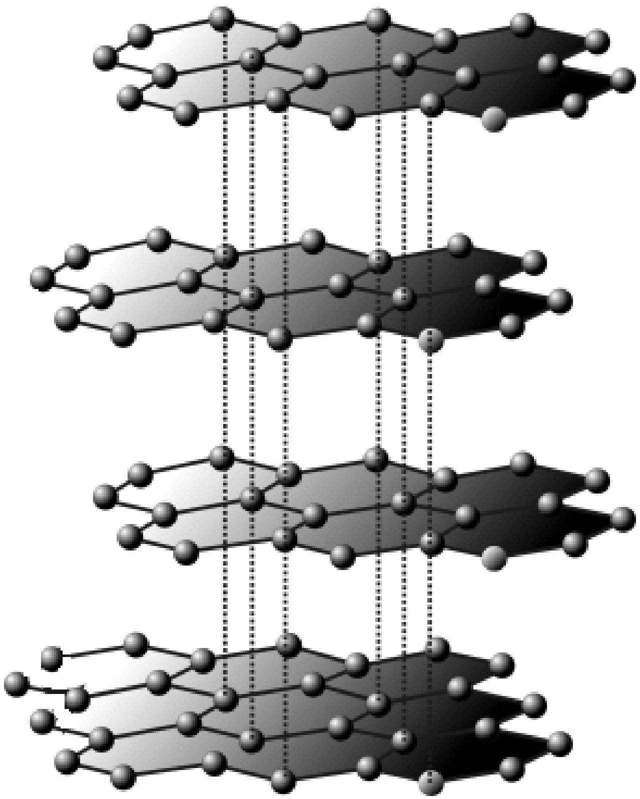
Simulation of Irradiated Graphite



Alex Theodosiou

Supervisors: Dr A. Carley / Dr S. Taylor

Background

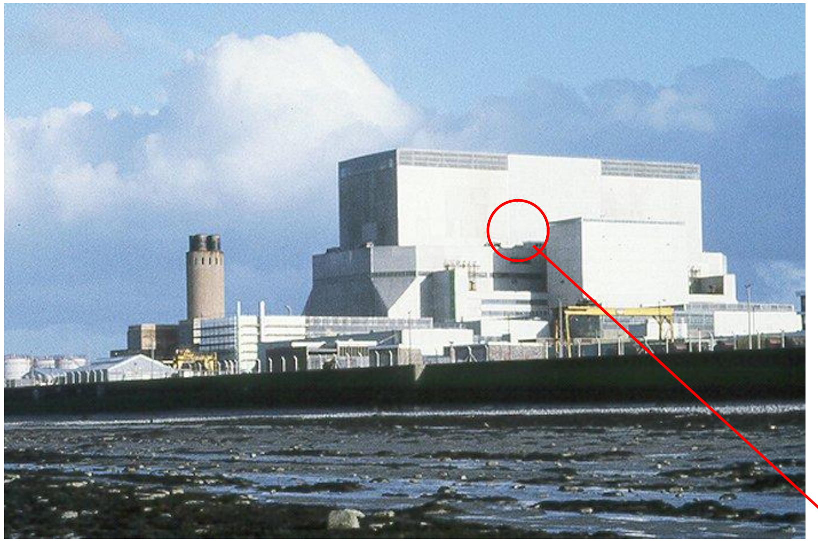
•Graphite is widely used as a neutron moderator in nuclear reactors.

•Fast, high-energy neutrons can cause a cascade of displacements within the crystal matrix via elastic collisions.

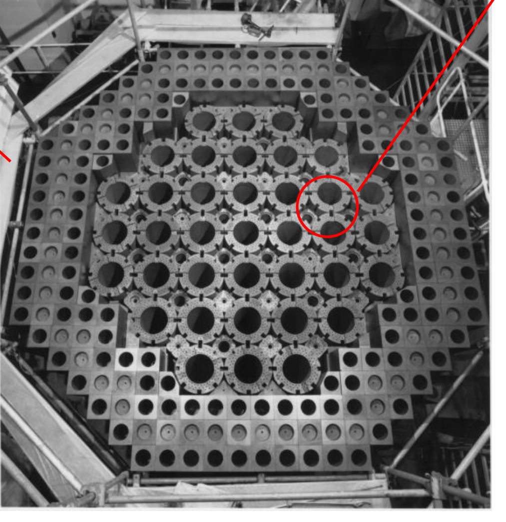
•This can lead to a build up of Wigner energy.

•c.f. Windscale Fire in 1957.

The UK currently has 7 operational AGR reactors (graphite moderated, CO_2 cooled)



