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SELF-DOPING AND HOPPING CONDUCTIVITY IN AMORPHOUS CARBON

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Graph theory is used to estimate the density of states near the Fermi level (E_F) of amorphous carbon (a–C) structure. There are topologically determined energy levels concentrated around the Fermi level. This phenomenon provides a possibility of self-doping. As the hopping conductivity is depending on the energy and spatial separations of the initial and final states the hopping conductivity between topologically determined states is regulated mostly by the spatial separation.

The amorphous carbon has different percentages of fourfold– and threefold–coordinated atoms. The π-electron network is determined by the threefold–coordinated graphitelike atoms. These atoms form three localized σ-states (sp^2 hybrid) plus a delocalized π-state near E_F. If we are respecting only the π–electron states of the graphitelike atoms the Hückel Hamiltonian H can be written in the following form:

$$H = \alpha I + \beta A,$$

where α and β are the interaction parameters, I is the unit matrix and A is the so-called adjacency matrix,

$$A_{ij} = \begin{cases} 1 & \text{if the atoms } i \text{ and } j \\ & \text{are first neigbours,} \\ 0 & \text{otherwise.} \end{cases}$$

Using the one-to-one correspondence

atom $\Longleftrightarrow$ vertex

bond between first neighbours $\Longleftrightarrow$ edge

a cluster of graphitelike atoms can be represented by a graph of adjacency matrix A.

The subset (the cluster) of graphitelike atoms in a-C structure can be described by a graph where each atom is a vertex of graph and each bond represents an edge. A Sachs graph[1] is such a subgraph of graph G which has only edge- and/or ring-type isolated components. If $P_G(x)$ is the characteristic polynomial of matrix A, then

$$P_G(x) = det|xI - A| = \sum_{n=0}^{N} a_n x^{N-n},$$

where N is the number of vertices in graph G. According to the theory of Sachs[2] the a_n coefficients are

$$a_n = \begin{cases} 0 & \text{if } 0 < n \leq N \\ & \text{and } S_n = \emptyset \\ \sum\limits_{S \epsilon S_n} (-1)^{C(S)} 2^{r(S)} & \text{if } 0 < n \leq N \\ & \text{and } S_n \neq \emptyset \\ 1 & \text{if } n = 0. \end{cases}$$

Here S_n is the set of all Sachs graphs S with n vertices. $C(S)$ and $r(S)$ denote the number of all components and of ring components in S, respectively.

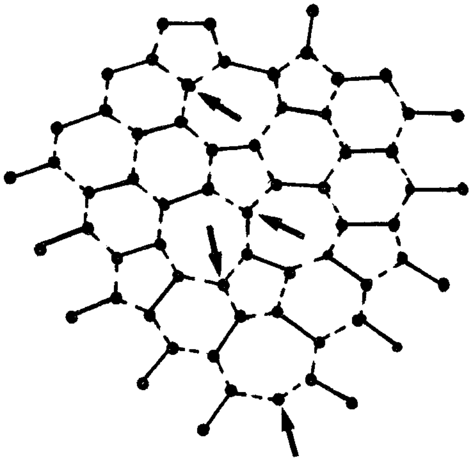

Figure 1.

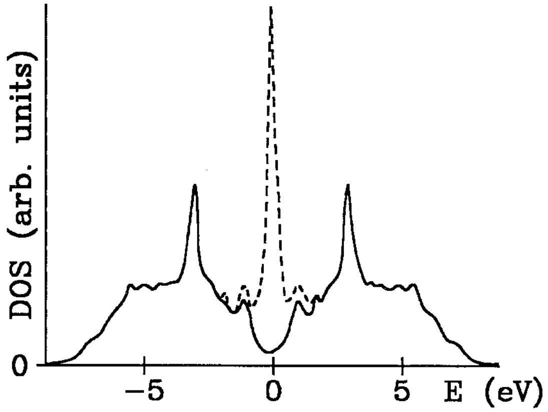

Figure 2.

In our previous paper[3] it was proved that the density of states around the Fermi level could be described by the non-existence of Sachs graphes. Here we introduce the topological degeneracy of electronic states. According to Sachs formula the degree of topological degeneracy is equal to the number of critical atoms[3,4]. Excluding these critical atoms the topological degeneracies disappear at E_F. This phenomenon provides the possibility of self-doping. Figure 1 shows a part of a model made by Beeman et al.[5] containing 64 sp^2 type atoms. Constructing S_n set of Sachs graphs (one of them represented by thick solid lines) there are four critical vertices of topology (marked by arrows). It leads to a fourfold topologycal degeneracy. The topology always determines the number of critical vertices without uniquely fixing their positions.

