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The contribution made by lattice vacancies to the Wigner effect in radiation-damaged graphite

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Abstract

Models for radiation damage in graphite are reviewed and compared, leading to a re-examination of the contribution made by vacancies to annealing processes. A method based on density functional theory, using large supercells with orthorhombic and hexagonal symmetry, is employed to calculate properties and behaviour of lattice vacancies and displacement defects. It is concluded that annihilation of intimate Frenkel defects marks the onset of recovery in electrical resistivity, which occurs when the temperature exceeds about 160 K. Migration of isolated monovacancies is estimated to have an activation energy of $E_a \approx 1.1$ eV. Coalescence into divacancy defects occurs in several stages, with different barriers at each stage, depending on the path. The formation of pairs ultimately yields up to 8.9 eV energy, which is nearly 1.0 eV more than the formation energy for an isolated monovacancy. Processes resulting in vacancy coalescence and annihilation appear to be responsible for the main Wigner energy release peak in radiation-damaged graphite, occurring at about 475 K.

(Some figures may appear in colour only in the online journal.)

1 Introduction

Owing to the discovery of fullerenes [1], carbon whiskers [2] and nanotubes [3], and the isolation of graphene [4, 5], our view of graphitic materials has advanced greatly in recent years from the simple Bernal model [6]. It is now understood that this family, based on threefold coordinated carbon atoms, can exist in a much wider variety of forms than rigidly stacked layers with hexagonal symmetry. In isolation, graphene sheets behave more like pieces of woven silk fabric, which can fold and wrinkle, than fixed, flat layers of a stiff mesh. The sheets can roll up into tubes, scrolls, balls, onion-like forms, and fold over upon themselves in complex ways [7–11].

In bulk form, graphite is an extremely resilient material, which along with several other properties, makes it ideal for many technological applications. One of these—which is the

underlying motivation for the present work—is as a moderator and reflector material in nuclear fission reactors. The response of the material at the atomic level to the intense radiation and high temperatures found in reactor environments is now informed by the advances in the understanding of graphitic materials described in the previous paragraph.

One of the phenomena observed in graphite irradiated by high-energy particles such as neutrons, is that of dimensional change [12]. A piece of highly-oriented pyrolytic graphite (HOPG) may expand in the crystallographic *c*-direction by as much as 20%, balanced by a corresponding, small shrinkage in the basal directions [13, 14]. Clearly, dimensional change has important implications for the structural integrity of graphite components in nuclear reactors. Radiation damage to graphite has many other well-documented effects, including changes to electrical and thermal conductivity, and elastic

Figure 1: Graph reconstructed from figure 1 in [19] showing the differential Wigner energy dH/dT released from pyrolytic graphite that was recrystallized by annealing at 2800 C under 19.6 MPa pressure, and subsequently irradiated with fission-reactor neutrons at 78 K. Reproduced with permission from Elsevier.

parameters [15].

The main purpose of this work is to examine the role played by point defects and defect complexes when irradiated graphite is annealed, emphasising the role of vacancies. Annealing of radiation-induced defects in graphite releases the potential energy stored within them, and restores the material properties nearly to the pristine state when a sufficiently high temperature is used [15]. For material which has been heavily irradiated at temperatures below room temperature this stored energy, known as Wigner energy, can be very large in proportion to the specific heat, which can lead to an uncontrollable, self-sustaining release of heat upon annealing [16]. Experiments have shown that the release of Wigner energy depends on the dose and the temperature of irradiation [17]. When irradiation occurs at low temperatures, the recovery behaviour is complex [16, 18]. Vacancies and self-interstitials can form pairs and larger aggregates; Frenkel defects can recombine [15], with each process being accompanied by the release of energy at different temperatures, corresponding to different activation energies. An illustration of this (from [19]) is provided in figure 1. Similar examples of Wigner energy release experiments can be seen in [20–23]. It has been concluded from measurements of electron-irradiated material that the peak at about 200 C, which is observed in many experiments, is due to annihilation of Frenkel defects [24].

The conventional model of radiation damage in graphite emphasises the role of self interstitial atoms rather than vacancies. When displaced from their normal lattice sites by an energetic particle colliding with them, interstitials are assumed to occupy locations between the layers. This pushes the layers apart, and hence causes expansion along the prismatic direction [25–30]. Upon annealing, the atoms aggregate into new graphene sheets between existing ones, taking the form of interstitial prismatic dislocation loops, while vacancies coalesce into lines which collapse, causing shrinkage in the basal plane [30, 31]. Thus, the response of graphite to damaging radiation involves the creation and accumulation of non-basal edge dislocation dipoles, and causes progressive reduction in long-range order [32, 33]. Details of the processes that are believed to occur have been captured by high-resolution transmission electron microscopy experiments showing the nucleation of prismatic dislocation loops [34]. These dislocations are observed to be unstable and undergo climb, resulting in the formation of new graphene sheets at the expense of existing ones.

