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Early Damage Mechanisms in Nuclear Grade Graphite under Irradiation

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Using Raman and X-ray photoelectron spectroscopy, we delineate the bond and defect structures in nuclear block graphite (NBG-18) under neutron and ion irradiation. The strengthening of the defect (*D*) peak in the Raman spectra under irradiation is attributed to an increase in the topological, sp^2 -hybridized defects. Using transmission electron microscopy, we provide evidence for prismatic dislocations as well as a number of basal dislocations dissociating into Shockley partials. The non-vanishing *D* peak in the Raman spectra, together with a generous number of dislocations, even at low irradiation doses, indicates a dislocation-mediated amorphization process in graphite.

Keywords: Graphite, Irradiation, Topological Defects, Dislocations, Amorphization

Introduction Currently pursued as a neutron moderator for the next generation, high temperature reactors, graphite has a rich history in nuclear energy dating back to 1942, when the first prototype reactor was developed by Enrico Fermi. Graphite has a lamellar structure, where the basal planes—constituted by strong, sp^2 -hybridized carbon atoms arranged in a hexagonal lattice—are held together through weak dispersion forces. The weak inter-layer interaction allows the graphitic layers to slip over each other promoting the formation of complex inter-layer defects [1,2]; recent investigations on graphene layers also show evidence for several classes of topological (planar) defects.[3,4] When irradiated, graphite exhibits asymmetric dimensional change that is generally attributed to the non-isotropic bonding characteristics.[1]

The mechanisms of defect formation in graphite during the early stages of irradiation are still not completely resolved. In the traditional view, a large number of interstitial and vacancy point defects are postulated to be generated under irradiation. Over time, point defects agglomerate and collapse into dislocation loops [1]; it is generally regarded that a number of prismatic dislocations are formed during irradiation. With continued irradiation, additional planes are formed between the graphitic layers, which contribute to an expansion perpendicular to the basal plane (along the *c*-axis).[1] In the nuclear graphite grades, the expansion along the *c*-axis

is initially masked by the collapse of micro Mrozowski cracks, followed by a rapid volume expansion [5] at higher irradiation doses.

Not all experimental observations fall in line with the above description. In a room temperature experiment with electron irradiation, large elongation along the *c*-axis (300%) has been observed on highly ordered pyrolytic graphite (HOPG) samples without concomitant observations on interstitial loops.[6] Solid-state disordering and amorphization [7–9] have also been observed in graphite with neutrons, ions and electrons, particularly at low temperatures and high fluences. The above observations are consistent with the reported bending and fragmentation of the basal planes into nanocrystallites with concomitant tilting [6]—perhaps, a precursor to amorphization. The early controversy on the role of amorphization,[10] to a large extent, is still unresolved.[1]

Recent experiments also show fascinating changes in the bond structure of graphite and graphene sheets under irradiation. While Raman spectroscopy studies with graphite at high doses show a saturating defect (*D*) to principal (*G*) intensity ratio (I_D/I_G) that is indicative of a significant proportion of residual ring-like sp^2 bonds, the I_D/I_G ratio for mono and few-layer graphene sheets exhibits a rapid decrease after passing through a maximum.[11,12] Thus the presence of a large number of layers in graphite appears to stall the complete trans-

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formation of planar sp^2 to non-planar sp^3 bond structures, unlike in few layer graphene sheets. To explain the process of defect generation, accumulation and amorphization, Niwase developed two models of differing physical origins.[13–15] In the semi-empirical, disordered-region model, changes in the Raman peaks are correlated to the generation and accumulation of vacancies, which transform into disordered and amorphous regions beyond a critical irradiation dose, or displacement per atom (dpa).[13] In the kinetic dislocation-accumulation model, Frenkel pairs generated by radiation give rise to divacancies, which morph into stable dislocation dipoles that multiply with increasing irradiation dose.[14] Given that both models have physically appealing features, a more cogent exposition of the pertinent mechanisms appears to be exigent. Experiments also show a rapid increase of stress intensity factor at very low neutron fluences,[16] perhaps, indicative of significant dislocation interactions. Thus, there is a lack of clarity on the mechanisms associated with the early damage processes.