Hinckley Point B

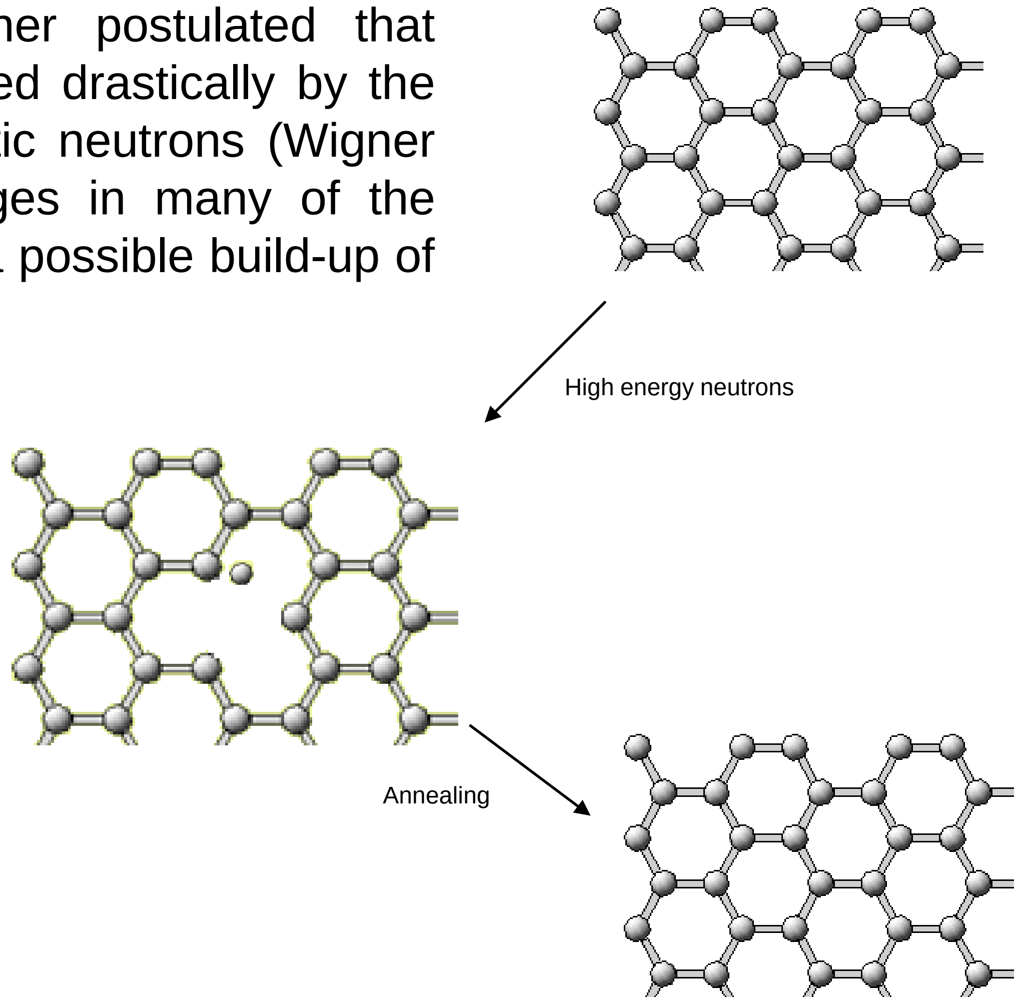


AGR core, before fuel insertion.

Typical AGR graphite brick

What is Wigner Energy?

In 1942, Eugene Wigner postulated that graphite could be affected drastically by the impact of highly energetic neutrons (Wigner effect) leading to changes in many of the physical properties and a possible build-up of internal (Wigner) energy.



Eugene P. Wigner

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Why is it important?

- The release of stored (Wigner) energy in graphite could lead to unexpected and dangerous results during processing, storage and disposal.

- Rapid and dramatic temperature rises of up to 1500 °C

- 200’000 tons of irradiated graphite worldwide that will at some stage require safe disposal

- “It is unacceptable to store or dispose of graphite containing significant releasable stored energy.” – IAEA TECDOC (2006)

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Literature Survey

"Approximately 20-30 eV must be imparted to a carbon atom in the graphite structure in order to displace it from its normal lattice position."[1]

"For every fast neutron (2 MeV) moderated in graphite approximately 20,000 atoms are knocked from their lattice sites."[2]

"Graphite becomes amorphized after a certain dose of irradiation, irrespective of the incident ion species". [3]

"Both interstitial defects and vacancy defect can be easily produced through ion bombardment".[4]

References: 1) R. Telling, M. Heggie; Radiation Defects in Graphite, *Philosophical magazine*, (2007).

2) R.E. Nightingale; Radiation Effects in Graphite

3) K. Niwase, T. Tanabe; *J. Nucl mat*, 170 (1990) 106

4) M. Portail, J.B. Faure et al; *Surface Science* 581 (2005) 24-32

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Aims

- To use ultra-high vacuum to irradiate nuclear grade graphite with inert gas ions.
- Can ions produce the same damage into graphite as neutrons do?
- What is the nature of this damage? Can we induce stored, Wigner-like energy?
- Use analytical techniques. Structural, thermal and spectroscopic, to try and answer these questions.

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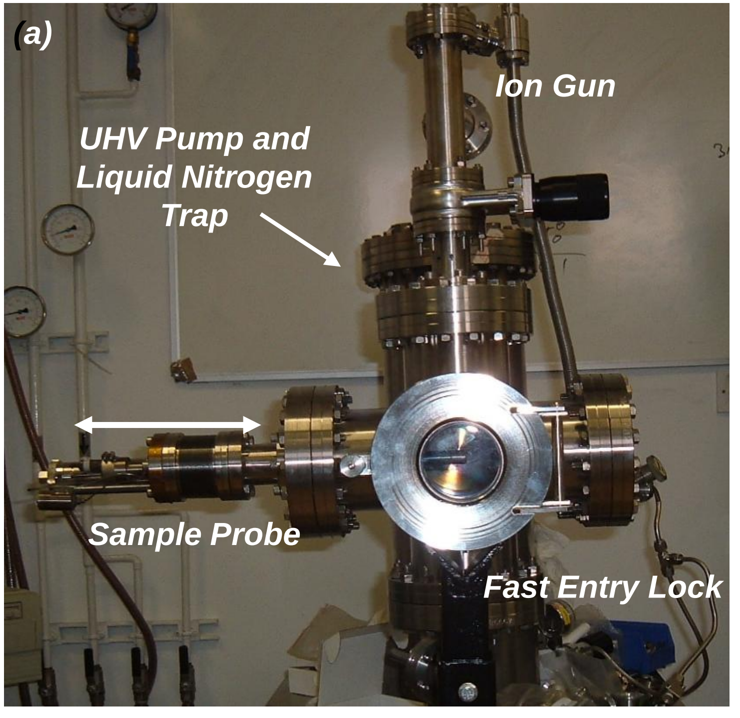
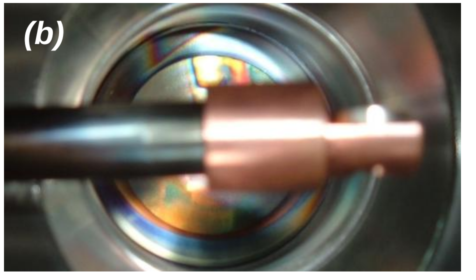
Experimental

