

Gap formation and defect states in tetrahedral amorphous carbon

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We present a model of tetrahedral amorphous carbon (with density 3.0 g cm^{-3}) obtained from self-consistent plane-wave (Car-Parrinello) methods. This model is closely related to one we presented earlier [Phys. Rev. B **49**, 16 415 (1994)], except for an even greater tendency toward sp^2 π pair and chain formation. We also discuss, in general terms, appropriate means for comparing models generated with different methods and emphasize the need for a proper relaxation of ionic coordinates. [S0163-1829(96)03032-9]

I. INTRODUCTION

Tetrahedral amorphous carbon, which typically contains about 80–90 % sp^3 bonded carbon with the remainder being sp^2 bonded, continues to attract broad interest in the semiconductor community. Since the landmark work of McKenzie *et al.*,¹ several papers have appeared on the structure, doping, and theoretical modeling. In our view the points of key interest are (i) the microstructure of the material including the large fraction of sp^3 sites, (ii) the microscopic reasons for why there is a nearly defect free gap of order 2.0 eV, (iii) the doping mechanism(s) in the material, and (iv) the conduction mechanism. This paper contributes directly to the first two points and provides a useful model for the other two. We also elucidate the relaxation of a network we proposed earlier obtained with local basis density functional² techniques, using Car-Parrinello forces with a converged basis. This work is an interesting complement to the very recent work of Marks and co-workers.³

The defect-free gap and high sp^3 count are the most impressive features of *ta*-C. Sizable clusters or rings of sp^2 in otherwise sp^3 amorphous material⁴ have been suggested as a model of the material. However, in earlier work based upon our molecular-dynamics (MD) simulations, we showed that the presence of isolated pairs or short chains of π -bonded sp^2 pairs was a viable explanation. Further, we showed that this model also led to an explanation of the sweeping of other defect states from the gap, in agreement with the experimental measurements that show a clean gap. This effect has been most thoroughly investigated by Stephan and co-workers.⁵ To our knowledge, sizable clusters and rings do not imply this property.

In this paper we discuss another supercell sample of 64 atoms, which, although it had its origins in our earlier supercell, is characterized by details that are distinct from it. However, the basic electronic properties of the two supercells are quite similar. In fact, one of the basic points of this paper is that the physics of the two supercells is the same, although the details differ. Of course this is not to say that inadequate

methods can capture the basic physics and yield, for example, the very special clean gap exhibited by this material. Our first model⁶ had only 6 sp^2 atoms out of 64, *all of which* were in π -bonded pairs. In the supercell we discuss here, there are a total of 18 sp^2 atoms, *all of which are in pairs or even membered chains of π -bonded atoms*. As before, we obtain a defect-free gap of about 2 eV even though there are other geometrical defects present. In this case, because of the greater number of π -bonded atoms, we can form a better picture of what is happening. In particular, the other defects are pushed to the edges of what would have been the diamond gap if the sp^2 atoms did not exist. We find no evidence for rings or substantial clusters, although we cannot rule them out since this discussion is limited to a 64-atom supercell model. Thus our work suggests a fantastic proclivity for the sp^2 atoms to pair and thus be swept out of the 2-eV gap and to *sweep out other defect states with them*. Besides this empirical observation, we have a simple model to explain this gap-forming “sweeping” mechanism. Finally, our two supercells are the only two constructed that contain some sp^2 bonded atoms and also a clean gap. We note that only one defect in a sample of 64 atoms corresponds to a defect density of 1.6% or about 1.25×10^{22} defects/cm³, or a density of states of 5×10^{21} cm³/eV, which is about four orders of magnitude greater than that which is experimentally observed.

II. COMPARISON OF METHODS

In this section we describe the details of the Car-Parrinello relaxation and compare our results to those obtained previously for local basis functions.

A. Self-consistent plane-wave method

The method of this paper is a conventional Car-Parrinello self-consistent plane-wave code⁷ restricted to Γ -point Brillouin-zone (BZ) sampling. In detail, we started with the coordinates of Ref. 6, obtained from calculations based on