In this Letter, we seek to delineate the nature of the bond and defect structures in nuclear block graphite (NBG-18) under neutron and ion irradiation using Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). We observe that the magnitude of the D peak in the Raman spectra increases with irradiation, which indicates an increase in the number of topological defect structures that are planar, ring-like and sp^2 -hybridized. Our experiments also show that the D peak does not shrink significantly in graphite even when irradiated to several tens of dpa, indicating the persistent presence of a defected layered structure with a high proportion of topological defects. Concomitantly, we also observe prismatic dislocations as well as a number of basal dislocations dissociating into Shockley partials. We conclude by noting that local disordering and amorphization are likely mediated through dislocations, and not through direct collapse of vacancies.

Experimental Details Neutron irradiation was conducted in the PULSTAR reactor at the North Carolina State University at a rate of 2.8×10^{-9} dpa/s. The samples were irradiated at a temperature of ~ 325 K with an average fast neutron flux of 2×10^{12} $n/(cm^2 \cdot s)$. Several specimens were also irradiated with carbon ions at the University of Wisconsin to several tens of dpa. Raman vibrational spectra were collected with a Horiba–Jobin Yvon LabRAM HR VIS high-resolution confocal Raman microscope using a 633 nm He-Ne laser as the excitation source. An elemental Si reference (520.7 cm^{-1}) was used for spectral axis calibration, and the zero position of the laser line and the Si line position were aligned prior to the data collection for each sample. Spectra were typically collected using a ten second measurement time with five

accumulations, and were processed using LabSpec software. XPS (SPECS, PHOIBOS 150) with Al/Mg dual anode source of 10–14 keV was employed to analyze the changes in the chemical bond structure following radiation. Samples for the transmission electron microscope (TEM) were prepared using focused ion beam in FEI Quanta 3D FEG-SEM microscope and HRTEM was performed in a Hitachi HF2000 TEM using an accelerating voltage of 200 kV.

Results and Discussion

Raman Spectroscopy. Figure 1(a) shows the Raman spectra for virgin and neutron irradiated (0.006 dpa) NBG-18 samples. The spectra for the samples are characterized by two prominent lines: a Raman active E_{2g} line at $\sim 1580\text{ cm}^{-1}$ (known as the G peak) and the disorder induced A_{1g} line at $\sim 1333\text{ cm}^{-1}$ (known as the D peak).[17] It is well-known that the D peak arises from the defects in the samples; the D peak for the virgin sample connotes the defects that were accumulated during the graphitization process. Under irradiation, the D peak strengthens considerably, indicating the accretion of defects that are solely radiation-induced. While Raman spectroscopic analyzes have been commonly employed for irradiated graphitic materials,[18,19] the nature of defects that contribute to the D peak have not been elucidated in adequate detail. On the basis of recent progress, especially on the theoretical front, we identify that the D peak arises exclusively from planar, ring-like, sp^2 -hybridized defects [17,20–22]—also known as topological defects. To understand the evolution of defects with irradiation, we will first discuss the origin of the main peaks observed in graphitic materials.

Even though NBG-18 is polycrystalline with a microstructure constituted by graphitic filler phase (pitch coke), binder (coal-tar pitch) and quinine insoluble particles, and punctuated by micro Mrozowski cracks, macrocracks and pores,[23–25] the Raman shift for the G peak is virtually indistinguishable from that in HOPG samples. This indicates that only the chemical bonds of the graphitic phase are activated by the incident laser. The G peak, which stems from a single resonance process, corresponds to E_{2g} phonon scattering with zero momentum ($\mathbf{q} = 0$) at the Γ point, with the intensity proportional to the number of sp^2 scattering sites.[26] In the molecular picture, the G peak represents the bond stretching of all pairs of sp^2 -hybridized atoms. The D peak is attributed to a higher order process that arises from a double resonance mechanism, which selectively activates a characteristic phonon wave vector.[27–29] The excitation of a phonon with momentum $\mathbf{q} \neq 0$ is not allowed in perfectly crystalline (HOPG) samples, but allowed in defected samples leading to defect D and D' peaks (Figure 1(a)). In the solid-state picture, the D peak is described on the basis