AGR reactor grade graphite (and HOPG), is irradiated with monocationic ions, typically Ar^+ and He^+, under Ultra-High Vacuum (UHV)





a) The UHV apparatus

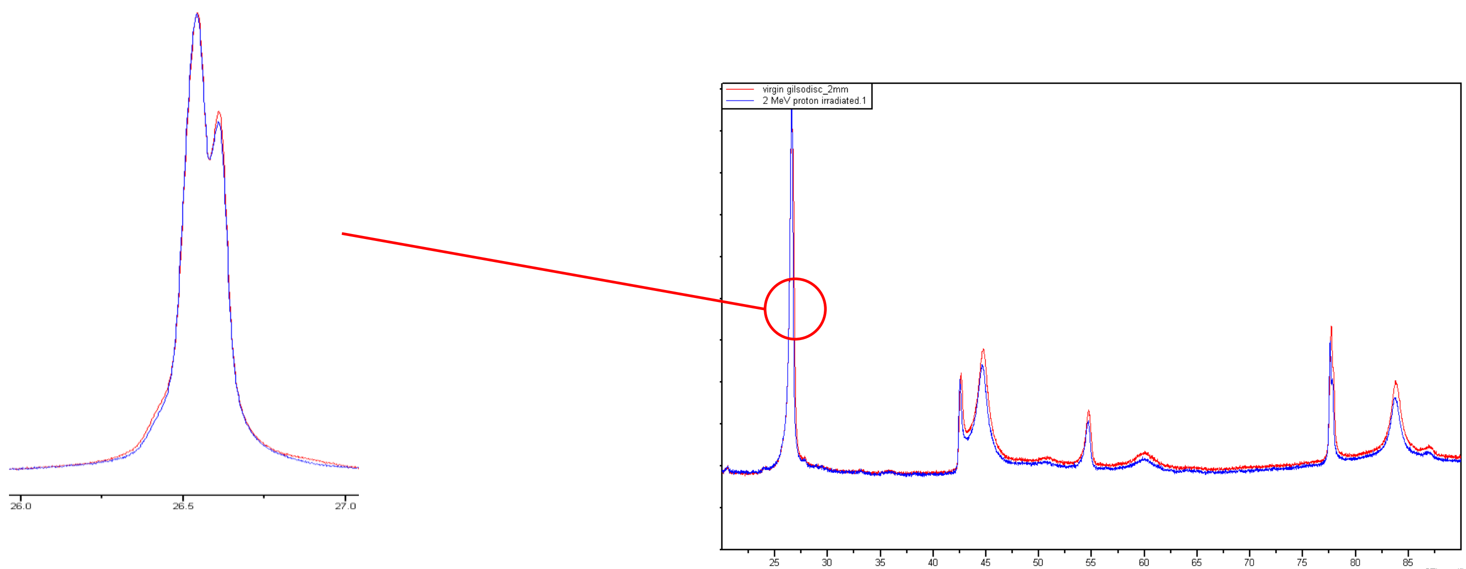
b) Close-up of the sample probe and holder

System was custom built at Cardiff and uses a diffusion pump to reach vacuum down to $3x10^{-10}$ mbar allowing for effective ion bombardment.

Results

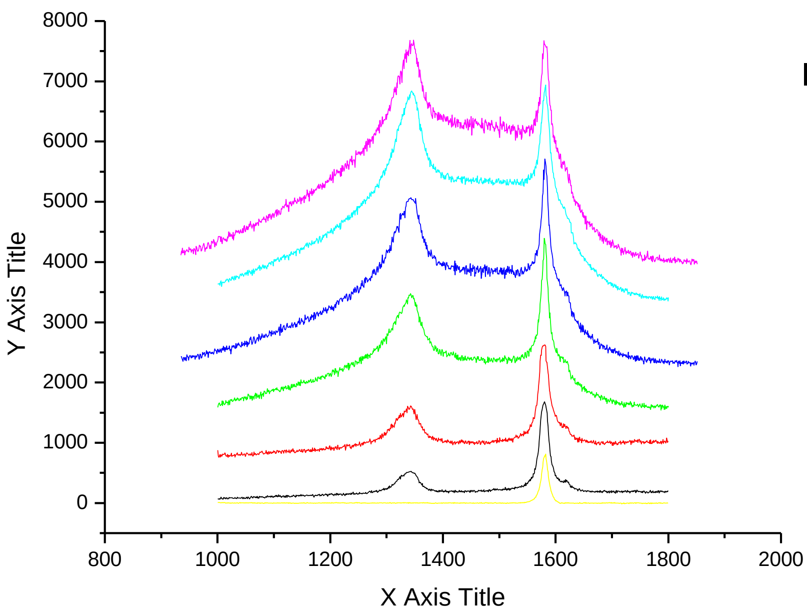
Published work has shown X-Ray Diffraction (XRD) to be a useful tool in assesing damage to the crystal lattice upon irradiation, through analysis of the 002 plane.

A broadening indicates a loss of order in the crystal structure tending to a more amorphous type structure.



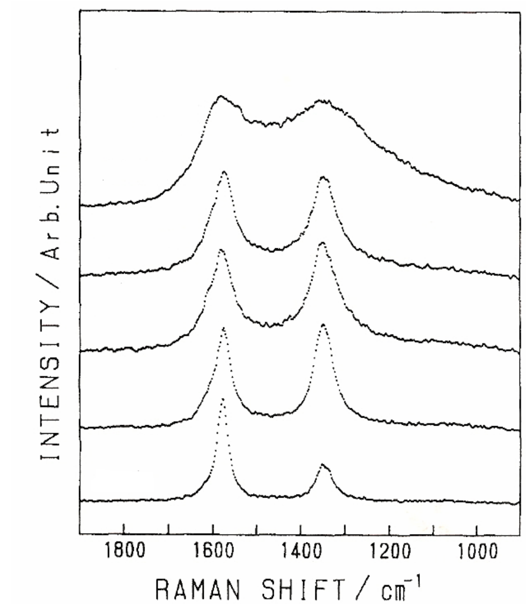
XRD results before and after 3 KeV Ar^{+} irradiation show negligable differences.

Raman spectroscopy uses the scattering of light (from a laser) to provide information on the phonon (vibrational) modes of a system.



Ar$^+$ Irradiated graphite

Increasing dose



Neutron irradiated graphite

K. Niwase, T. Tanabe; *J. Nucl mat*, 170 (1990) 106

Both spectra exhibit an increasing dissorder band (1355 cm^{-1}) upon irradiation, consequently a larger I_G/I_D ratio and hence a smaller crystallite size.

