FIRST PRINCIPLES MODELLING OF DISLOCATIONS IN AA GRAPHITE

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General Abstract

Graphite is widely used as a moderator in nuclear industry. Blocks of graphite are placed in nuclear reactor in order to slow down the fast-neutrons from fission processes. Neutron irradiation can lead to properties changes, such as dimensional changes which provides information for estimating longevity of graphite moderated reactor.

Fast-neutrons may knock-out atoms from the graphite lattice producing vacancies and interstitials. These defects can aggregate forming extended defects, such as vacancy lines or dislocation loops which produced dimensional changes.

We investigate defects in graphite at an atomic level in order to understand these observed properties changes. Computer models of a number of defects in graphite are studied and formation energies and atomic structures are determined within the formalism of Density Functional Theory (DFT).

Technical Abstract

Graphite is widely used as a moderator in nuclear reactor. The primary irradiation defects in graphite are interstitials and vacancies, but they can aggregate forming extended defects, such as vacancy lines or prismatic dislocation loops.

We investigate the structure and energetics of prismatic edge and screw dislocations in AA graphite within the formalism of Density Functional Theory (DFT).

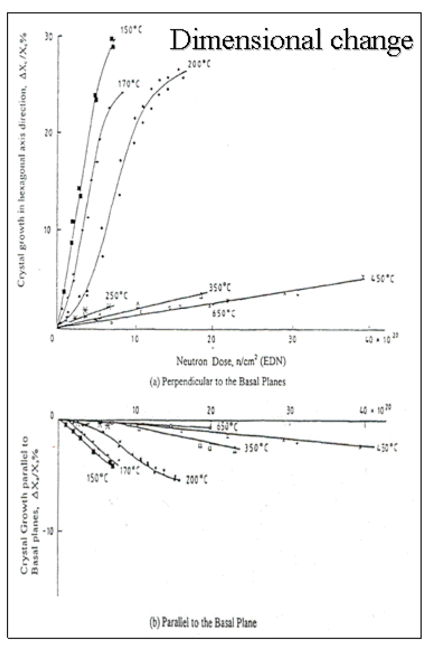
Tetra coordinated carbon atoms are found to be stable only at the core of zigzag prismatic edge dislocations, while in the rest of the studied structures carbon atoms remain sp^2 hybridised.

The dimensional change produced by irradiation at high temperatures can be interpreted due to dislocations.

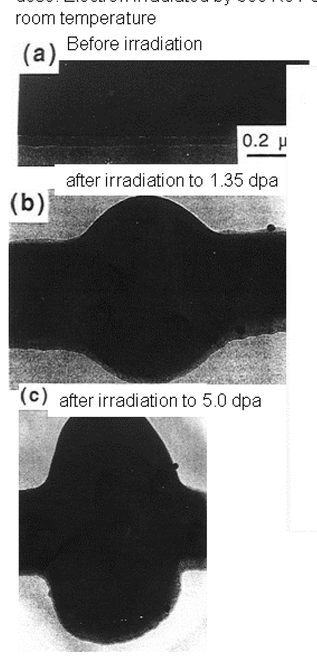
Methodology

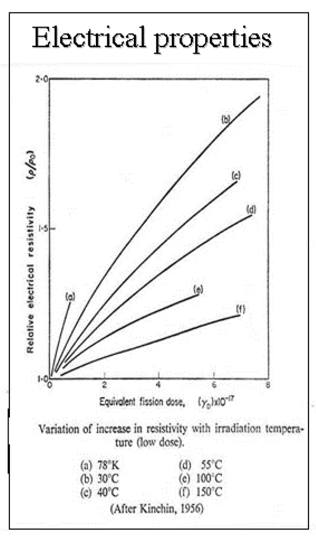
- Initial atomic positions obtained by **Isotropic Elastic Theory.**
- Use the formalism of the **Density Functional Theory (DFT)** to obtain total energy, calculate forces and iteratively optimise geometry.
- Solution to Schrödinger equation time independent, $\hat{H}\psi=E\,\psi$ assuming only atom types and starting positions.
- AIMPRO package is used with the periodic approach.
- Defect system:
  - supercell- with periodic boundary conditions: dipoles
  - cluster- periodic along dislocation line direction and hydrogen saturated in the others: isolated dislocations