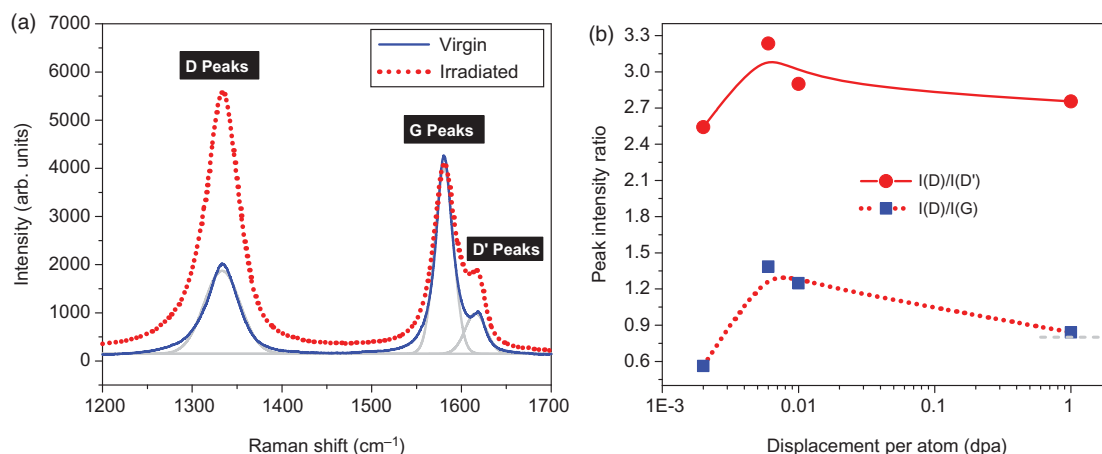


Figure 1. (a) Raman spectra of virgin and neutron irradiated (0.006 dpa) nuclear grade NBG-18 samples. Grey lines for the virgin sample are Gaussian fits to the peaks. (b) Peak intensity ratios for different levels of radiation damage. The data for 1 dpa is from ion irradiation at 300 K.

of an electron–hole pair excitation with a photon, followed by electron–phonon ($k \approx 1/2 q$) scattering near the **K** point and electron–hole recombination.[20] From the symmetry involved in the resonant transitions, the transverse optical branch near the **K** point corresponds to the *D* peak while the longitudinal optical branch near the Γ point corresponds to the *D'* peak [30]; both features are visible in the virgin and irradiated NBG-18 samples. The molecular picture gives a relatively straightforward interpretation for the *D* peak—it arises from the breathing modes of the defected sp^2 atom sites having a planar, closed ring structure,[17,20–22] when excited by laser wavelengths that are in the visible range. The converse is also true—any defect, which does not constitute a planar, ring structure (such as a three dimensional, cross-linked defect), does not activate the *D* peak in graphite and graphene layers.[17]

Irradiation, typically, creates a large number of point defects, a fraction of which will condense over time to form extended defects. It is known that several types of point defects are energetically possible, many of them involving closed planar structures (sp^2 -hybridized) or three dimensional structures (sp^3 -hybridized or a combination of sp^2 and sp^3).[2–4,31] In-plane interstitials do not exist in graphite as the energy penalty for placing an atom in the hexagonal ring is extraordinarily high. Planar defect structures can however, simply arise from the rearrangement of carbon atoms in the basal plane. The most common planar defect is the 55–77 Stone–Wales (also known as Thrower–Stone–Wales) defect configuration, which is formed by the rotation of a C–C bond by 90° . [4,32] Double vacancies can result in closed planar structures without dangling bonds; tight binding simulations show that two vacancies can coalesce into a 5–8–5 divacancy configuration followed by a transformation to a 555–777 structure that is more energetically favorable.[33] Interstitials, typically, are trapped between