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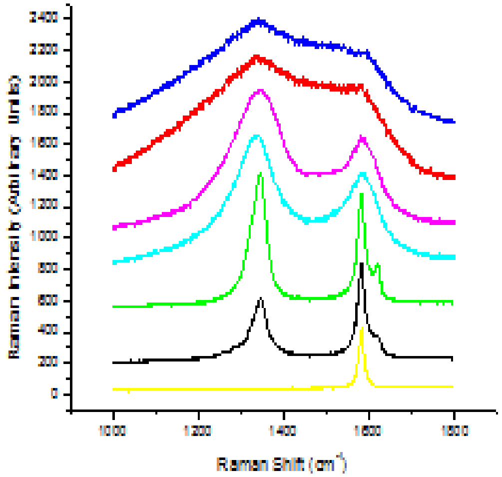
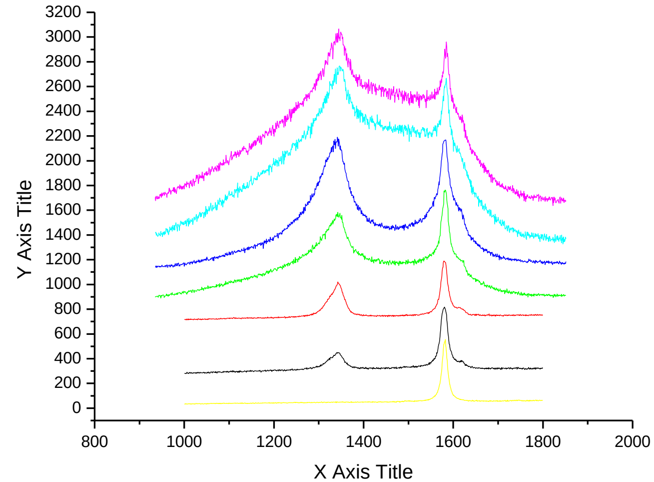
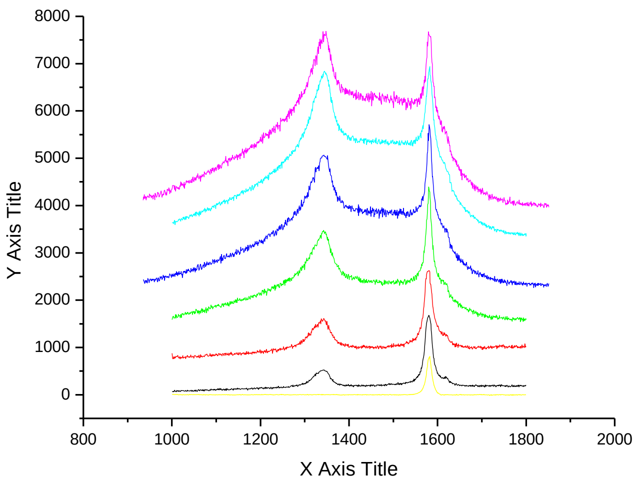
He+