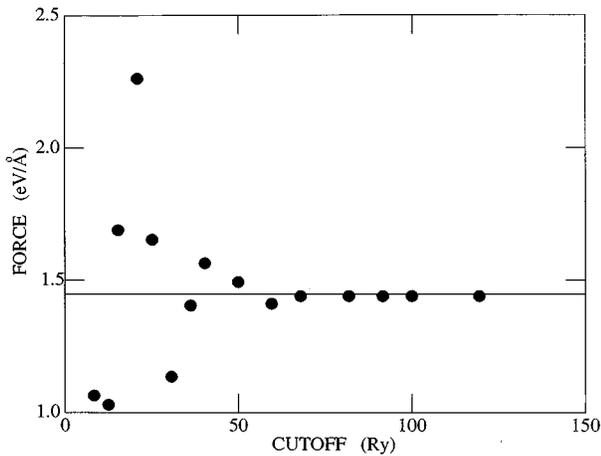


FIG. 1. Convergence of the forces on displaced atom in a diamond cell plotted against the plane-wave cutoff for the smooth Vanderbilt pseudopotential. The force is fully converged at 70 Ry.

four \mathbf{k} points, and performed a relaxation of the ionic coordinates using a 45-Ry cutoff for the smooth Vanderbilt pseudopotential.⁸ Because the Hamann *et al.* pseudopotential⁹ is *very* hard for carbon, the authors of Ref. 10 had to use *very* large cutoffs. Reliable smooth or, even better, ultrasoft¹¹ pseudopotentials obviate the need for such enormous cutoffs for work involving disordered phases of carbon. To demonstrate this we have used the smooth Vanderbilt potential to compute the restoring force on a displaced atom within a two-atom diamond cell. The irreducible Brillouin zone is sampled with ten special points. Figure 1 shows the magnitude of the force as the plane-wave cutoff is increased. We find that the force is fully converged at 70 Ry, while an error of $\sim 7\%$ is incurred at 45 Ry. As we first pointed out,¹² Γ -point sampling can lead to errors in small cells; the magnitude of this error is described in Ref. 10. Substantial topological changes associated with BZ sampling are unlikely here since our models have fully occupied bands at the Fermi surface.

Two quenching regimes were employed: (i) by quenching all atomic velocities whenever $\mathbf{F} \cdot \mathbf{v} < 0$ for any individual atom and (ii) letting the system freely evolve until the total kinetic energy reaches a maximum and then quenching all atomic velocities and repeating until all forces were smaller than 0.025 eV/\AA . Method (i) was used for the first 1300 steps, method (ii) for the subsequent quench (another 2700 steps). We employed two methods because the relaxation was tortuously slow; we hoped that method (ii) would be faster, but both methods seem to converge at comparable rates. We describe the network rearrangements in Sec. II C. To be certain that the cutoff was adequate, we then quenched this cell using method (ii) and a 70-Ry cutoff. The converged 45-Ry cell had a maximum force of 0.4 eV/\AA and quickly relaxed to a structure with forces smaller than 0.025 eV/\AA and exhibited *no additional topological rearrangements*. Tests on distorted diamond indicate that a 70-Ry cutoff is converged with respect to forces for the smooth pseudopotential. Other inaccuracies (such as Γ -point BZ sampling) introduce much larger errors than one could attribute to the plane-wave cutoff. The calculations reported here were car-

ried out on an IBM workstation, with the exception of the short 70-Ry quench that was performed on a Cray Y/MP-8 supercomputer.

B. Local basis density-functional method

Here we compare our first model⁶ generated by local basis local-density approximation (LDA) methods. The approximations are (i) density-functional theory in the local-density approximation, using the (ii) Harris functional, (iii) the full Hamann *et al.* pseudopotentials⁹ without approximations (for example, the assumption of a Kleinman-Bylander separable form), and (iv) a minimal *s-p* basis representation. (A comprehensive discussion of this scheme, approximations used, and a description of various tests can be found in Ref. 2.) The available data are quite clear that the method is transferable, as seen in the phase diagram, which is in very good agreement with plane-wave calculations,^{13,6} including the difficult metallic phases of the material.¹⁴ A spilling analysis has also been performed by Sanchez-Portal *et al.*,¹⁵ which shows (relative to plane waves) that the confined pseudo-atomic orbitals are optimal within a controlled range of interaction. Our scheme is also efficient enough to enable *proper* Brillouin-zone sampling,¹² longer simulations, and calculations on much larger systems (relaxations on up to 512-atom models of *a*-diamond¹⁶ have been performed,¹⁷ without even resorting to quantum order- N methods,¹⁸ which are implemented for this methodology).

C. Results from different methods

In connection with methods, we feel compelled to discuss a recent paper of Nelson *et al.*¹⁰ By using coordinates of a tetrahedral amorphous carbon (*ta*-C) model, which we provided,⁶ that were obtained from local basis density-functional (LBDF) calculations,² they suggested the following. (i) Converged force calculations and particularly relaxations of 64-atom supercell models of *ta*-C were computationally prohibitive on supercomputers, even for Γ -point BZ sampling. (ii) The existence of a force *by itself* on atoms in models studied with a different method implied that the model in question is unrealistic. (iii) The paper implicitly claims that a 46-Ry cutoff is inadequate for other calculations in highly disordered (amorphous or liquid¹⁹) environments.