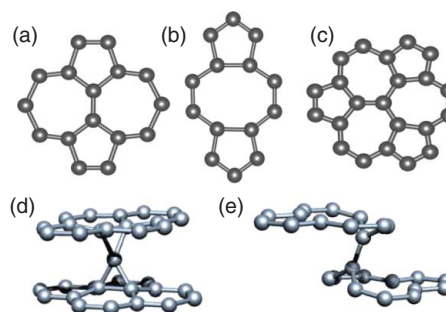


Figure 2. (a–c) Topological defects: Stone–Wales (55–77), 5–8–5 and 555–777 configurations [4,32] (d, e) inter-planar defects: spiro and divacancy configurations (reproduced from [2]). The 5–8–5 and 555–777 structures are also known as the double pentagon–octagon, and T5T7, respectively. The defects in the top panel maintain their sp^2 connectivity—each carbon atom has exactly 3 neighbors. Only bonds with sp^2 connectivity can activate the *D* peak in the Raman spectra.

the basal planes and several configurations such as *spiro*, *bridge* and *ylid* are energetically favorable.[32] Of particular interest is the effect of low threshold for shearing the basal planes [2]—on account of the weak interlayer bonding energy, which allows interstitial atoms to bond between the basal layers. Such formations are essentially three dimensional and are non- sp^2 bonded structures. Figure 2 shows five defect configurations—the top panel ((a)–(c)) shows three defect structures on the basal plane [4] while the bottom panel ((d), (e)) depicts cross-planar, three dimensional defect structures.[2]

In general, graphite has the remarkable property of accommodating *topological* defects, which maintain the connectivity of the sp^2 lattice sites.[3] Thus, the defects portrayed in the top panel of Figure 2 are all topological, with each carbon atom having exactly three neighbors. Because of dangling bonds, a single vacancy, on the

other hand, is not a topological defect. Since the bonds of the topological defects form a closed ring-like structure, they can participate in a breathing vibrational mode. The planar, closed ring defects that activate the Raman D peak therefore, are topological in nature. Stated equivalently: The Raman D peak is activated by topological defects having sp^2 connectivity. Other types of topological defects, in addition to Stone–Wales configuration, are: double pentagon–heptagon (D5D7), triple pentagon–heptagon (T5T7), grain boundary loops [34] and line defects on the basal plane. The configurations portrayed in the top panel of Figure 2, which are three-coordinated, sp^2 -hybridized, therefore, can be considered as strongly Raman active and those in the bottom panel as null or weakly Raman active.

Coming back to Figure 1(a), the augmentation in the D peak is a reflection of an increase in the number of topologically defected sp^2 bonds. In Figure 1(b), we have plotted the ratio of the maximum intensities of G and D peaks (I_D/I_G). With increasing dose, I_D/I_G increases; it reaches a maximum at a dpa of 0.006 and then decreases to a value of 0.8 at 1 dpa (obtained from ion irradiation). A residual I_D/I_G , in the range of 0.5–0.8, has also been reported at large irradiation doses with HOPG samples.[11,35] Further, NGB-18 samples that were irradiated to 25 dpa with ions, albeit at 900 K, also exhibited a I_D/I_G ratio of ~ 0.8 (results not shown). Thus, there is respectable evidence for a non-zero D peak intensity in graphite, even at high irradiation doses. Furthermore, the width of the D peak does not register a significant increase (even at larger doses), which perhaps, is indicative of structurally sound basal layers. The interpretation is quite illuminating—graphite maintains its layered structure under large doses of irradiation, however, with accumulated topological, sp^2 -hybridized defects.

