Theoretical and EELS study of Nitrogen doping of carbon nanotubes

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Nitrogen doping of carbon nanotubes is of crucial importance if the dream of carbon nanotube based molecular electronics is to be realised. Doping of carbon nanotubes should lead to a variety of interesting electronic and optical properties[1,2]. Previous attempts to dope carbon nanotubes have met with mixed success, often resulting in nitrogen gas incorporation in the tube cores.

We present a theoretical and microscopic study of nitrogen doped carbon nanotubes. Both single walled (SWNT) and multi-walled (MWNT) nanotubes have been grown using an aerosol injection chemical vapour deposition system at Montpellier University.

Core-loss electron energy loss spectroscopy (EELS) coupled with high-resolution transmission electron microscopy (HRTEM) allows two-dimensional chemical mapping of the resultant tubes with near atomic resolution. The tubes show nitrogen incorporation in the tube walls, both in single walled and multi-walled tube samples. Particular spectral features in the nitrogen and carbon absorption edges are noted, corresponding to nitrogen present with different coordination.

Computer modelling using a supercell density functional technique, AIMPRO, is used to characterise the behaviour of nitrogen within the carbon lattice. We show that whilst substitutional nitrogen is stable (formation energy of 0.4eV), there is a strong binding energy between N and carbon vacancies (3.1eV), which become stabilised with nitrogen cores. Weak repulsion is seen between substitutional N atoms, and indeed N is strongly repelled by structural lattice defects such as the Stone-Wales bond rotation defect. We calculate EELS spectra for various N lattice defects and identify prominent features in the experimental spectra. We examine defect formation and behaviour as a function of curvature. Substitutional nitrogen is increasingly stable in smaller radii tubes to the extent that lattice substitution is exothermic for some very small diameter tubes. Various cross-sheet structures are possible in multi-walled tube structures.

Finally we examine the behaviour of P and B impurities in the graphite / nanotube lattice, and discuss their potential for doping of carbon nanotubes.

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[1] X. Blase, J. C. Charlier, A. De Vita, R. Car, Appl. Phys. A 68, 293 (1999).
[2] E. Hernandez, C. Goze, P. Bernier, A. Rubio, Phys Rev Lett 80, 4502 (1998).