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Experiment (NEXAFS) versus simulation (DOS) for carbon allotropes

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A description of a set of comphrehensive comparisons between experimental NEXAFS measurements and computed DOS results for many carbon allotropes is given.

1. INTRODUCTION

Nanodiamond has an enormous potential for industrial applications, but nanodiamond films can be marred by impurities and grain boundaries. The non-destructive characterization of these films is complex; a central issue being the elucidation of the nature of amorphous graphitic regions that surround nanodiamonds, as well as the role hydrogen plays in their formation. Experimental measurements, especially Near Edge X-ray Absorption Fine Structure (NEXAFS)[1], yield results that enable building a hypothesis for the film structure. However, only in simulations can we achieve a full characterization of the atomistic structure. Since the experiments yield curves that have features related to the DOS (Density Of States), we need to calculate the DOS of our samples. Therefore must use simulation methods such as tight-binding molecular dynamics (TBMD). Relative to using classical potentials this limits our sample sizes, but relative to using ab-initio it substantially expands them and in this project sample sizes of up to 1728 atoms were used. By comparing DOS simulation results for systems where we have a detailed description of the structure to the measured NEXAFS we may confirm (or deny) predictions from the experiments. These issues are being studied in a long-term collaboration between groups in the Chemistry and Physics departments at the Technion.

Studies of DOS of relatively small nanodiamond/graphite/amorphous carbon composites with and without hydrogen have been made in several Technion projects, ([2] [3][4]). Our initial efforts toward the DOS/NEXAFS comparisons were presented in [5]. Important aspects (described more fully in [6]) included new approaches to obtaining samples with amorphous cores in a diamond sample, and a new color code typification for atoms and bonds. Recently, detailed results [7] [8], with an emphasis on the important role of hydrogen in a set of samples with 512 atoms with a nanodiamond core have been obtained. In the present manuscript we present results for diamond and graphite, with a wide range of sample sizes (between 64 and 1728 C atoms) and different K-point selections to provide

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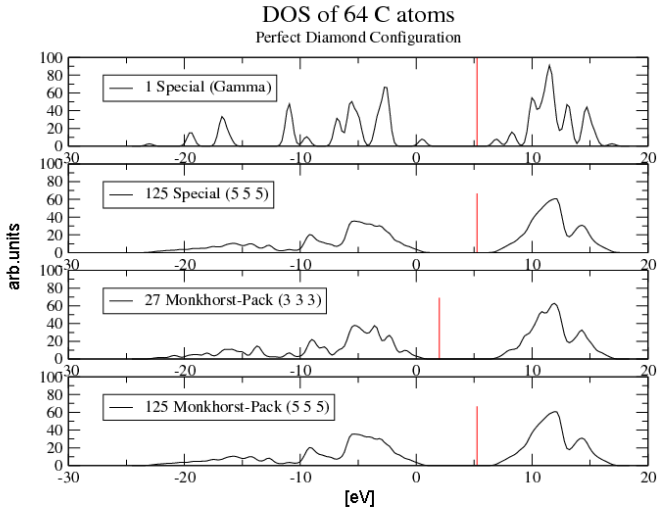

Figure 1. Diamond DOS (arbitrary units) as a function of energy in eV for different selections of K-points, with the Fermi energy shown as a vertical line.

a comphrehensive validation of our approach.

2. NEXAFS

The NEXAFS spectrum near the core level excitation edge may be described to a first approximation by a summation over all optical transitions between the C(1s) and the unoccupied electronic states. Therefore it is expected that the NEXAFS intensity at each point in the energy scale will depend on the specific geometry determined by the sample surface crystallographic orientation, incident photon source and detector orientation.

For the case of pure diamond the DOS/NEXAFS comparison may be less justifiable a priori than in amorphous carbon [8] since optical transition selection rules may have an important effect on the NEXAFS spectrum. However a general qualitative comparison may be made between the calculated DOS and the NEXAFS of diamond [1]. NEXAFS for Highly Oriented Pyrolithic Graphite, HOPG, [9] and DOS results were compared in Fischer et al [10] and we agree with both the experimental and computational results reported therein.

3. CODE VALIDATION, VARIATION IN SAMPLE SIZE AND K-POINT SELECTION

There are several different tight-binding codes, we have worked with two of these, OXON (Oxford Order-N Tight-Binding Package) [11] and PLATO (Package for Linear-combination of ATomic Orbitals) [12]. We experienced problems with larger samples in