We will now briefly discuss why the basal plane (sp^2) defects are more likely than the cross-planed (sp^3) defects in irradiated graphite. As discussed before, a number of topological defects can be formed on the basal planes simply through the rearrangement of bonds—for example, 55–77 Stone–Wales defects, which are commonly observed in graphene layers, can be formed by the rotation of a C–C bond through 90° . [4] Such topological defects are unique because they are Raman active and can be formed without generating vacancy and interstitial defects. From theoretical studies, it is shown that extended clustering of elementary topological defects is possible in graphene; a recent investigation using *ab-initio* simulation and scanning tunneling microscopy shows extended lines of pentagons, heptagons and octagons.[36] Extended clustering and loops are also observed in graphene under controlled electron irradiation.[37] Using a tight binding simulation, four single vacancies are shown to rearrange into two 555–777 configurations, which incidentally, are the unit structures for the haeckelite configuration [38]—a form

of two dimensional carbon crystal that is characterized by hexagons, pentagons and heptagons. Multivacancies can also be accommodated on the basal layers; for example, a formation energy of 2.7 eV/atom is reported with *ab-initio* simulations,[31] which is much lower than that for 555–777 (3.5 eV/atom) and 5–8–5 configurations (4 eV/atom).[4] With the exceptional ability for reorganization following perturbations, the atoms on the basal plane, following irradiation, can morph into multitudes of topological defect positions, several of which can be formed simply through bond rearrangement.[3]

In the seminal work of Tuinstra and Koenig,[39] I_D/I_G is regarded to be proportional to the inverse of a characteristic crystallite length (L_a) in the sample, which can be expressed as: $I_D/I_G = C(\lambda)/L_a$, where C is a constant that depends on the wavelength (λ) of the laser. This relationship is known to be valid for crystallite sizes greater than 10 nm, but breaks down at smaller sizes.[11,12] The characteristic length can be interpreted as the distance over which phonons (atomic vibrations) get decorrelated.[15] Using the empirical relationship developed by Cancado et al.,[40] L_a can be expressed as

$$L_a(\text{nm}) = 2.4 \times 10^{-10} \lambda^4 \left(\frac{A_D}{A_G} \right)^{-1}, \quad (1)$$

where A and λ are the integrated peak intensity and the laser wavelength (in nm), respectively. For neutron irradiated samples (dpa ≤ 0.01), the characteristic size is estimated to lie between 18–21 nm using a 632 nm He–Ne laser. The rather low phonon confinement spacing indicates the presence of topological defects that are able to scatter the phonons over atomistic dimensions. With continued irradiation, the phonon correlation length becomes smaller and approaches the planar bond dimensions. The Raman spectra also show a minor D' peak adjacent to the G peak. Figure 1(b) shows that I_D/I_D' is correlated to I_D/I_G with a maximum observed at a dpa of 0.006, followed by a gradual decrease. There is one recent investigation, which correlates I_D/I_D' to the type of defects in mono-layer graphene.[35] While such metrics are promising—as discussed by Terrones et al.,[3] more evidence is needed to make an assessment for three dimensional graphitic defect structure.

X-ray Photoelectron Spectroscopy. The Raman spectra for graphite do not show a discernible peak for sp^3 type defects. Therefore, we have directly assessed the different types of bond structures at the surface (Figure 3) using XPS (although defect information is not readily available). In XPS, the electronic states of the sample surface atoms are excited by photons and the resulting energy spectra of the electrons are analyzed for resonance peaks that are characteristic of the chemical bonds. A dominant peak at 284.4 eV represents C1s sp^2 bonds while the resolved peak at 285.6 eV indicates the presence of sp^3