It is our contention that *almost nothing can be said in the absence of relaxation*. A simple example will suffice to illustrate the point. Consider two Hamiltonians and a crystal lattice. Suppose that these Hamiltonians are identical except for a scaling factor causing one to have bond lengths differing by 0.1 \AA . Uniform distortions of this magnitude would lead to forces greater than 1 eV/\AA , and yet obviously a relaxation would not lead to a topological rearrangement; yet forces would appear to be “large.” For *ta*-C we find that highly defective sites are *very* sensitive to small displacements in ionic coordinates, according to LBDF calculations. It is of course just such a configuration that yields different looking forces for slightly different Hamiltonians, but this by itself means very little. It is also relevant to recognize that there is a “domino effect” at work—since the bonding is obviously highly correlated, one local change can lead to a rearrangement—so that one must be careful in interpreting

the results of these studies. The existence of a vast number of nearly degenerate, topologically similar minimum-energy conformations is a fundamental property of topologically disordered networks, as we have explicitly demonstrated for *a*-Si:H.²⁰ The number of such metastable minima can only be larger for *a*-C with the richer chemistry of carbon. The existence of this large set of local minima suggests that conformational changes are quite possible for small differences in interactions. An interesting illustration of this point is afforded in a vastly simpler system—small Si clusters—by Grossman and Mhas,²¹ who performed quantum Monte Carlo, configuration-interaction and LDA calculations for Si₂₀ and found that each method led to significantly different ground-state conformations: this despite the fact that each of the three highly respected methods was implemented very carefully with painstaking care to ensure convergence of the basis. Some recent work of ours²⁰ is also relevant in that we showed that annealing an *a*-Si sample at any finite temperature induces minor changes in the basic equilibrium or quenched state, although it does not change any of the average properties.

The relaxation described in Sec. II A led to an enhancement in *sp*² bonding: the starting 64-atom cell had six *sp*² atoms, the fully relaxed cell had 18 (seven bonds broke and one formed over the course of the relaxation). Three of these bonds that broke were quite weak (with bond length greater than 1.65 Å) and were already strongly *sp*² in character. To emphasize the minor nature of the change, the electronic density of states and the radial distribution function were both essentially unchanged. The highest occupied molecular-orbital–lowest unoccupied molecular-orbital energy gap, a sensitive measure of the structure of defects, changed by 0.3 eV with the supercell with more *sp*² bonds having the smaller gap. In addition, the band tail states were *sp*² before and after the relaxation and were localized on much the same sites.

When we compare the energies of the Car-Parrinello relaxed cell *with LBDF methods* we find it to be 0.2 eV/atom lower in energy, compared to about 0.25 eV/atom for the Car-Parrinello Hamiltonian. This suggests that the annealing and quenching regime used may be more important than the Hamiltonian. This may also be inferred from the work of Stephan *et al.*,⁵ who carefully investigated several different annealing methods and found that very extended annealing led to longer and longer π chains and of course more *sp*² bonding. Energy, however, *is far from the whole story* in this material, grown under the most extreme nonequilibrium conditions, and exhibits more than 85% *sp*³ bonding.¹ The only model, as far as we know, with an experimentally appropriate *sp*³ concentration is ours.⁶ It is quite possible that some badly strained bonds are present in the real material to yield this high *sp*³ concentration.

III. ELECTRONIC STRUCTURE OF *ta*-C

The cell with 18 threefold coordinated C atoms and 46 fourfold coordinated atoms has been extensively investigated. The 18 threefold coordinated C atoms are configured in the following ways. There are eight atoms comprising four nearest-neighbor π -bonded pairs. There are four atoms in a chain of nearest-neighbor π -bonded atoms. Finally, the re-

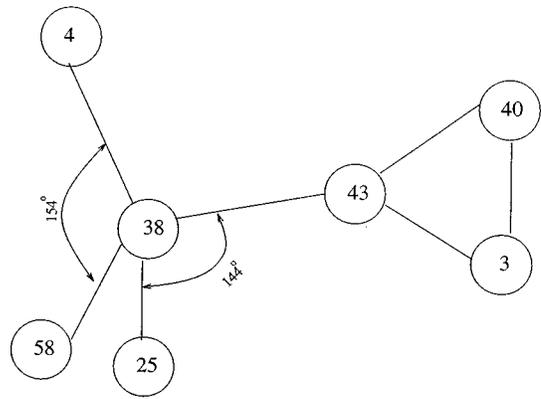


FIG. 2. Two-dimensional representation of a geometrically odd configuration of atoms occurring in the supercell. Note the threefold ring and the large bond angles.