Experimental observations



Bright-field images of HOPG at different dose. Electron irradiated by 300 KeV at room temperature

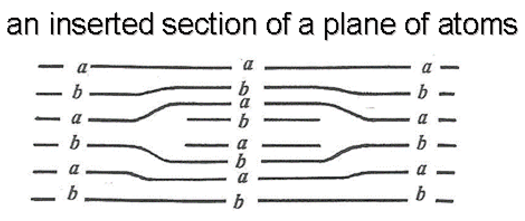




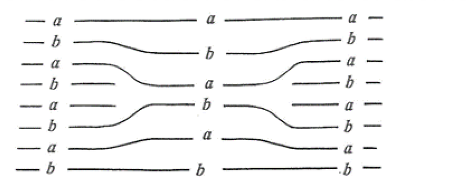
Prismatic Edge Dislocations

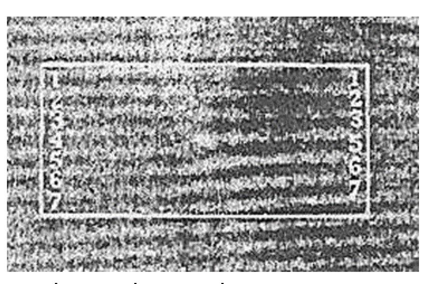
These dislocations, eventually formed during the irradiation process, are mainly composed of prismatic dislocation loops:

Interstitial loop:
an inserted section of a plane of atoms

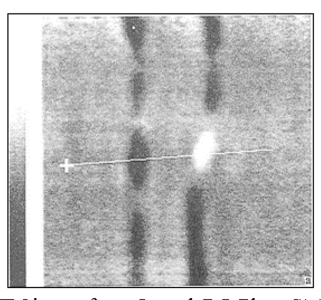


Vacancy loop:
a removed section of a plane of atoms

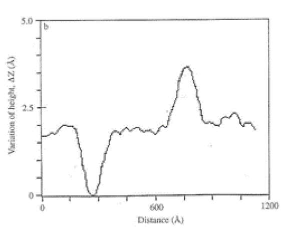




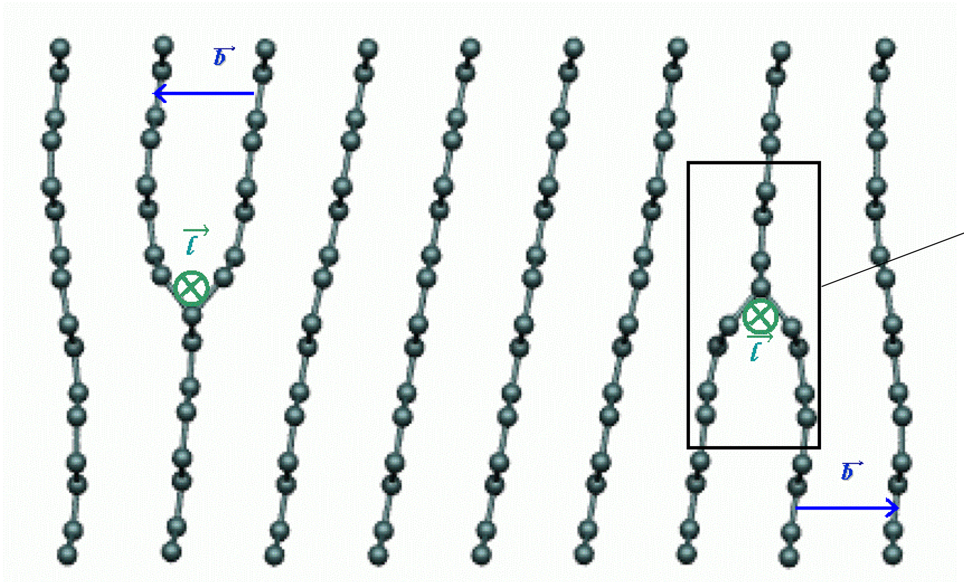
Electron microscope image. Dawson IM. Proceeding of the Royal Soc of London. 1959 A253 390