To check our idea two different types of quantum chemical calculation were carried out on C356 model containing 356 carbon atoms of which about 50 % are three coordinated. The π-DOS curve, as obtained by smoothing

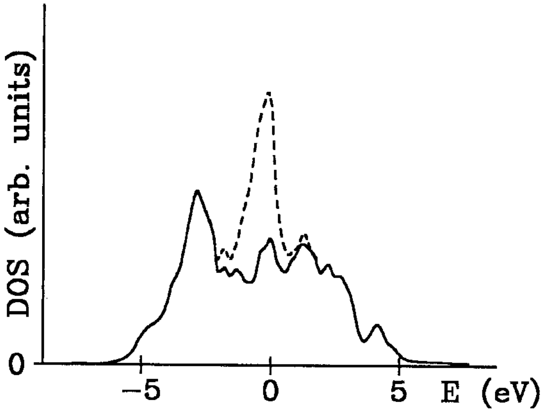

Figure 3.

the Hückel one electron energies with Gaussian line broadening that corresponds to a full width of 0.2 eV at half maximum, is presented in Fig.2. Optical gap of a-C:H increases in the presence of H. As the hydrogen-carbon bond is σ type we suppose that in a process of saturation the hydrogen atoms can transform three–coordinated carbons into four–coordinated carbons. Saturating the topological degeneracies of electronic states by hydrogen the huge narrow peak at the Fermi level disappears. In the second type of calculation the π-orbital axis vector analysis[6] was applied to define the π-states and the orbital orthogonality relationship was used to define the π-orbital hybridizations and directions. In this more realistic calculation a similar large peak appears around the Fermi level and the previous saturational process eliminates this peak as well (see Fig.3).

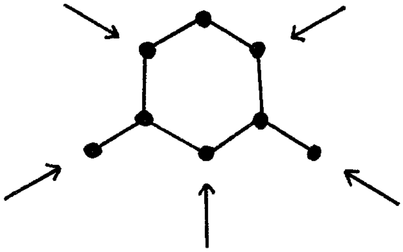

Figure 4.

Usually it is supposed that the midgap states of a-C are produced by clusters with an odd number of atoms. The mostly mentioned clusters regarding this matter are the five-and seven-fold rings[7]. Our cluster in Fig.4 is a counter-example, because it has two midgap states contrary to the fact that it is an eight atomic cluster with a hexagonal ring. These midgap states can be explained by the topological degeneracies of the cluster. In Hückel approximation the hopping conductivity σ_{ij} between clusters having topologically determined midgap states depends only on the distance R_{ij} . Where R_{ij} is the distance between the clusters i and j. Namely

$$\sigma_{ij} \approx exp - [aR_{ij} + b(\varepsilon_i - \varepsilon_j)]$$

and $\varepsilon_i = \varepsilon_j = \alpha$. Some topologically determined energy levels are localized to a separated part of the cluster. Numerical calculations[8] for a-C showed that these topologically determined energy levels are mostly localized at the circumferences of the clusters. There are, however, other topologically determined energy levels that are not severely localized. See for example Fig.4, where the atoms which are contributing to these states are marked by arrows. The hopping constant of π electrons found by Shimakawa and Miyake[9,10] can be attributed to such topologically determined energy levels that are not severely localized.

We conclude that the metallic behavior of amorphous carbon clusters can be explained by the degree of degeneracy due to topology defined by the three coordinated carbon atoms. It means, that based on topology it is possible to estimate the π-band DOS at the Fermi level without any quantum-mechanical calculation. Thus topological structure plays a more important role than angle distortion in amorphous systems containing π-electron islands. In practice, most of the three–coordinated carbon atoms can be critical atom. Varying the H content in a given amorphous structure the number of critical atoms in–creases or decreases and the one electronic states appear or disappear around the Fermi level. This is very close to experimental results because around the Fermi level in a–C 0.4–0.7 eV and in a–C:H 1.6–2.7 eV optical gap was measured[11]. Midgap states which can be produced by clusters having special topology improve the hopping conductivity of amorphous carbon.

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