maining six atoms form another chain of nearest-neighbor π -bonded atoms. Note that none of the threefold coordinated atoms is isolated by itself and that all chains are of an even length. Further, two of the pairs are separated by only one fourfold coordinated C atom and the chain of length 6 is separated from one of the remaining pairs by only one fourfold coordinated C atom. The axes of the π bonds are within 30° of being parallel for all *sp*² neighbors and the same is true for the chains separated by only one *sp*³ atom. These chains are neither close to being rings nor close to being straight. The longer ones could be said to wander around.

There are other geometrically odd configurations of fourfold coordinated atoms that should be identified as geometrical defects. The most glaring example is depicted in Fig. 2, where the extended defect contains a threefold ring connected to a fourfold group of atoms with extremely large bond angles. There are other less glaring geometrical oddities in the supercell. These geometrical defects would have lead to defect states in the gap in *a*-Si or in *a*-C without the threefold coordinated atom pairs. This point will be explained in more detail shortly.

The electronic properties are described well by Figs. 3–5. The electronic density of states is shown in Fig. 3. Each bar on the figure represents an energy eigenvalue. Note the clean Γ -point gap of about 1.7 eV. The quantity $Q_2(E)$ is a measure of the localization of a state

$$Q_2(E) = \sum Q(n, E)^2, \quad (1)$$

where $Q(n, E)$ is the localized charge associated with the eigenvalue E at the site n . For a perfectly uniform extended state $Q_2(E)$ would be 1 and for a perfectly localized state it would be N , with $N=64$ here. The fact that Q_2 never gets near N is because none of the eigenstates is particularly well localized. That is, the *sp*² states hybridize extensively among themselves and to some degree with the *sp*³ states. The *sp*³-like states are extended but not perfectly in that the weight on various sites is not uniform. This is to be expected in an amorphous material and has been noted in MD generated models of *a*-Si:H.²²

A simplified view of *ta*-C is one where the *sp*³ bonded atoms form diamondlike bands of extended states with a gap

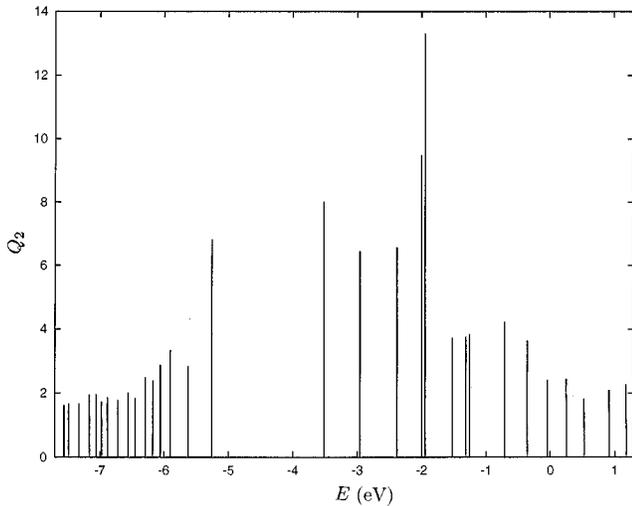


FIG. 3. Electronic density of states of the supercell in the region around the gap. Each bar on the figure represents an energy eigenvalue and the height is a measure of the localization of the state.

of about 6 eV and the sp^2 bonded atoms form two graphite-like bands of localized state. One of these bands is just below the conduction band of the diamondlike states and the other is just above the valence band of the diamondlike states. Further there is a gap between these graphite-like bands. While this picture is somewhat naive, the idea is basically correct. The fraction of sp^2 (the fraction associated with threefold coordinated sites) associated with each eigenvalue is shown in Fig. 4. The horizontal line corresponds to a fraction of 0.28, which is the fraction of sites that are threefold coordinated. There is a clear distinction between eigenvalues that are primarily sp^2 and those that are primarily sp^3 with the sp^2 eigenvalues lying closer to the gap as expected. However, none of the states are 100% either sp^2 or sp^3 . On the conduction-band side, the line between the types of eigenvalues as a function of energy is sharp. On the valence-band side, the line is not quite so sharp. Nor is there any *a priori* reason why the demarcation should be sharp. However, we have denoted the approximate extent of the sp^2 eigenvalues by arrows in the figure.

