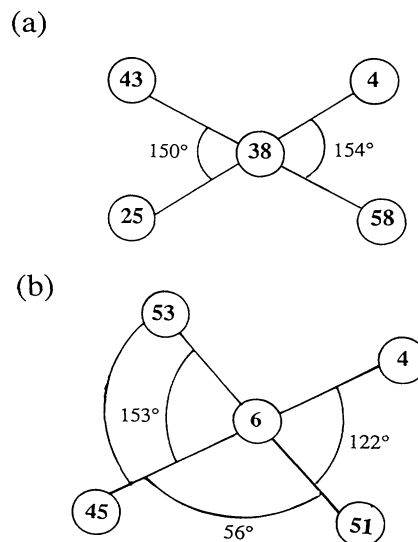


FIG. 4. Sketches of the two strained bond defects described in the text. Only bond angles that are extreme are noted.

2. TBMD structure

Recently, Wang and Ho¹⁰ have presented their 216 atom structure. We have analyzed their structure and find a very different topology from the structure that we have generated. Using a coordination radius of 2.0 Å, the TBMD structure as we received it contains 42 threefold coordinated C atoms. These threefold coordinated atoms are clustered but are not paired to the extent that ours are. That is, their structure contains three isolated, ten pairs, two triplets, one quartet, and one octet of connected threefold coordinated atoms. We find that there is a large number of states in their pseudogap with no substantial region free of spectral defects and, thus, no true gap. There is no tendency for the defects to arrange themselves in order to produce a gap as was observed with our supercell. Further, their supercell sample changed substantially when we performed a steepest descent quench with *ab initio* methods. The unrelaxed cell had 42 threefold atoms, and the relaxed cell contained only 28. Clearly the TBMD forces are significantly different than our *ab initio* forces and lead to different network topology. We attribute the discrepancy between the present density functional theory and TBMD to a major difference in transferability. The phase diagram of Fig. 1 shows close agreement with self-consistent LDA (SCLDA) calculations for all phases studied, whereas there is a serious discrepancy between TBMD and SCLDA for the cubic phases of C. This is discussed in more detail in Ref. 25. When we quenched the *a*-C cell of Galli, Martin, Car, and Parrinello (GMCP) (Ref. 33) with our code, the structure underwent only very minimal changes, certainly involving no topological changes. The GMCP sample was constructed with the Car-Parrinello self-consistent plane wave code and this minimal change is strong evidence that the forces from both *ab initio* codes are quite close.

3. WT cell

Here, we briefly describe the electronic properties of the relaxed WT cell. This model was obtained by a bond-switching method, not the result of a dynamical simulation. This bond switching mechanism is described more completely in Ref. 34. By construction, the starting cell was entirely fourfold coordinated. This state of affairs persisted after a steepest descent relaxation of the original coordinates. The gap was large: about 4.1 eV after relaxation, and the gap was completely free of states. There were many strained bonds in the network. It is interesting that the WT cell relaxed to a much smaller degree than the TBMD cell. This is impressive given the relative simplicity of carbon interactions used in constructing the WT model.

The WT cell presumably displays such a large gap because there is no *sp*² bonding in the material. This differs from experiment, but the relaxed WT cell is a plausible model for ideal fourfold topology. We will discuss the WT model in more detail in a subsequent publication.

D. Gap formation in ta-C

Without question the most interesting scientific question connected with ta-C is the presence of a large (≈ 2.0 eV) state-free gap, unknown in other elemental amorphous semiconductors. At its simplest, any system being quenched into a metastable solid state structure rearranges itself to a local minimum in the total energy. The accessible configurations attainable to the atoms depends on (1) the detailed chemistry of the material: this determines energetically favorable bonding configurations, (2) the temperature, since higher temperatures allow the system to explore a more diverse range of configurations, and (3) the presence, or lack thereof of nucleation sites which favor the growth of favored structures. We have seen that the gap is due to the formation of special defects as described above with the property that a state free 2.0 eV optical gap is maintained. That is, the defects arrange themselves to lower the total energy by pushing occupied states lower and unoccupied states higher.

Robertson³⁵ has argued that the existence of the gap in *sp*² *a*-C is due to large, isolated islands of graphitic regions interconnected by smaller *sp*³ domains. This has been discussed in detail in the medium range order theories of amorphous semiconductors. Since Robertson's arguments were designed for materials with a higher density of *sp*², it is not clear that they are relevant here. However, an extreme extension of his argument is that clusters of only two *sp*² atoms form a minicluster with a gap. However, as discussed above, the gap is not so simple. That is, a variety of defects all interact with each other to form the gap. It is not due to isolated pairs.

E. Vibrational properties

In Fig. 5 we reproduce the vibrational power spectrum of the paired-defect cell. The results are rather simi-

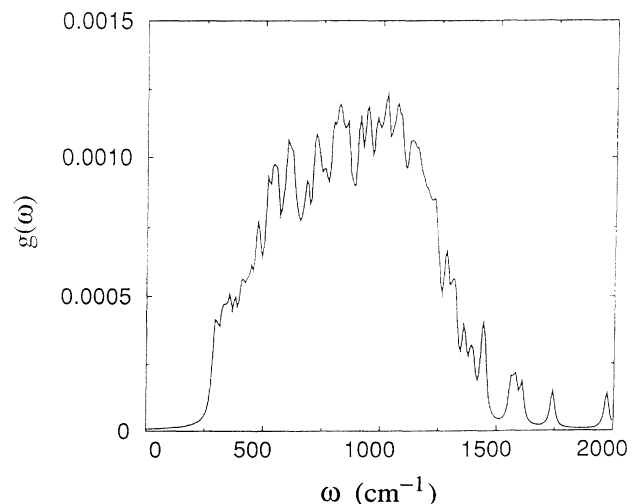


FIG. 5. Vibrational power spectrum for paired-defect cell. Modes with frequencies higher than about 1300 cm⁻¹ show strong localization. The spectrum is Lorentzian broadened with width 12 cm⁻¹.

lar to the work of Ref. 10 including the conclusion that modes with frequencies higher than about 1300 cm^{-1} are strongly localized. This is an interesting indication of how insensitive the vibrational power spectrum is to differences in the local structure. Unfortunately, it is difficult at present to measure the vibrational spectrum of this material because of sample size limitations: for example, inelastic neutron scattering requires a much larger sample than those presently available. The modes above 1300 cm^{-1} are all rather localized and the localization is always associated with a geometrical anomaly. These include strained bonds, stretched bonds, and the expected sp^2 pairs. Evidently any geometrical irregularity can lead to a high frequency well localized mode. Thus, the vibrational spectrum sheds very little light on the electronic properties of the supercell sample.

V. CONCLUSION

We have used *ab initio* density functional methods to model the microstructure of quaternary *a*-C. We have shown that first-principles methods are *essential* to describe the subtleties of topology on the sp^3 *a*-C topology.

While these structural effects are not very evident in the radial distribution function or vibrational spectrum, they are of prime importance to the electronic states. The primary new discovery of this paper is the pairing of three-coordinated defects in the amorphous network. When this happens, a large optical gap of more than 2.0 eV appears, completely free of defect states, in gratifying agreement with experiment. This work will be extended in several ways: to larger cells, and to models with dopants present. Coordinates discussed in this paper are available upon request.³⁶

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