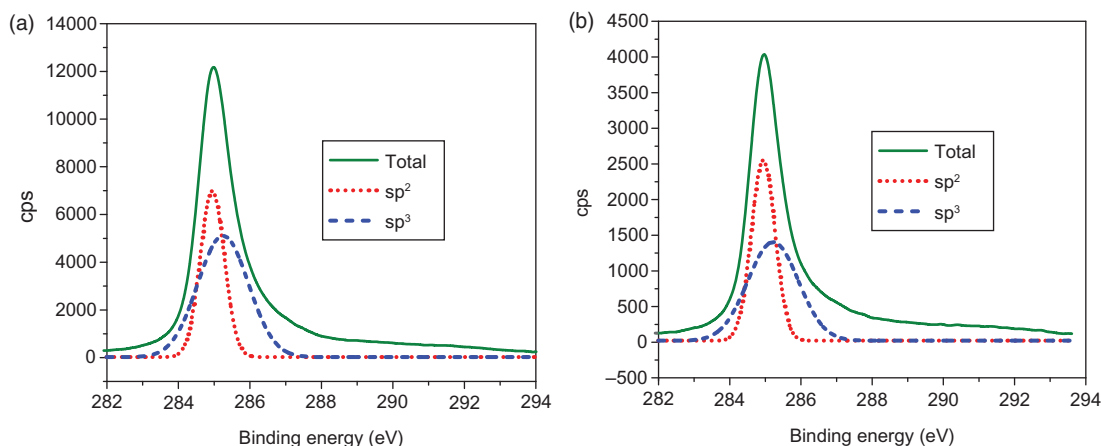


Figure 3. XPS spectra (a) virgin NBG-18, (b) neutron irradiated NBG-18 (0.006 dpa).

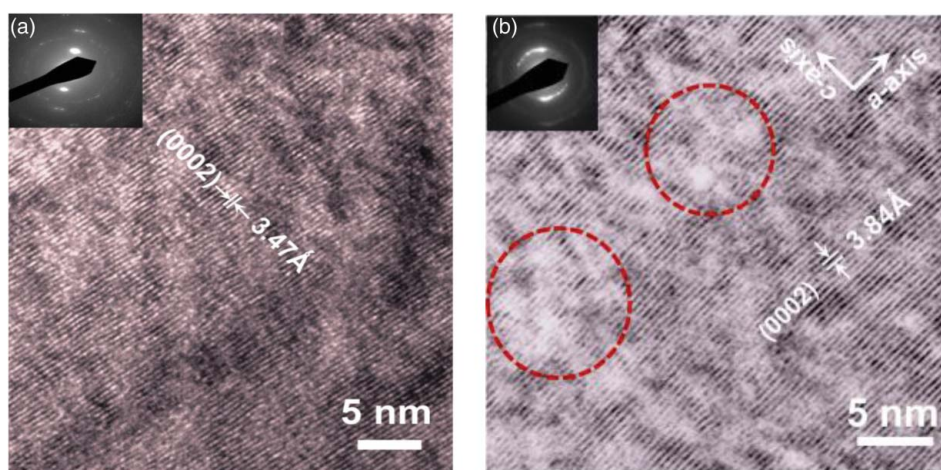


Figure 4. HRTEM images showing (a) the basal planes in the virgin NBG-18 sample, and (b) localized pockets of disordered basal planes (shown by broken circles) in neutron irradiated NBG-18 sample at 0.002 dpa. Insets correspond to SAEDP.

bonds.[41] Unlike in Raman spectroscopy, where certain peaks are activated only in the presence of defects, XPS does not provide specific information on the defect structures. Figure 3, which contrasts the resolved peaks for sp^2 and sp^3 bonds for virgin and irradiated (0.006 dpa) samples, indicates that virgin samples have a high proportion of sp^3 content, likely engendered during the heating and cool-down stages of the graphitizing process.[42] Interestingly, there is a discernible drop in the sp^3 content, relative to sp^2 , for the irradiated sample, even though the Raman spectrum shows an increase in the number of defects.

With continued irradiation, sp^3 defects that typically arise from interstitials will increase. The Raman analysis, however, shows that sp^2 defects are not significantly reduced, even at large doses, indicating the versatility of the topological defects to rearrange and morph into several different configurations. While there is evidence for a large number of topological defects, there is no definitive information, at present, on the proportion of topological defects (sp^2), relative to other defect types, at different irradiation doses. We are currently investigating

the mechanisms of defect formation and transformation under irradiation using molecular dynamics simulations.