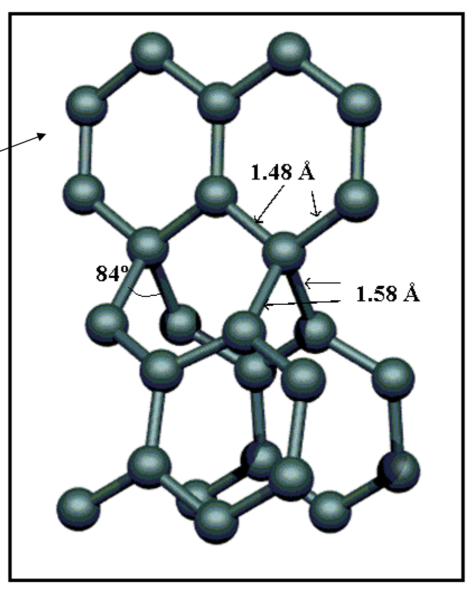


STM image from Ouseph P.J. Phys. Stat. Sol. (a) 169, 25 (1998)



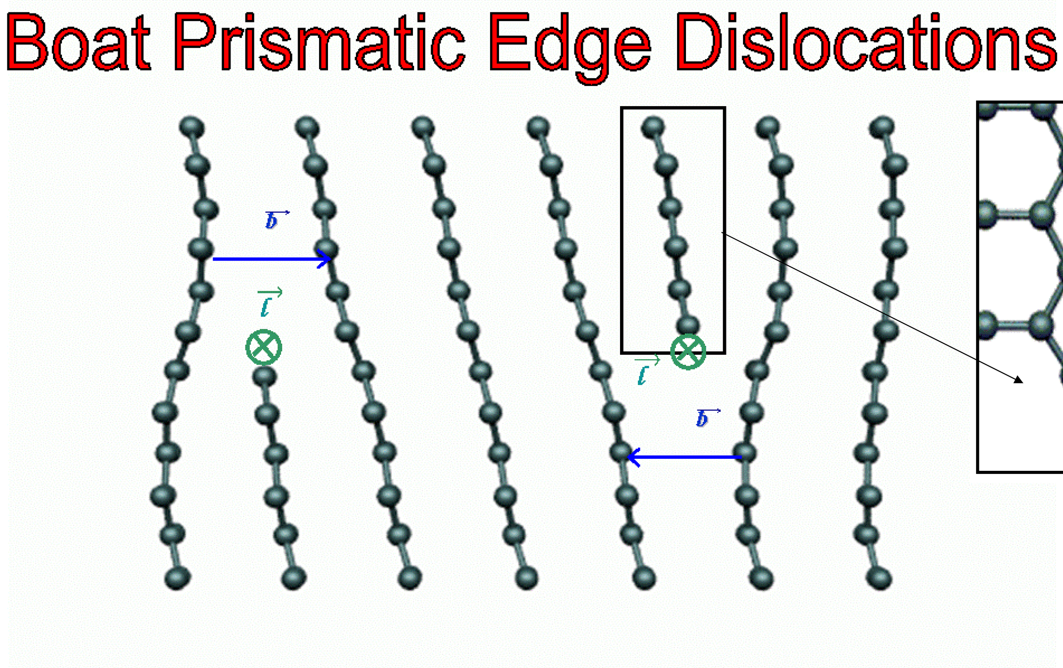
Zigzag Prismatic Edge Dislocation

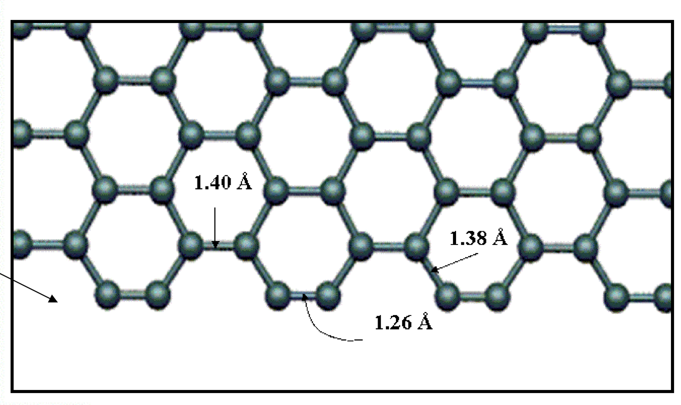




- There is sp^3 contribution with one tetra coordinated carbon atom per lattice parameter along the dislocation line.
- Initial dangling bonds: 2/ 2.46= 0.81 dangling bond/ Å
- Elastic energy: ~ 0.9 eV/ Å (Radius cut off =b/2 Å)
- Core energy: ~ 2.3 eV/ Å
- Formation energy: ~ 3.2 eV/ Å