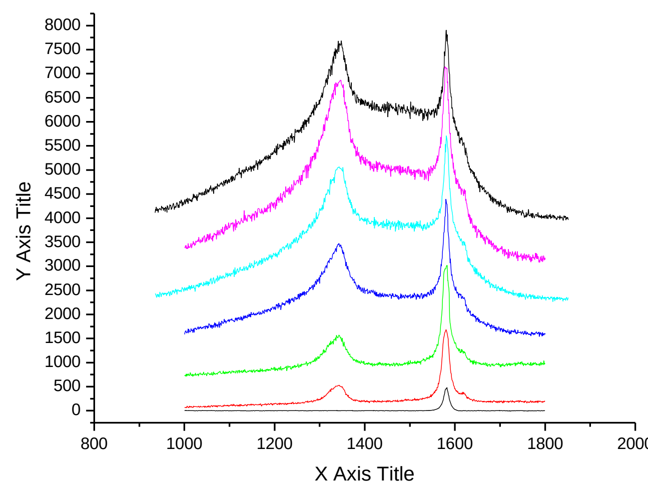
Ne+



Increasing Dose

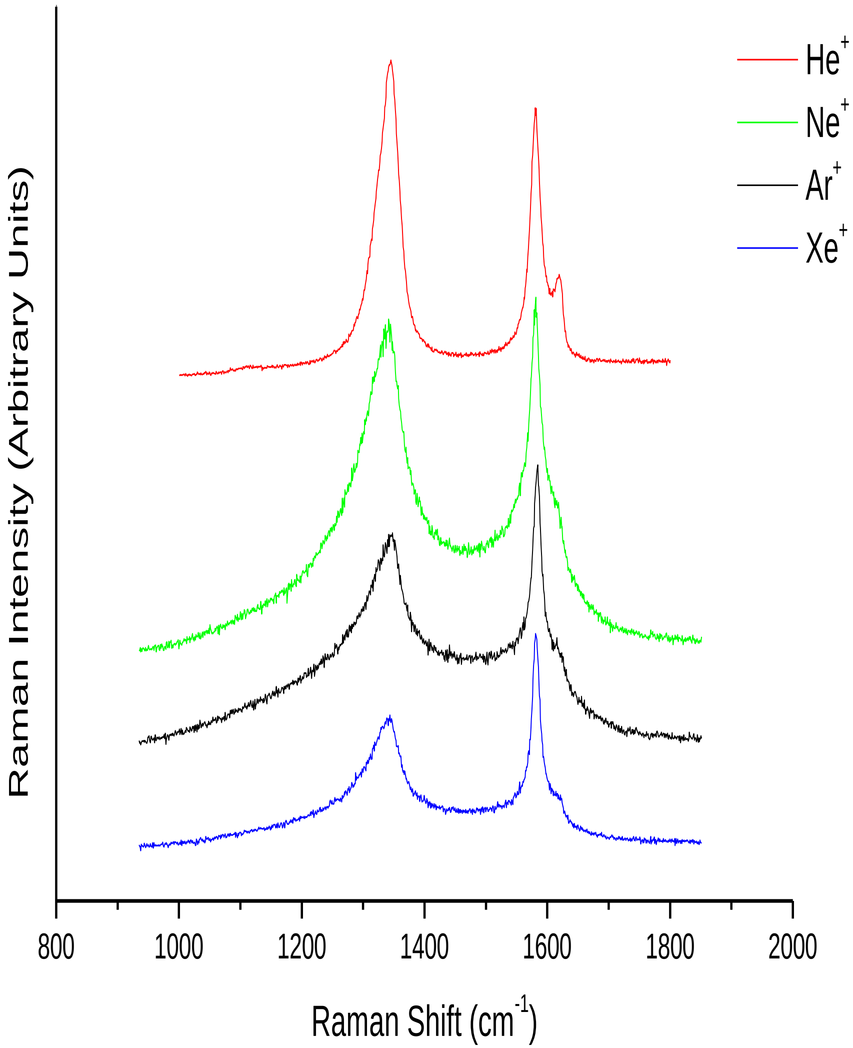


Ar+



Xe+

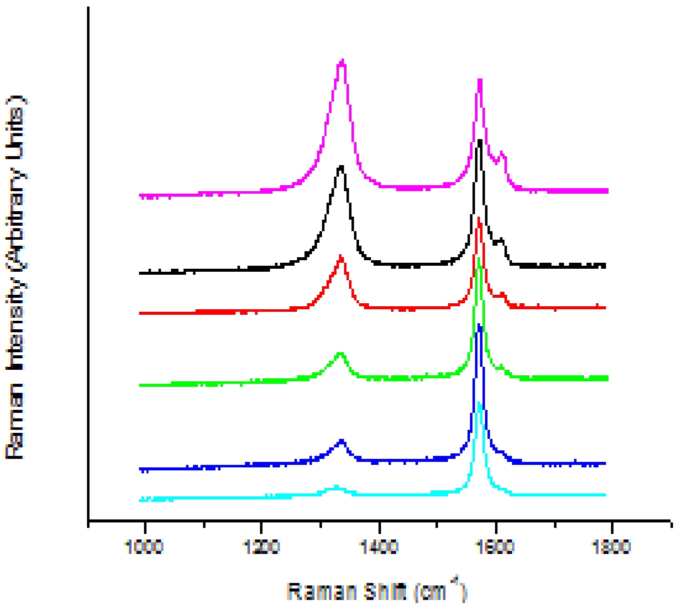
Effect of Ion Mass



Constant Dose of $1x10^{15}$ ions/cm^2 at 5 KeV

Ion	Ion Mass (amu)	Projected Range at 5 KeV (nm)	I_D/I_G Ratio
He^+	4.003	42.6	1.21
Ne^+	19.992	9.8	0.95
Ar^+	39.962	7.1	0.74
Xe^+	131.904	7.1	0.57

Annealing of Ion-Irradiated Samples

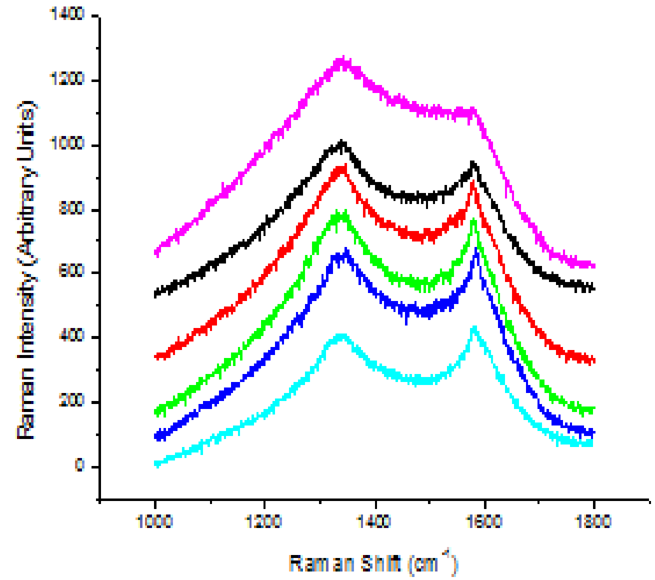


He+ Lower Dose

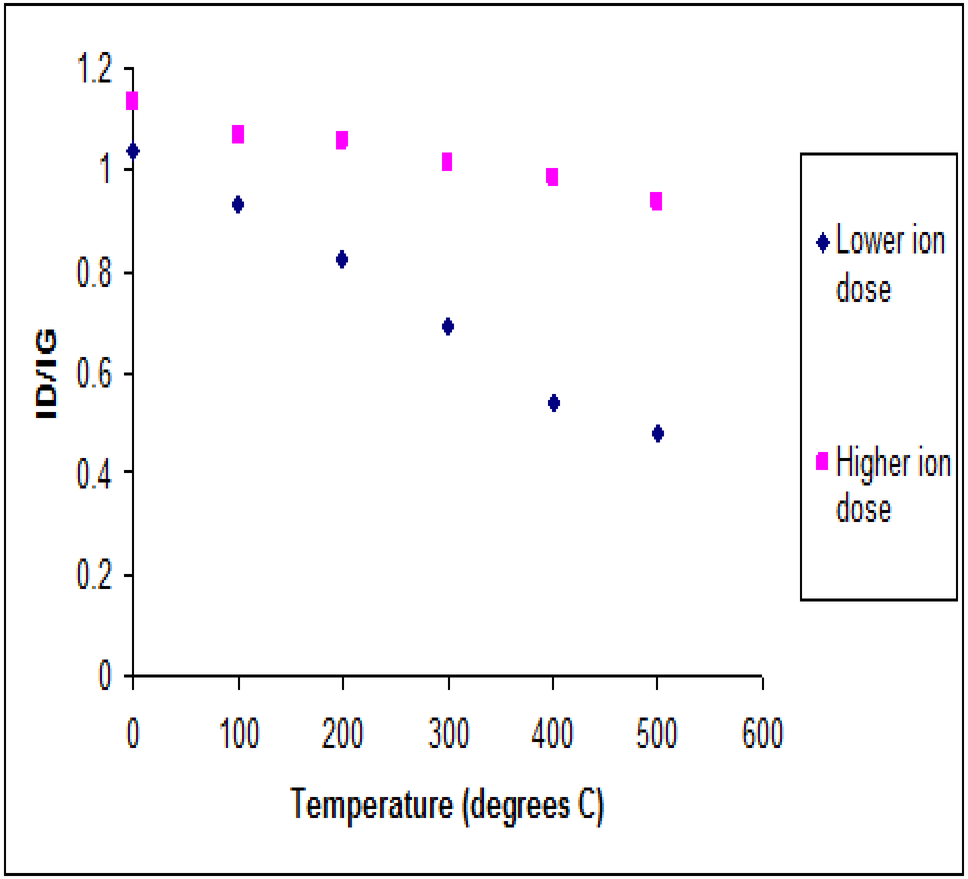
Temp

25 °C

500°C



He+ Higher Dose



I_{1350}/I_{1580} ratio decreases in an almost linear fashion with increasing annealing temperature.