Accretion of elementary defects will eventually lead to extended defects. In the next sub-section, we will discuss the evidence gleaned from HRTEM on extended defects.

Electron Microscopy. Figure 4 portrays HRTEM images for (a) virgin and (b) irradiated samples with the insets showing the corresponding selected area electron diffraction pattern (SAEDP). While the basal planes are clearly visible in the virgin sample, distortions without loss of long-ranged order can also be observed. As discussed before, the sp^2 defects on the basal plane appear as the *D* peak in the Raman spectra. Noticeably, the irradiated sample shows heavy distortions and interconnected disordered regions that have a characteristic size of ~ 5 nm; SAEDP (see inset) also shows spreading of spots into arcs for the irradiated sample. Such ripples and distortions can arise from topological defects such as Stone–Wales defects.[3]

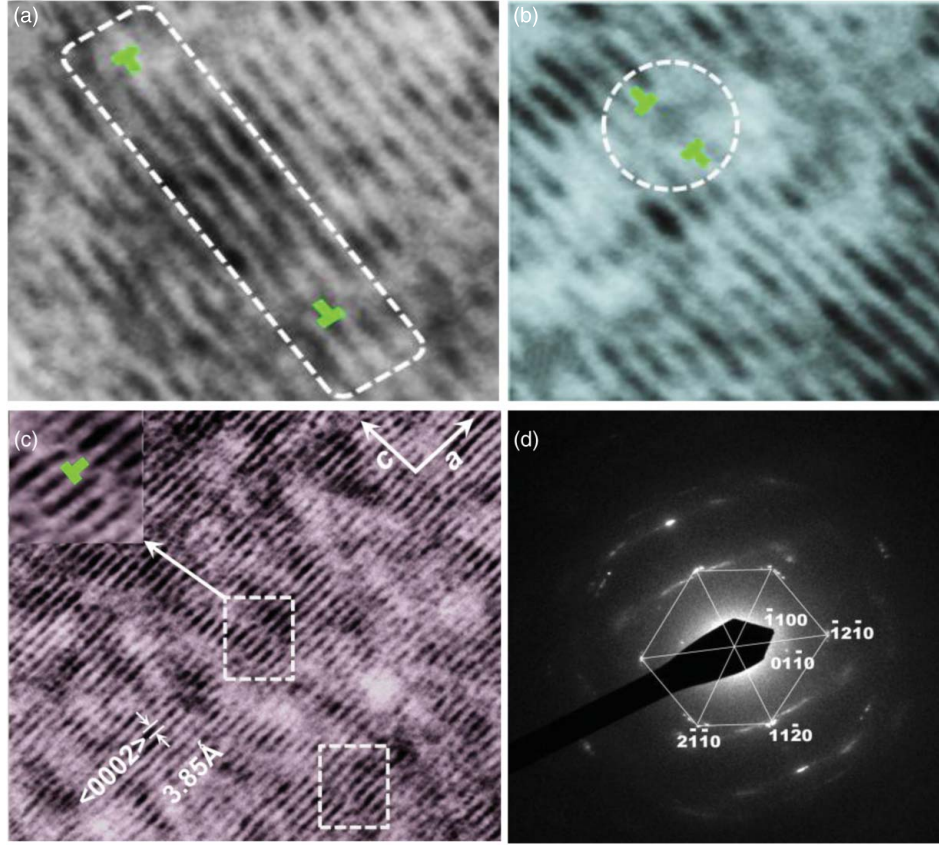


Figure 5. HRTEM images showing extended defects, (a) an interstitial loop, (b) a vacancy loop, (c) prismatic dislocations in, (inset) magnified view and (d), SAEDP indicating basal dislocation dissociating into Shockley partials. The defects are imaged using diffraction contrast.

