Mechanical Behaviour of Intrinsic Point Defects in Graphite and Carbon Nanostructures

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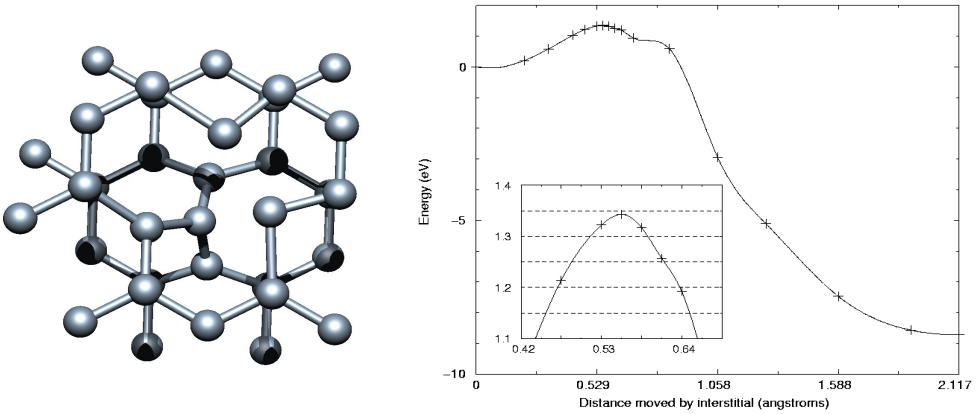
The build-up of structural defects in an irradiated crystal increases the internal energy and can alter physical properties and microstructure.

We discuss the behaviour of various intrinsic point defect aggregates in graphite and carbon nanostructures, including interstitials (I), vacancies (V), and interstitial-vacancy aggregates (I_2, V_2, I-V). Our density functional calculations[1] suggest that many of these defect complexes form bridges between graphitic layers[2], which has profound implications for the mechanical and electronic properties of the system.

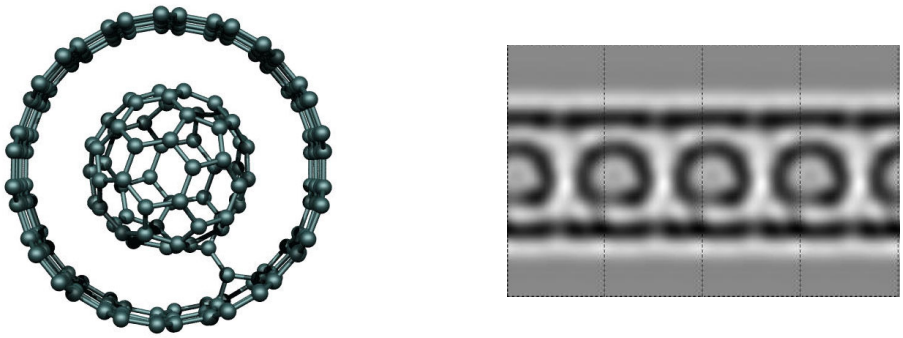
Interstitial atoms form different structures depending on whether they lie in single- or multi-layer graphitic systems. This affects both binding and migration energies.

In particular we show how interstitial and vacancy behaviour should vary between single- and multi-walled carbon nanotubes, in principle leading to different growth behaviour and response to applied stress. As an example of defect behaviour in graphites we consider the formation of I-V complexes and show their relation to the Wigner energy effect in graphite[3].



Interstitial-Vacancy complex responsible for 200°C Wigner energy release peak. Calculated barrier for recombination to perfect graphite is 1.38eV, releasing over 10eV in the process.

