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Optical properties of tetrahedral amorphous carbon nitride

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Abstract

We calculated the optical properties of three amorphous tetrahedral carbon-based clusters of the type $a-C_{21-i}N_iH_{28}$ with 6-atom boat-type rings. The 28 hydrogens passivate the outermost dangling bonds and i is 0, 1 or 4. The theoretical DFT-LDA based method used minimizes the energy of the clusters and provides the energy spectrum and the optical transitions for the minimum energy structures. The optical absorption spectrum is analyzed for each cluster and is consistent with previous results obtained by the authors for the behaviour of the energy gap.

Keywords: Amorphous semiconductors, Clusters, Tetrahedral carbon, Ab initio density functional calculations

1. Introduction

In general, amorphous carbon is a material in which both sp^3 and sp^2 hybridizations coexist. Attempts to characterize its structure have produced results that indicate a wide spectrum of bonding types, coordination numbers and bonding angles, that make experimental and theoretical studies sample dependent [1]. However, the discovery of tetrahedral amorphous carbon, $ta-C$ [2], indicates that it is possible to produce an amorphous form of diamond since it has bond lengths, bond angles and coordination number of 0.153 nm, 110° and 3.7, respectively, determined from neutron scattering experiments [3] in comparison to 0.154 nm, 109.47° and 4.0 for diamond and 0.142 nm, 120.00° and 3.0 for graphite. When this type of carbon is doped with nitrogen it becomes an n-type material for low concentrations having a structure amenable for analysis by quantum chemistry methods.

Dealing theoretically with an amorphous material in bulk becomes more difficult when the structure is very bond-type dependent. In order to circumvent this difficulty we have undertaken a systematic study of amorphous clusters that simulate the bulk by forcing the outermost atoms to be fixed to account for the inertia of the bulk, fitting gaussian functions to the energy levels, for a variety of bond angles, bond lengths and atom ring topologies, in covalent four-fold coordinated specimens [4-6] . Here we apply these techniques to the study of the optical properties of carbon clusters, pure and contaminated with nitrogen, to better comprehend the electronic processes that take place when an electromagnetic field is applied to the bulk.

2. The Clusters and the Method

The three amorphous tetrahedral clusters are of the type $a-C_{21-i}N_iH_{28}$, where i=0, 1 or 4, and contain 6-atom boat-type rings, Fig. 1. The 28 hydrogens are used to passivate the outermost dangling bonds. Recently the role of nitrogen in tetrahedral amorphous carbon was discerned by using a variety of clusters and *ab initio* methods [4] demonstrating the effectiveness of this approach since it allows the analysis of particular characteristics, specific restrictions or geometries that may contribute to understanding the relevance of different factors on the electronic structure of these materials. The clusters were constructed using the builder module of the *InsightII* graphical user interface of MSI [7] and have one central atom, four nearest neighbors nn, 12 second neighbors, $2n$ and 4 third neighbors, $3n$. The clusters have the T_d point group symmetry with 8 degrees of freedom. The 28 hydrogens are the outermost circles. For the lower concentration, one nitrogen was placed at the center of the cluster substituting a carbon; for the higher concentration 4 nitrogens substituted carbons in the nn positions. Geometry optimizations were carried out for all clusters maintaining the $2n$, the $3n$ and the hydrogen atoms fixed.

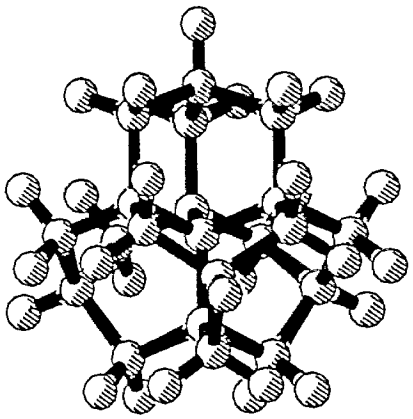

Fig. 1. $a-C_{21}H_{28}$ cluster used in the present work.