We will now discuss the formation of extended defects that have been identified with HRTEM. Since graphite has a layered structure, it can accommodate several types of dislocations. In general, there are two types of stacking disorder in graphite: basal or prismatic.[43] In the former, the Burgers vector lies on the basal plane while in the latter, it is perpendicular or at an angle to the basal plane.[43] Recent investigations on graphene reveal that planar dislocations can be formed through combinations of topological defects, which generally are considered to be energetically favorable over the haecelike structures.[31] Prismatic dislocations in graphite often are detected after irradiation or heat treatment,[43] and are formed either by the insertion of segments of lattice planes, or through collapse of vacancies.[1]

In a recent review, Telling and Heggie [1] have summarized the mechanisms behind the formation of extended defects in graphite. Aided by an in-plane slip, disc vacancy clusters can collapse into a prismatic dislocation with a Burgers vector $\frac{c}{2}(0001) + \frac{a}{3}(\bar{1}2\bar{1}0)$. [44] However, line-type clusters typically collapse into a pair of edge basal dislocations without the formation of dangling bonds. Recently, Karthik et al. [45] found evidence for the formation of dislocation dipoles from vacancy loops in NBG-18 under electron irradiation.

Using *in-situ* measurements with HRTEM, the formation of a vacancy loop is observed first, followed by a dissociation into a set of dislocations and the formation of incomplete planes through a climb mechanism. In our HRTEM analysis, we have found several interstitial and vacancy loops as shown in Figure 5(a) and 5(b). Prismatic dislocations (see boxes in Figure 5(c)), which are typically reported in radiation investigations, are also observed. Given the likelihood of sp^2 vacancy-like topological defects on the basal plane during irradiation (as evidenced by the *D* peak in Raman), the formation of prismatic dislocations is possible through a vacancy collapse mechanism. As noted by Karthik et al.,[45] such dislocations are continuously created and annihilated during irradiation; only a few stable dislocations remain at the end of irradiation. Interestingly, we also see evidence for a number of basal dislocations dissociating into Shockley partials, given by $(a/3)[\bar{1}2\bar{1}0] \rightarrow (a/3)[\bar{1}100] + (a/3)[01\bar{1}0]$ (Figure 5(d)). The partials enclose a stacking fault with a rhombohedral (*abc*) stacking sequence,[46] which is created by a glide process along the basal plane. Basal dislocations, generally, do not break the strong in-plane atomic bonds, rather they are created by distorted carbon-carbon bonds on the basal plane. First principles simulations show that the

Peierls stress barrier for basal dislocation glide is quite small (10^{-17} Pa); the shear strength, therefore, is largely dependent on the pinning of dislocations,[47] which constrains the motion of the basal planes to short segments while accommodating significant distortions. Heggie and coworkers [48] have proposed that the pinning mechanism can result in folding, or the ‘ruck and tuck’, of the basal planes. This new model indicates that basal planes can warp and additional planes that lead to an expansion along the c -axis can be formed through basal dislocations. Currently, we are investigating the possibility of such formations through electron microscopy analysis.

Conclusion The nature of the bond and defect structures in nuclear grade graphite (NBG-18), under neutron and ion irradiation, has been characterized using Raman spectroscopy, XPS and HRTEM. The magnitude of the defect D peak in the Raman spectra increases with irradiation, which indicates an increase in the number of topological defect structures that maintain the sp^2 bond connectivity. Our experiments also show that the D peak does not shrink significantly in graphite, even when irradiated to several tens of dpa, indicating the persistent presence of a layered structure with topological defects. Thus, a direct condensation of the topological defects (which are initially formed during radiation) into three dimensional vacancy pores or amorphous pockets (which will manifest as vanishing I_D/I_G) can be deemed highly improbable for doses that are expected in the high temperature reactors. The non-vanishing D peak in the Raman spectra, together with a generous number of dislocations, even at low irradiation doses, indicates a dislocation-mediated amorphization process in graphite. The Niwase dislocation model [14] for amorphization, therefore, is more consistent with the above picture than the direct amorphization model [13] in which vacancy accumulation is regarded to amorphize the graphite layers without the formation of extended defects.

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