Boat Prismatic Edge Dislocations



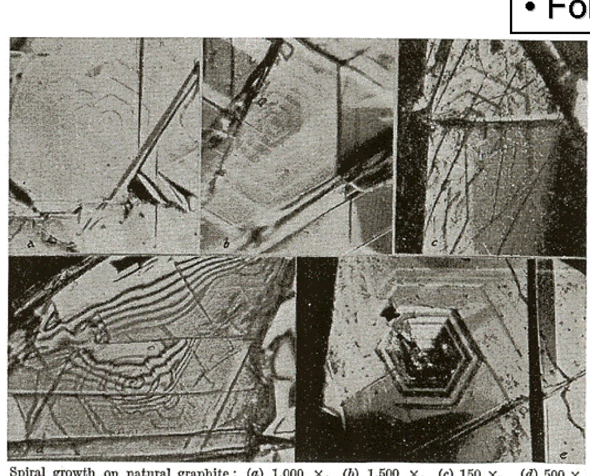


- Reconstruction of the dangling within the layer with a contribution of triple bond (sp contribution) at the core of the dislocation.
- Initial dangling bonds: 4/ 4.26 = 0.94 dangling bond/ Å
- Elastic energy: ~ 0.7 eV/Å (Radius cut off =b/2)
- Core energy: ~ 1.9 eV/Å
- Formation energy: ~ 2.6 eV/Å

Screw Dislocations

Spiral patterns have been observed on graphite surface by optical microscope.

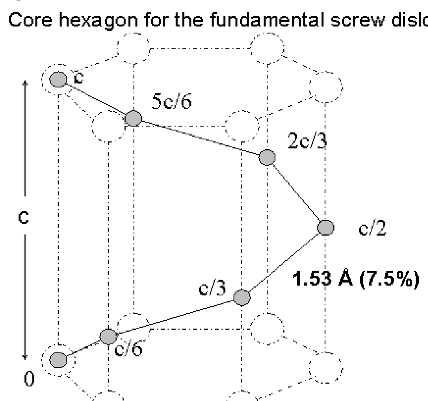
The spiral height (which directly relates with the dislocation Burgers vector) can be up to 2000 Å.



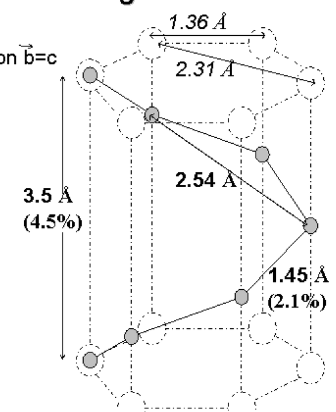
Spiral growth on natural graphite: (a) 1,000 ×, (b) 1,500 ×, (c) 150 ×, (d) 500 ×, (e) 150 ×.
F.H.Horn. Nature 170 p.581 (1952)

Fundamental Screw

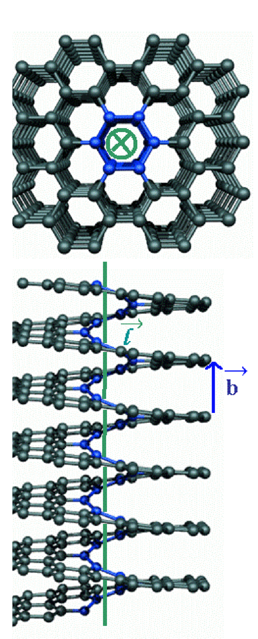
A fundamental screw dislocation presents a Burgers vector of one interlayer distance c=*3.35 Å*



Isotropic Elastic Theory predicts that a screw dislocation is invisible in a basal plane projection