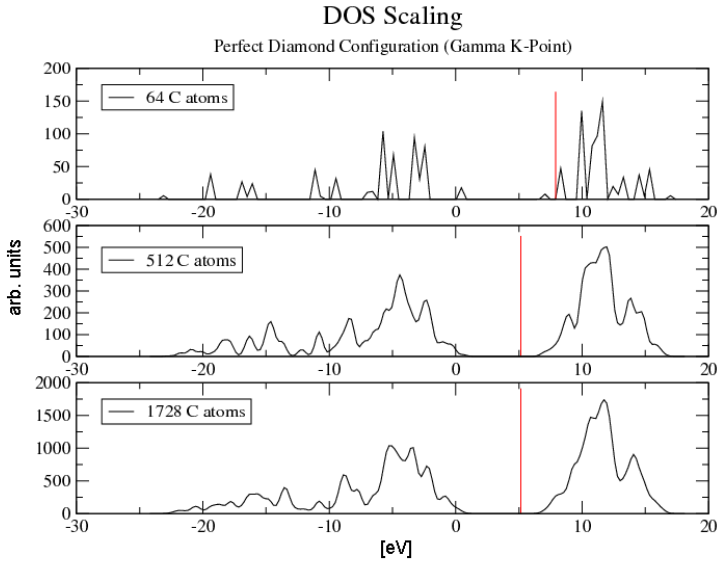

Figure 2. Scaling of diamond DOS for different lattice sizes

OXON which motivated our decision to move to PLATO, issues with OXON analyses for graphite confirmed this decision. When the tight-binding approximation is used to solve the Schrodinger equation, several different methods for selecting the k points that appear in the wave function have been proposed. The basis of the atomic orbitals in the wave function is not, in general, orthogonal. We have used include orthogonal or Fraunheim basis sets andspecial Γ point,and Monkhurst-Pack K-points, with varying numbers of points and sample sizes. These comparisons are summarized in Figures 1 and 2, all figures showing DOS in arbitrary units as a function of energy in eV. The results above the Fermi level (which falls as expected in the gap below the 10eV mark on the x-axes) have a remarkably similar structure to the experimental NEXAFS shown in [8].

4. RESULTS FOR GRAPHITE

DOS calculations for grahite are given in Figure 3, with a detail of the relvant region above E_f. The closest experimental system for which we have NEXAFS data [9] is HOPG (Highly Oriented Pyrolitic Graphite) as shown in Figure 4.

5. MIXED SAMPLES OF AMORPHOUS CARBON, GRAPHITE AND DIAMOND

CVD grown diamond films contain nanodiamonds in an amorphous carbon matrix. In simulations several geometries for mixed samples have been utilised. In [7,8] a central

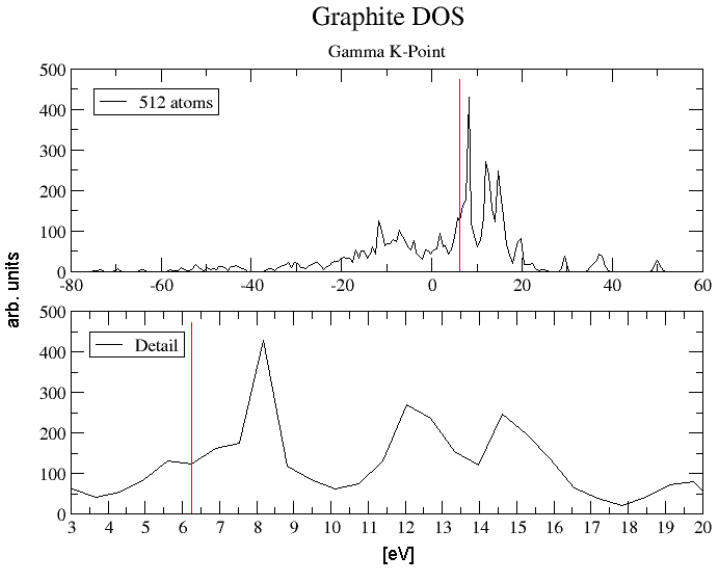

Figure 3. DOS (arbitrary units) results as a function of energy in eV for graphite with detail

diamond core was frozen in place and the surroundings melted and quenched and in [6] a spherical region in the centre of the sample was melted. With periodic boundary conditions these approaches give equivalent results. An interesting mixed sample is that from [2] where a diamond lattice was bombarded and found to have graphitic regions after annealing. The DOS here exhibits a mixture of diamond and graphitic features.

6. CONCLUSIONS AND SUMMARY

This report summarises results that validate the comparison between DOS results obtained with PLATO and experimental NEXAFS measurements.

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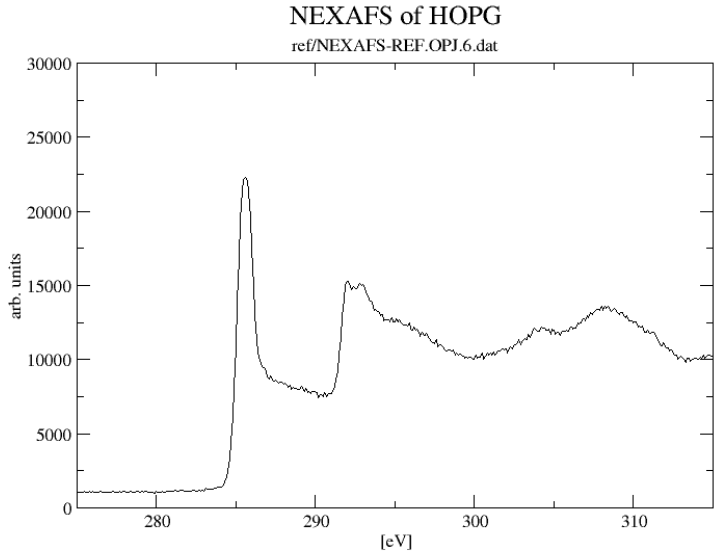

Figure 4. NEXAFS (arbitrary units) as a function of energy in eV for HOPG

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