

Nanodiamonds : their Structure and Optical Properties

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Nanometer sized diamond is a constituent of diverse systems ranging from interstellar dusts and meteorites to carbonaceous residues of detonations and diamond-like films. While many of the properties of bulk diamond have been well understood for decades, those of nanodiamond are mostly unexplored.

We present a combined theoretical and experimental study showing that diamond has unique properties not only as a bulk material but also at the nanoscale, where size reduction and surface reconstruction effects are fundamentally different from those found, e.g. in Si and Ge. We have performed ab-initio calculations using Density Functional Theory (both within the Generalized Gradient Approximation and the Time Dependent Local Density Approximation frameworks) and carried out x-ray absorption and emission experiments. Our theoretical results show that the optical gap of hydrogenated nanodiamonds with diameter larger than 1 to 2 nm is the same as that of bulk diamond. Consistently, the measured nanodiamond K-edge absorption and emission spectra for 3-4 nm clusters show the same features as the bulk material and no blue shift is observed, at variance with previous experiments. In addition, calculations show that the surface of bare nanodiamond particles larger than 1 nm reconstructs in a fullerene-like manner, giving rise to a new family of carbon clusters : bucky diamonds. Possible signatures of these surface reconstructions were identified as pre-edge features in the measured absorption spectra. As the particle size increases and their curvature decreases, the surface adopts a graphitic structure, with an energy barrier between the ideal and the reconstructed geometries increasing with size. The effect of nitrogen impurities on the stability and optical properties of nanodiamonds is finally discussed.

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