Although prismatic dislocation loops are observed to form

and grow following high-temperature annealing of irradiated graphite [35–37], and evidence for the existence of vacancy lines has been found [38], the interstitial loops are insufficient in size and number to account for the expansion along the *c*-direction [39, 40].

A key assumption of the conventional model is that the interstitial atoms do not form covalent bonds with their neighbours in the host [27, 41, 42], and this allows them to migrate freely in the interlayer spaces, either as individual atoms or in small clusters [28]. Early on, calculations using the complete neglect of differential overlap methodology (CNDO) showed that this hypothesis is unlikely to be correct [43]. The merit of the CNDO scheme here is that the wavefunctions of molecular orbitals are used to estimate the total energies of the valence electrons, and, unlike empirical potentials, it contains no assumptions about chemical bonds. Later, the results of *ab initio* atomistic modelling based on density functional theory (DFT) confirmed the view that strong bonds do form between interstitial atoms and the host, and found that the activation energy for interstitial migration ($E_a > 1.5$ eV [44] and either $E_a = 1.88$ or 2.12 eV [45]) is too high for aggregation to occur at the temperatures where the onset of dimensional change occurs. This energy is much larger than earlier estimates, which all lie below 0.5 eV for isolated interstitial atoms [21, 27, 46–48]. Other recent work based on DFT offers an alternative interpretation, where it is proposed that two populations of interstitial atoms exist at low temperatures, one of which is a metastable state that can migrate easily, and cannot convert to the other stable, immobile form owing to an activation energy barrier [49, 50]. However, it is our view that this model appears to have been constructed as a way to force agreement with the conventional model, which has been shown to have several flaws [51]. DFT calculations also predict that self-interstitial pairs in graphite are particularly stable defects which cannot migrate easily [52].

A consequence of assuming that the binding between interstitial atoms and the host is weak, is that the interstitials occupy a large effective volume, about 3.3 times the volume per carbon atom in a graphite crystal, which reproduces dimensional change data [29]. This is also not supported by DFT calculations, which predict that the volume per interstitial atom is much smaller than that postulated by the conventional model [52]. Moreover, expansion occurs in *both* prismatic and basal directions of a graphite crystal when interstitial atoms are present, according to the DFT calculations [52].

In transmission electron microscopy experiments, *in situ* electron irradiation of highly graphitized carbon fibres is observed to produce expansion of the d_{002} lattice spacing by up to about 11% [53,54]. Similar experiments on HOPG yield an expansion of up to 4% in the lattice spacing, while the specimens grow by up to 300% along the c -direction [55]. The form of the damaging radiation (electrons, ions, neutrons) is found to have little effect on the resulting microstructure [56]. Evidence for the aggregation of interstitial atoms into new sheets as a cause for this expansion was looked for in these experiments, but not found. The idea that interstitial atoms migrate and coalesce into new graphene sheets between existing ones is ruled out [56]. Instead, breaking and bending of the graphene sheets in graphite appears to provide a better model for dimensional change [56,57]. According to one proposal, this can be explained by the creation of a disordered network of sp^2 -bonded atoms [58]. Other research suggests that some displaced carbon atoms adopt sp^3 bonding configurations, possibly in the form of three-dimensional clusters, both within the graphene sheets and bridging neighbouring layers, which produces distortion and breakage of the sheets [56,59]. The presence of these defects can also explain changes in electrical and thermal conductivity which are observed when graphite is damaged by radiation, and annealed, according to the model. Electron energy loss measurements on HOPG are consistent with this model as well [60]. Later work reiterates the point that vacancies and interstitial atoms in radiation-damaged graphite have unsaturated chemical bonds, which will usually be reconstructed [61].

Another model for dimensional change divides the processes that are responsible for it into low- and high-temperature regimes [62]. According to this model, radiation damage at low temperatures creates strong cross-links between the layers. The existence of such defects in neutron-irradiated hot-worked pyrolytic graphite has been inferred from measurements of the elastic shear modulus C_{44} [63], and it was anticipated that this would generate an enormous strain in heavily damaged material, causing the layers to buckle [64]. It was realised later that if radiation damage caused crinkling or blistering of the sheets, then this would produce an expansion in the prismatic direction [62]. Buckling of graphite layers induced by the presence of defects has even been observed to occur in unirradiated graphite [65]. Furthermore, it has been argued that expanded regions in a radiation-damaged graphite crystal would tend to repel each other, owing to their long-ranged elastic interactions; hence, they would not be randomly distributed, and this produces the diffuse, asymmetric X-ray diffraction spots observed in radiation-damaged graphite [13]. The original interpretation was that interstitial atoms propped the layers apart; however, this argument could equally well apply to the kind of blister-like structures that would be produced by a system of interlayer cross-links. At high temperatures, the cross-links break, and dislocations become active. The measurements of C_{44} cited previously find that this occurs above about 200 C, and it was postulated that subsequent accumulation of defects led to the formation of new graphene sheets [63]. In the present model, basal dislocations accumulate in a manner that