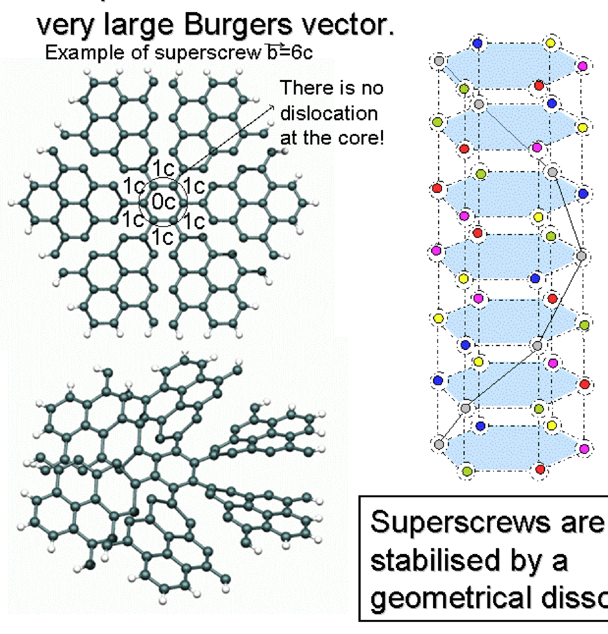


DFT
Predicts a contraction in the basal which reduces the stretch of C-C bonds and an expansion in the c-direction.



Superscrew

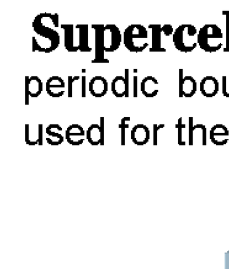
A superscrew is a screw dislocation with very large Burgers vector.



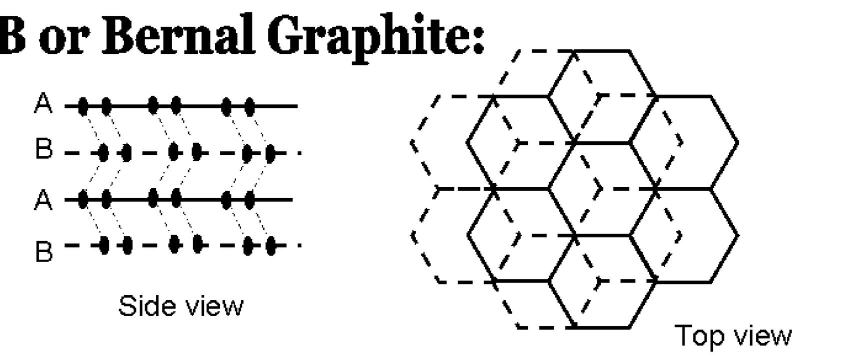
Superscrews are stabilised by a geometrical dissociation

Glossary

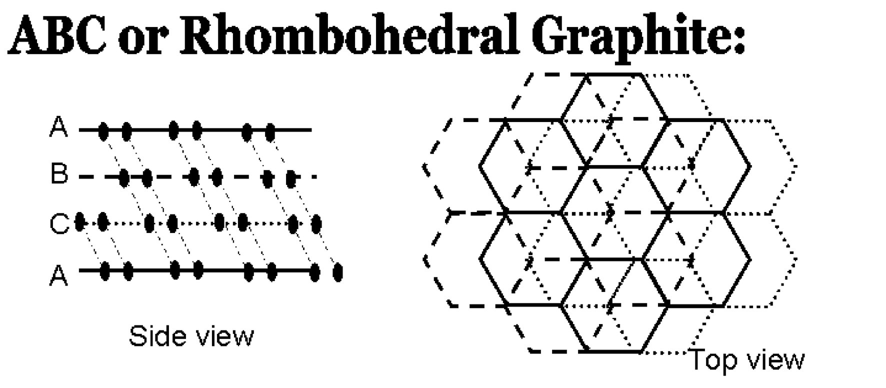
Graphite: Soft black lustrous mineral. The thermodynamically most stable allotropic form of carbon. It is made of carbon atoms bound hexagonally in sheets (like honeycomb).