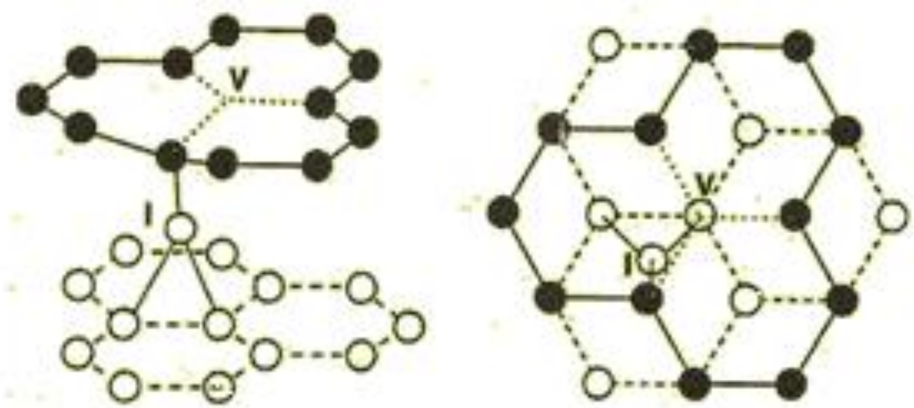
Indicates that higher temps encourage a reversal of the irradiation induced changes hence tending to the original structure (i.e. No D-band).

Results suggest that higher ion fluences lead to different damage processes that seem to be 'harder' to reverse. Can investigate this further.

Measurement of Stored energy:

Any stored (Wigner-like) energy can be detected through simple calorimetry (DSC).

Iwata[7] and Lexa[8] et al have employed DSC effectivley to monitor stored energy release from neutron irradiated reactor graphite.

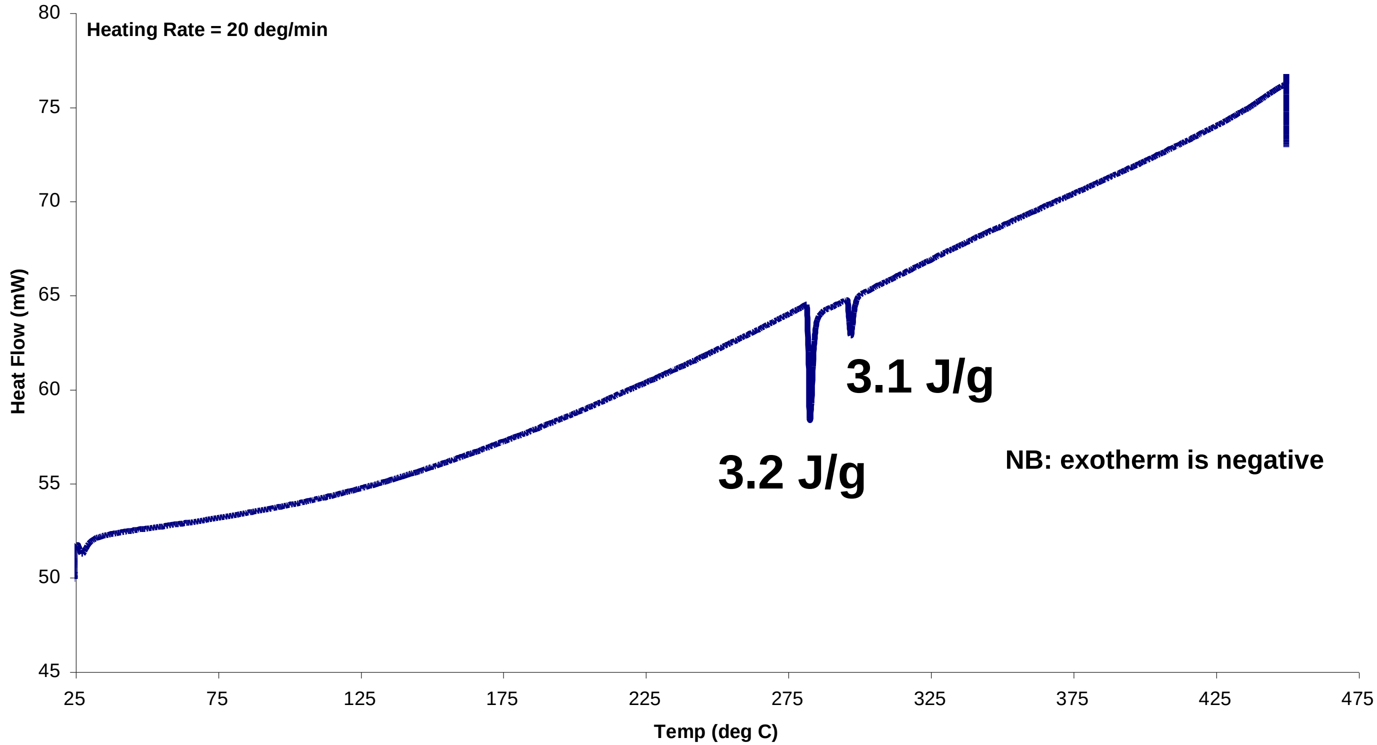


An exotherm observed between 200-300ºC is common amongst neutron irradiated graphite – and has been widely attributed to the intimate Frenkel Pair defect (shown)[9].

The metastable, intimate Frenkel-pair I + V* defect.