first creates structures analogous to a ruck in a carpet or sheet of fabric, then fold over completely upon themselves [62]. Hence, the material expands in the c -direction at the expense of the basal dimensions. Simulations [62] show that these folded structures are consistent with previously unexplained diffuse features seen in X-ray diffraction experiments [66,67]. Thus, this model accounts for the fact that dimensional change at low temperatures is not volume-conserving, while at high temperatures it is [14].

The formation of cross-links in the low-temperature radiation damage regime is demonstrated in molecular dynamics simulations [68]. Although this employs a classical potential, where the well-known shortcomings are acknowledged, the simulations are able to illustrate the effects of accumulated damage in a model that mimics the results of DFT calculations fairly well, where comparisons are possible. Blisters form in the graphene sheets around the sites of cross-linking defects, and evidence of longer-ranged bending and buckling can be seen, even though this is necessarily constrained by the finite size of the model.

The models for radiation damage in graphite presented so far have concentrated on the role of interstitial atoms, owing to their status in the conventional model for radiation damage in graphite. Unlike self interstitials, the conventional view holds that isolated lattice vacancies have a high activation energy for migration [46]; hence, they are a largely immobile entity at temperatures below 1470 K, meaning that they do not become active participants in the annealing process until the temperature exceeds this level [69,70]. However, it will be seen in Section 3.2 that there is growing evidence that this is not the case. The remainder of this work is a re-examination and review of the role of vacancies in radiation damaged graphite.

2 Method

The total energies E_{total} of supercells are calculated using a method based on self-consistent density functional theory, AIMPRO. Only a brief summary of the main points is provided here. For a more detailed explanation see [71–74].

In previous work [52], the exchange-correlation energy contribution was evaluated according the formula for the local density approximation (LDA) described by Perdew and Wang (PW92) [75] only. The present work uses both the PW92-LDA and the generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof (PBE96) [76]. The basis sets [72], pseudopotentials [77], band-structure sampling [78], filling of Kohn-Sham levels [79], structural optimization, and other parameters and procedures all follow the method in [52].

Model defects are constructed in supercells of various sizes with either hexagonal or orthorhombic crystal symmetry. The orthorhombic supercells are approximately square in the basal plane; hence, a point defect has four nearest neighbouring images sharing the same basal plane, in contrast to the six images for a hexagonal supercell of the same size. Formation energies of defects are given by the same formula as used previously [52]. Local vibrational modes for defects are calculated by using the second derivatives of energy with respect to the positions of the atoms to calculate

the dynamical matrix for selected atoms close to a model defect. Three methods are used to simulate the migration of atoms, according to the geometry of the problem. In some cases, symmetry can be exploited to hold a structure at the mid-point between the initial and final state. A second method calculates the total energy of the system subject to several values of a fixed constraint(s) $C = r_{ab}^2 - r_{ac}^2$ for selected atoms, where r_{ax} is the distance between an atom a , and a second atom x . The third method is nudged elastic band with optional climb [80, 81].

Under some circumstances, defects generate shear forces that have a component in the basal plane which, for a small model system, are greater than the weak interlayer bonds in graphite are able to resist. If these forces are left unchecked, then a relative translation by up to half a C-C bond length of the graphene layers in the host crystal would occur. In order to counter this effect, one atom in each layer, furthest from the defect region, can be constrained so that it may only move along the prismatic direction of the crystal.

3 Results

3.1 Interlayer bonding

DFT calculations show that the weak interatomic forces, which bind the graphene sheets of a graphite crystal together, arise from the overlap of the partially occupied p -orbitals projecting perpendicular to the planar sp^2 -hybridized orbitals within the sheets [82]. This can be understood in terms of the band structure. Dispersion of the π -bands along the prismatic direction in graphite is significant, which implies that there is a chemical bond between the layers [82]. Hence, in strained graphite crystals, redistribution of electrons and holes at the Brillouin zone boundaries is found to be the main contribution to the elastic coefficients with prismatic components, C_{33} and C_{44} [83]. However, the development of methods based on density functional theory has, in recent years, provoked a new debate about the origin of the interlayer forces in graphite.