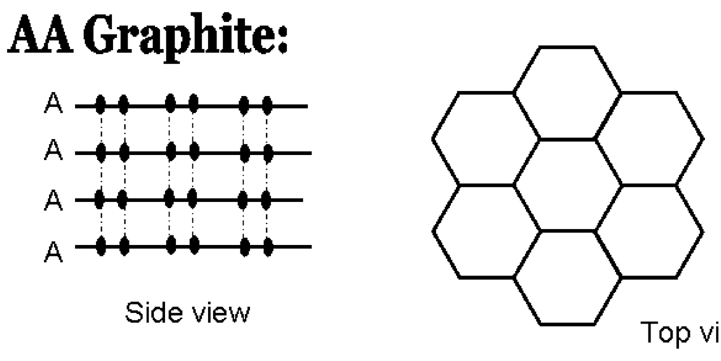
AB or Bernal Graphite:



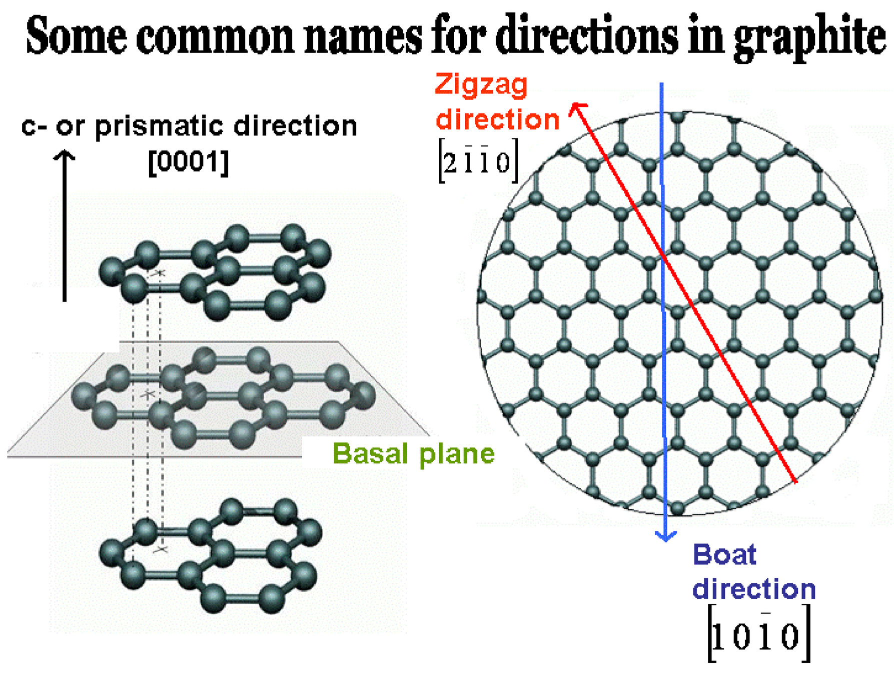
ABC or Rhombohedral Graphite:



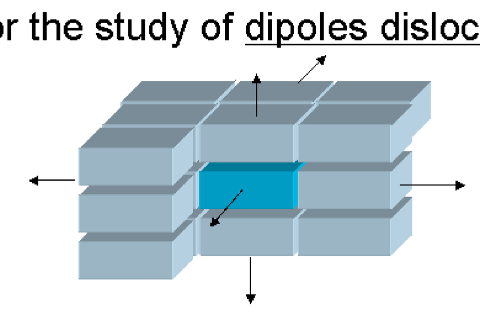
AA Graphite:



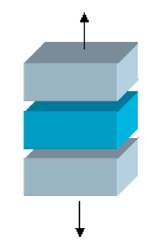
Some common names for directions in graphite



Supercell calculation: Calculation where periodic boundary conditions are applied. It is used for the study of dipoles dislocations.



Cluster calculation: A cluster calculation in a periodic approach is a calculation where the periodicity occurs only in one direction and the other directions are hydrogen saturated. It is used for the study of isolated dislocations.



Density Functional Theory (DFT):

It is one of the most popular *ab initio* approaches to quantum mechanical many-body electronic structure calculations of molecular and condensed matter systems with large number of atoms due to the short computer time required.

It is based on derived all of the electronic properties of a chemical system, including the energy, from the electronic density.

It assumes that the exchange-correlation (XC) energy of a single electron at any position is equal to the XC energy of an electron in an homogenous electron gas of a density equal to the local electron density.

Isotropic Elastic Theory:

This theory considers all the bonds as 'springs' that follow Hooke's law. The isotropic approach is the simplest, the interactions in all the directions are considered equivalent.

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