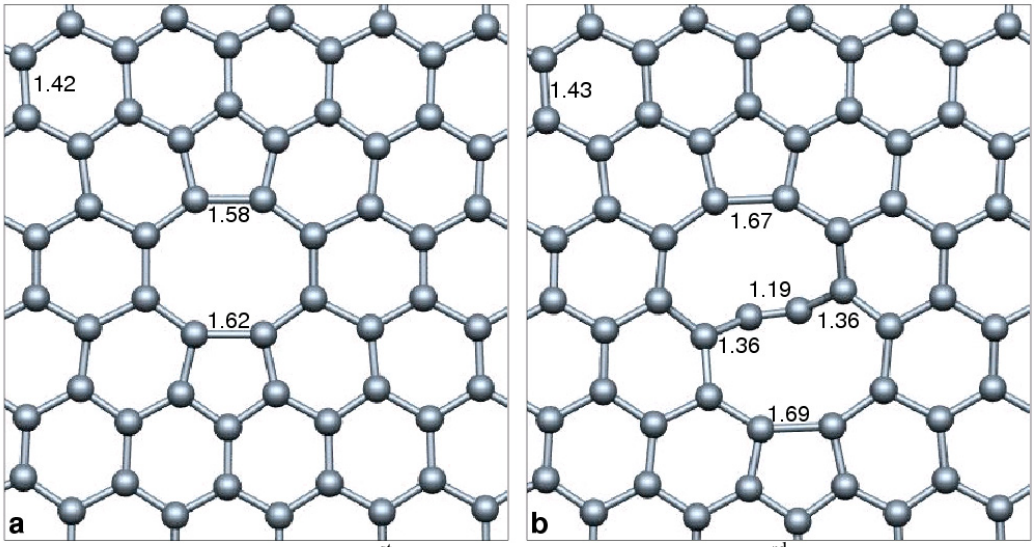
For the first time it is becoming possible to directly detect individual defect species using high-resolution transmission electron microscopy (HRTEM), and image their evolution over time[4]. We show the formation and development of point defects in various carbon nanostructures and compare these with structural calculations.



Preliminary HRTEM simulations of "peapods", C_{60} molecules in the core of carbon nanotubes, showing I-V bridging defect between C_{60} and the tube wall.

Material processing requires a detailed understanding of the diffusion and aggregation of defects and impurities. It is possible that rates of aggregation can be profoundly affected by the energy landscape of interacting defect pairs. In particular it is important to know whether there is thermodynamic bias to drift or whether aggregation is controlled by simple thermal diffusion until trapping occurs.

We show that when impurities are located at 3rd neighbour sites they can be stabilised due to rehybridisation of the two intervening carbon atoms. Although not as stable as next neighbour pairings, these 3rd neighbour structures present considerable barriers to the aggregation of defect pairs, and have a significant effect on defect aggregation rates.



Vacancy pair in graphite, (a) 1st neighbour (ground state), (b) 3rd neighbour, 4.43eV less stable. (b) nonetheless stabilised through formation of a strong C-C triple bond. 2nd neighbour 5.40eV less stable than (a), spontaneously relaxes into (a).

Different defect species can be implicated in shape change in graphitic materials, and can be used to either strengthen or weaken carbon nanostructures. We discuss the implications of these findings for microstructure evolution and physical property change during irradiation and the insights gained into defect-mediated processes in related carbon materials.

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[1] We employ a first principles approach with AIMPRO, a code using the local density functional formalism, and apply this typically to a 64 atom supercell of graphite containing the defect. Two d- and three p- like atom centred Gaussian functions are used as a basis, performing a Bloch sum over lattice vectors. Matrix elements of the kinetic energy and the pseudopotentials are found in real space while the Hartree and exchange-correlation energies and potentials are found from a Fourier expansion of the charge density. Brillouin Zone sampling is performed using the k-point generation scheme of Monkhorst and Pack and minima in the total energy are found using a conjugate gradient algorithm.

[2] R. H. Telling, C. P. Ewels, A. A. El-Barbary, M. I. Heggie, Nature Materials **2**, 333 (2003).
[3] C. P. Ewels, R. H. Telling, A. A. El-Barbary, M. I. Heggie, Phys. Rev. Lett., **91** 025505 (2003).
[4] A. Kimura-Hasimoto, K. Suenaga, A.Gloter, K. Urita, S. Iijima, submitted (2004).