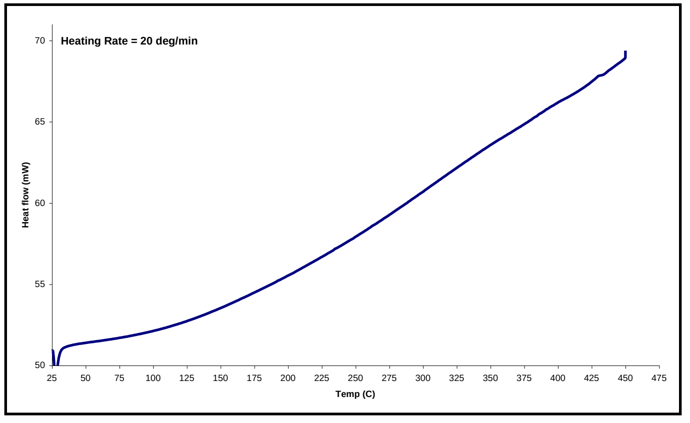
Refs: 7) Iwata, *J. Nucl. Mat.,* 133-134 (1985) 361
8) Lexa, D; J. Nucl. Mat, 122-132 (2006) 348
9) Ewels, C.P, Telling, R.H; Phys Rev lett, 91 (2003)

Previous experiments at Cardiff have shown two exotherms in the DSC trace (below):

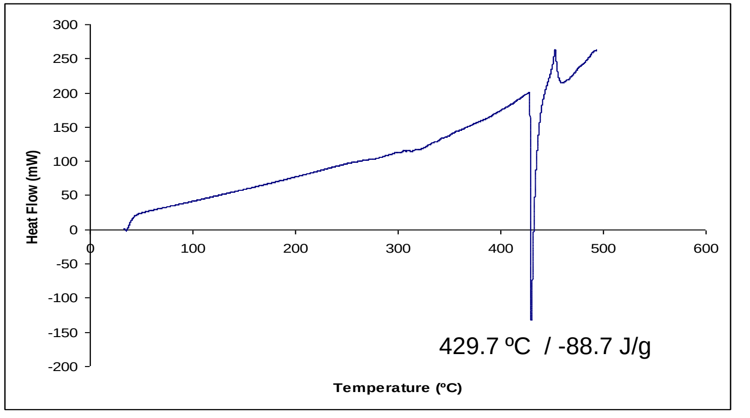


Indicates the presence of stored energy (Wigner?)

DSC Studies



Virgin Graphite



Ar^+ Irradiated at 2.5 KeV with ion gun.

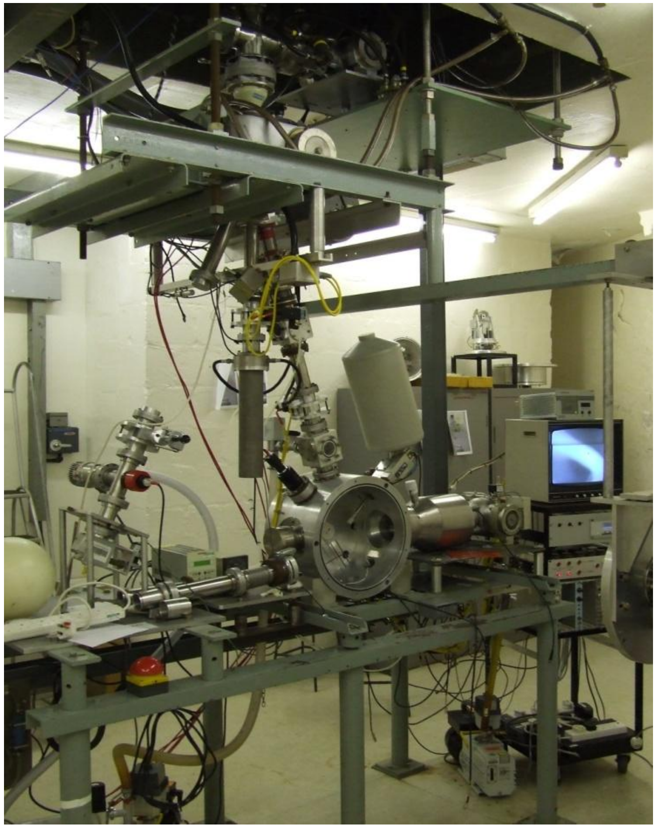
DSC trace for the virgin graphite shows no peaks – no stored energy.

Ar^+ irradiated graphite displays a large exotherm – indicative of stored energy release??

However, the intensity and temperature are different from previous exotherms observed at Cardiff. *Issues with consistency and reproducibility.*

Particle Induced X-Ray Emission (PIXE)

Powerful elemental analysis technique

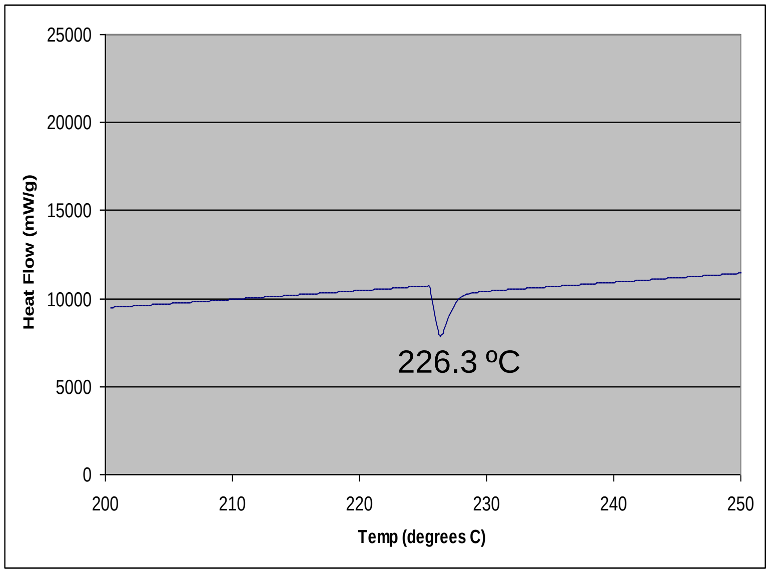


Uses a Van DeGraff accelerator to produce high energy ion beams, typically H^+ and He^+ up to 2.5 MeV.