In Fig. 5 we have plotted the fraction of the various eigenvalues that correspond to the atoms in the large defect in Fig. 2. The horizontal line corresponds to a fraction of 0.109 since that defect contains 7 out of the 64 atoms. The arrows from the Fig. 4 are reproduced there. We see that the heavy concentration of weight is at the band edges of the sp^3 band. This forms the band tail of the diamondlike gap. In *a-Si* or all fourfold coordinated C atoms, these states would be around midgap.

Thus a picture emerges that is a somewhat clarified version of the picture we presented before. That is, the sp^2 “defects” form pairs in which one of the two hybridized states is pushed lower in energy and one is pushed higher in energy. Since only the lower-energy state is occupied, the total energy is significantly lowered. Further there is some tendency for the π -bonded pairs to form short chains. We see no evidence of rings or cluster formation and indeed the cost in free energy for this to happen would be considerable because of the rather extensive ordering that it would entail.

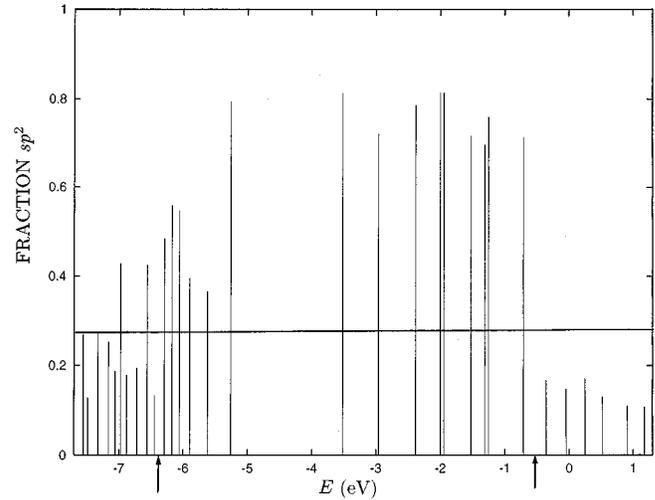


FIG. 4. Fraction of sp^2 character associated with each energy eigenvalue. The horizontal line corresponds to a fraction of 0.28 that is the fraction of sites that are threefold coordinated. The arrows denote the approximate extent of the heavily sp^2 eigenvalues.

Thus single sp^2 atoms, or dangling bonds, do not occur in substantial numbers as they do in *a-Si*. It also appears that defect states associated with geometric anomalies are also pushed out of the sp^2 gap into the band edges of the diamond or sp^3 gap, that is, what would have also hybridized with the sp^2 states and are thus pushed out of the gap. This can be understood as follows. The large number of π active C atoms form sp^2 bands. These bands have their energies near that of other topologically different defects such as strained or even certain dangling bonds. As there is a reasonably large concentration of sp^2 atoms (of order 15%), there are large matrix elements between the π and π^* bands and the other topological defects. In addition, there are small energy denominators because some of the π and π^* states will lie close in energy to the other defects. Thus these other defect states will mix strongly with the threefold coordinated

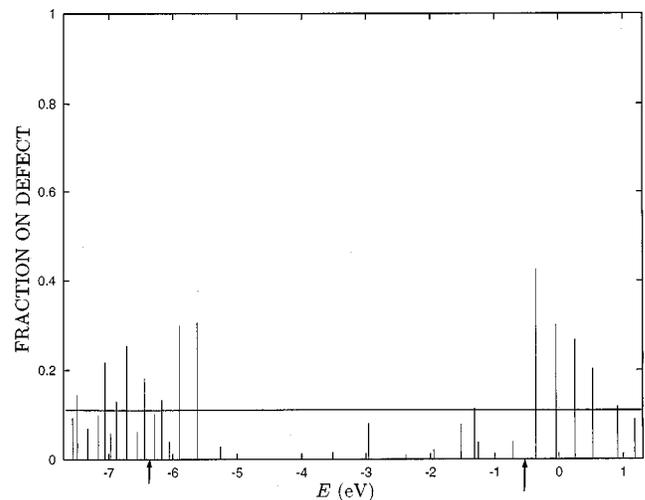


FIG. 5. Fraction of eigenvalues that correspond to the atoms in Fig. 2. The horizontal line corresponds to a fraction of 0.109 since the defect contains 7 atoms out of 24. Again, the arrows denote the approximate extent of the heavily sp^2 eigenvalues.

C atoms and the states will be pushed up or down in energy depending on whether or not they are occupied. It follows that in this view, the clean gap in *ta*-C is *made possible* because of the existence of a reservoir of extended π and π^* states, resonant or nearly so with defect states.

ACKNOWLEDGMENTS

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