The theoretical DFT-LDA based method used allows the

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minimization of the energy of each cluster and provides the energy spectrum and the optical transitions for the minimum energy structures implemented in *DMol* [8] . All minimizations were carried out for unrestricted spin using the local density approximation (LDA) of Vosko, Wilk and Nusair [9]. The solutions to the DFT equations were calculated variationally and self-consistently and these solutions provide the molecular wave function, the electron energy levels and the intensity of the dipole transitions that allow the evaluation of the optical properties of the system *without* relaxing the cluster when electrons are in excited states.

3. The Optical Absorption

The pure cluster has an absorption spectrum with an optical gap of 5.42 eV, Fig. 2. There are six transitions at this energy value and each one has an intensity of 0.2. For i=1 the single nitrogen impurity induces transitions with very low intensities and low energies: three with an intensity 0.01 at 1.66 eV and three with 0.05 at 1.90 eV, Fig. 3. For an optical gap of 2.17 eV there appear three transitions with an intensity of 0.99. These low energy transitions are due to the nitrogen located in the center of the cluster. Fig. 4 shows the spectrum for i=4. It has even lower energy peaks, 1.24 eV and 1.31 eV, with strong intensities, 1.75 and 3.65, all within an overall more complicated structure. As reported in Ref. 4, the energy values for the LUMO and the impurity levels are: -0.43 eV, and -1.36 eV for i=1, and -0.70 eV and -0.96, -1.10 and -3.33 eV for i=4.

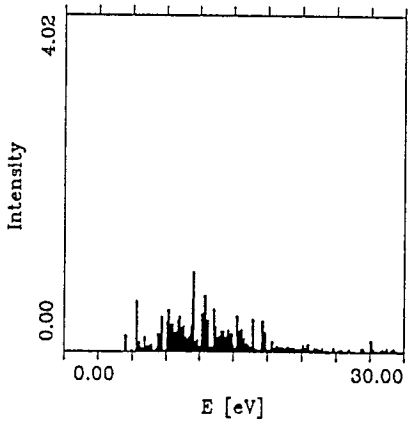

Fig. 2. Optical absorption spectrum of $a - C_{21}H_{28}$.

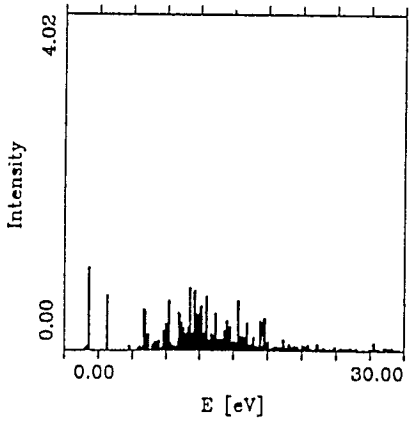

Fig. 3. Optical absorption spectrum of $a - C_{20}N_1H_{28}$.

4. Conclusions

The effect of impurities on the optical absorption spectrum of the contaminated clusters is clear. Since each nitrogen contributes an extra electron to the overall count, the impurity levels introduced reveal their presence by the low energy transitions that appear in the overall optical spectrum. Thus, even for the small clusters used here one can see that with one nitrogen the highest energy level that participates in the allowed transitions is 1.66 eV below the conduction band which, within our approximation, can be described by the position of the LUMO. For 4 nitrogens these levels are 1.24 and 1.31 eV below the conduction band. This indicates that the optical gap is different from the energy gap for these clusters [4]. Clearly, in this calculation we have assumed that the energy levels for the excited states are obtained from the minimization supposing that the structure does not change when electrons are excited. Also one must bear in mind that DFT calculations tend to underestimate the gap values and no "cut and shift" operator has been applied to our results.

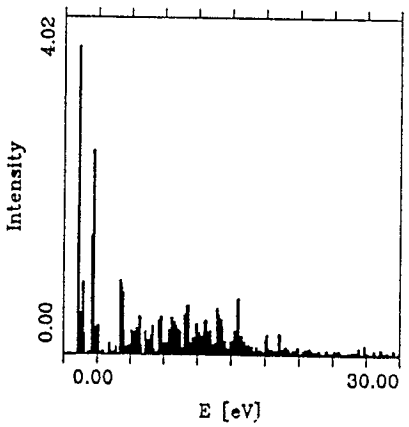

Fig. 4. Optical absorption spectrum of $a - C_{17}N_4H_{28}$.

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