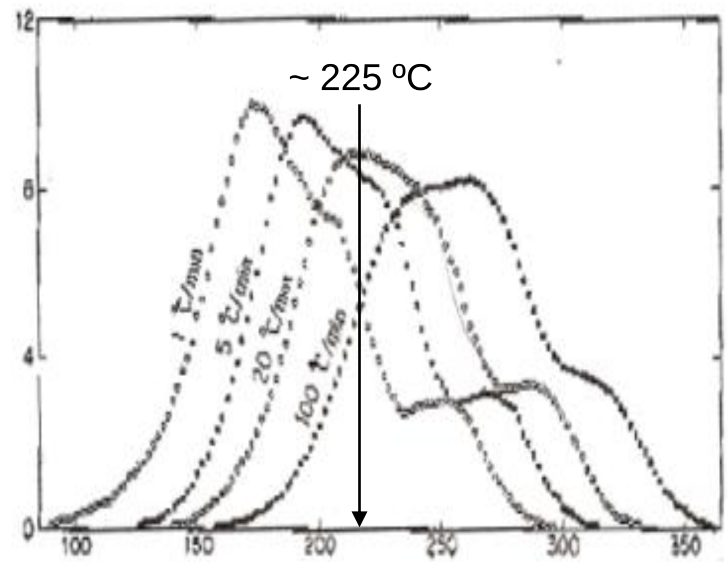
It is hoped that such protons (similar mass and energy to neutrons within a reactor core) will cause similar damage to the graphite lattice.

Results of PIXE experiments

The DSC trace of the graphite sample irradiated with protons (1 MeV, 15 mins) is shown below:



H^+ Irradiated graphite

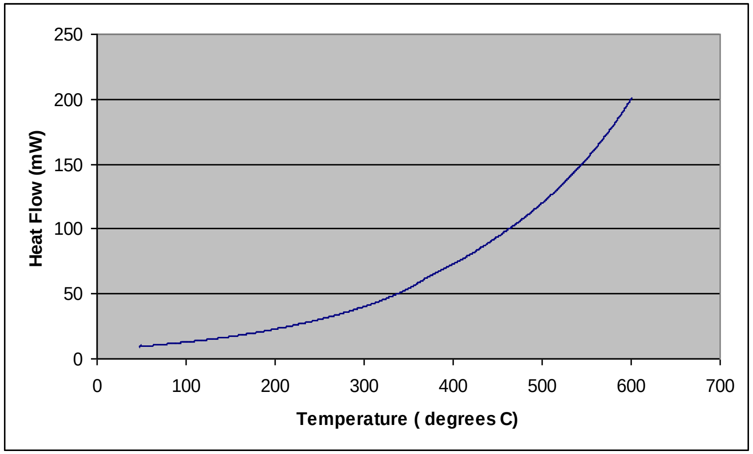


Neutron irradiated graphite
c.f. Iwata, *J. Nucl. Mat.*, 133-134 (1985) 361

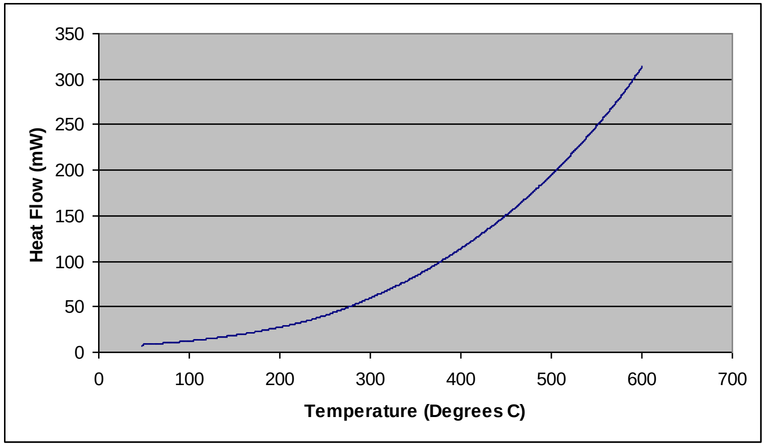
Interesting result! Both graphs show a heat release at very similar temperatures.

Several samples were irradiated at various energies for various lengths of time.

Unfortunately many of the samples displayed no exotherms upon heating with the DSC:



H^+, 2 MeV, 60 mins



He^+, 2 MeV, 60 mins

The question now is:

Why did this experiment display an exotherm while the others did not?

Possible Explanation:

Other samples were irradiated at higher energies for longer durations. This could mean that such high energies and high beam currents could cause significant localised heating, leading to self-annealment[10].

Also, the possibility of overlapping collision cascades and the increased probability of channeling could lead to a reduced number of atomic displacements.

Refs:
10) D.F. Peach, D.W. Lane, M.J Sellwood; Nucl Instr Meth Phys Res B, 249 (2006) 677-679

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Conclusions

- DSC results have shown the release of energy upon heating of ion irradiated samples – Wigner energy? – i.e It can be done (but is not as straight-forward as one might think)

- Raman results indicate disruption of the graphite lattice upon ion irradiation, similar to that observed through neutron irradiation, with higher ion doses lead to more pronounced damage that is harder to 'anneal out'. Likely due to the formation of more complex multi-atom/vacancy clusters – investigate further!

- Early studies at MeV energy show promising results. Need to investigate this further.

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Other Pieces of the Jig-Saw

- Grazing Incidence XRD (information from c.a. top 100 microns) has shown a drop in intensity of the 004 plane upon irradiation.

- XPS has shown an increase in the FWHM of C 1s peak after irradiation. Perhaps indicative of bond breaking and the appearance of some sp3 character.

- Work carried out at low temp (~ 100 K) has shown an increase in radiation damage. Perhaps expected since Frenkel pairs become less mobile and more stable.

- A collaboration with Oxford Materials Dept is underway to try and utilise HR-TEM to try and 'see' irradiation induced damage, on the atomic scale.

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What Next?

- Carry out analysis on samples irradiated (MeV) at Ion Beam Centre at Surrey University and at facility in Lyon, France. Will utilise Grazing-incidence XRD and DSC.
- Continue work with UHV system at Cardiff focusing on different inert gasses and plasmas. Look further at the effects of sample temperature.
- Carry out further analysis on irradiated samples, using various microscopy techniques (STM/AFM, TEM) XRD and DSC.

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