IRRADIATION EFFECTS AND BASAL SHEAR IN GRAPHITE

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Introduction

Irradiation damage in graphite has been the subject of intensive research in the latter half of the twentieth century, driven by nuclear applications. Nevertheless, even parameters as fundamental as the interstitial and vacancy migration energies are still controversial. In general the reason for this is inherent in the usually poor quality of graphite crystals and its delocalized π system which frustrates many characterization techniques common in semiconductors. In particular, it is because indirect measures of irradiation damage (changes in crystal dimensions and in electrical and thermal resistance) have been directly attributed to point defects or small clusters thereof [1].

First principles calculations of the structure and energetics of irradiation damage defects afford a direct interrogation of point defects and their clusters. In previous work [2] we have shown that the ground state of the self-interstitial is a spiro form bonding between graphene sheets, forming a core of five carbon atoms analogous to the spiropentane (apex sharing triangles) structure. A basal shear of approximately 0.7Å along a <11-20> direction is required for this, and this provides the strong interaction with basal dislocations.

The vacancy migration energy has been found to be 1.7 eV, much lower than the experimental value (3 eV), but it was proposed this could be reconciled if intervacancy binding is taken into account (either across planes as in [2] or in-plane third neighbour interactions as in [3]). The interlayer binding can also give rise to shearing forces between planes.

Theory

We apply density functional pseudopotential supercell calculations (AIMPRO code) where the wavefunctions are expanded in a Gaussian basis, the charge density in a plane wave basis and the pseudopotential of Bachelet, Hamann and Schlüter-type for carbon and Troullier-Martins type for boron. Geometry optimization is performed by the conjugate gradient method.

Results and Discussion

We find an interstitial formation energy of 5.5 eV and vacancy formation energy of 8.3 eV, giving a Frenkel pair energy of 13.8 eV in good agreement with 14 eV obtained from experiment [1]. Our initial calculations on the migration of an interstitial give a *ca.* 1 eV barrier, which leads us to suspect that the experiments giving apparent migration energies in the range 0.02 to 0.5 eV [1] are complex, secondary effects of interstitials such as shear and buckling of graphene planes. Preliminary geometry optimization on basal dislocations demonstrate that shear and buckling can give rise to substantial dimensional changes. Dislocations involve mismatch between lattice planes, which means that planes must either stretch or compress to accommodate the mismatch. For graphene planes the easy deformation is compression by buckling.

The direct evidence comes from electron microscope observations of the growth of interstitial prismatic dislocation loops and reveals an activation energy of *ca.* 1.2 eV [4]

Ref. 4 suggests that boron traps self-interstitials (figure 1), giving the large apparent migration energy – we have confirmed that such a trap exists with a trap energy of 1.1 eV, rather close to the experimental activation energy, but release rate from this trap could involve an activation barrier, which is the subject of further investigation.

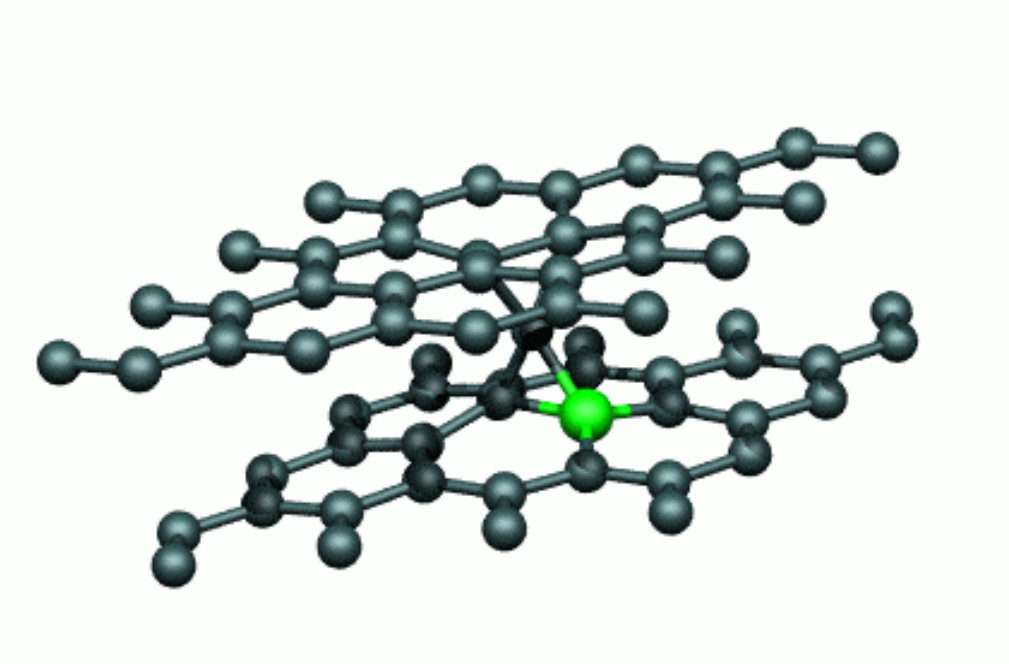

Figure 1. Self-interstitial pinned at a boron impurity

Similarly, the vacancy is trapped by boron (Figure 2) with a trap energy of 2.7 eV, providing yet another possible cause for the elevated vacancy migration energy observed in experiment. The activation barrier for release from this trap is also under investigation.

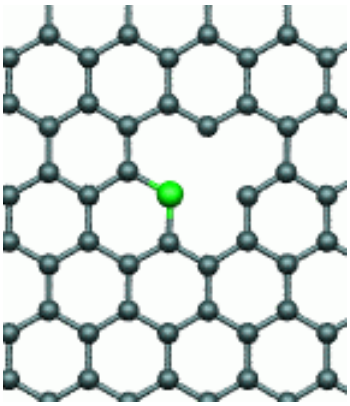

Figure 2. Lattice vacancy pinned at a boron impurity

Conclusions

The energetics of point defects in graphite and historical interpretation of many experiments on them could be need of revision in the light of first principles calculations, especially questioning the origin of indirect measures of radiation damage and of the role of boron.

Acknowledgements

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References

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