There is a natural assumption that the inclusion of gradient terms in GGAs means they are a better approximation than the simpler LDA. Owing to the neglect of contributions to the exchange-correlation energy from multiplet terms for free atoms [84], atomization energies of small molecules, and cohesive energies of crystals are usually overestimated by the LDA, while GGAs usually yield results that are closer to their measured values for these quantities, appearing to support the idea that they are better. For example, the measured cohesive energy of diamond is about 7.37 eV/atom [85], while the values obtained using the AIMPRO method are about 8.76 eV/atom for the LDA, and about 7.64 eV/atom for the PBE96-GGA. However, estimates for some quantities, such as band gaps of semiconductors, are nearly always worse with GGAs than the LDA, and the relative performance in other areas is inconsistent [86]. Graphite is one case where the LDA appears to perform significantly better than GGAs. The LDA yields a good description of the interlayer binding energy [82, 87], and is able to reproduce the observed lattice parameters and elastic properties [88], while GGAs perform very poorly (figure 2). The failure of GGAs for graphite is

blamed on the omission of London dispersion forces from the theory, and the success of the LDA, which also neglects London dispersion, is believed to be due to a fortuitous cancellation of errors. Nevertheless, it has been shown that it is not possible to describe fully the interlayer forces by using an interatomic potential of the form applicable to London dispersion, as would be the case if this were the main source of these forces [83, 89, 90]. The possibility that the fault with GGAs may lie elsewhere is overlooked.

Figure 2: Graph illustrating the interlayer binding energy versus c lattice parameter for graphite. The observed lattice parameter is $c = 6.7079 \pm 0.0007$ Å; the calculated values are $c_{\text{LDA}} = 6.5186$ Å, and $c_{\text{GGA}} = 7.5290$ Å.

According to quantum Monte Carlo calculations (which do include London dispersion) GGAs do not provide consistent improvement over the LDA because errors are closely correlated with the Laplacian, rather than the gradient of the electron density [91]. The calculations, for model systems with a sinusoidal density modulation along one dimension forming sheets of charge in the two other spatial dimensions, show that there is some cancellation of errors for the LDA, which is best for regions of slowly varying density, and worst for density maxima. However, the way in which GGAs are constructed means they tend to magnify rather than reduce this error. Thus, in some cases GGAs provide a poorer approximation than the LDA. This suggests that errors arising from the neglect of Laplacian terms in density functionals may be more important than the omission of London dispersion.

General-purpose density functionals with Laplacian terms are not available at present. In their absence, a practical approach to correct the interlayer binding of graphite for GGAs is to modify the energy functional either on an empirical [49, 92–95], or an *ab initio* [50, 96, 97] basis, so that the experimentally observed lattice parameters are reproduced. However, this is based on assumptions which, it has been seen here, are not necessarily correct. Moreover, although corrections to GGAs have a significant effect on the weak interatomic forces responsible for the interlayer binding

Figure 3: The isolated monovacancy in graphite: (a) ground state; (b) transition state for migration.

of graphite, this is small in comparison with the strength of bonds between atoms in defects and their host [98, 99]. An equally practical approach to this problem is to accept that the LDA provides a better description of interlayer binding in graphite than GGAs. Calculations based on the random phase approximation (RPA) appear to support this idea [100]. The RPA is thought to give an accurate description of weak, non-covalent bonding; however, its application is restricted by the high computational cost of the method. The RPA calculations demonstrate that even the more sophisticated *ab initio* density functionals with van der Waals terms fail to reproduce well lattice parameters, binding energies, and the C_{33} elastic parameters simultaneously for weakly-bonded layered materials, owing to the compromises needed to construct the functionals.

Finally, it is possible to assess the relative performance of density functionals by constraining all calculations to use the LDA-derived lattice parameters. These are $a = 2.4458 \text{ \AA}$, and $c = 6.5186 \text{ \AA}$, which are close to the observed values. This is the protocol adopted for the present work.

3.2 Lattice vacancies

An ‘ideal’ lattice vacancy in graphite on either an α or β site possesses D_{3h} symmetry, with a threefold axis through its centre. This leaves it with a doubly degenerate $2E'\sigma$ state occupied by one electron, making the defect unstable against a Jahn-Teller distortion [101]. The predicted ground state of the defect adopts a structure with C_{2v} symmetry, where two of the three atoms neighbouring the vacancy form a bond between them, with the remaining atom on the mirror plane of the reconstructed defect (figure 3(a)). Graphene is often used as the basis for models of vacancies in graphite, and this yields similar results [45, 102–107]. In this instance the distinction between α and β sites vanishes, and interlayer bonding no longer applies. The present work uses both graphite and graphene monovacancy models to facilitate comparisons, and assess the validity of the calculations. Supercells of different sizes and types are also considered. A summary of results is given in table 1.

Formation energies for vacancies in graphite and graphene when calculated using the PBE96-GGA are lower by about 0.6 eV than they are with the LDA. This is of similar

magnitude to the difference in cohesive energy of graphene for these functionals, which is about 0.97 eV, according to our calculations.

While there is generally good agreement between calculated and measured values for the formation energy of monovacancies in graphite (experiments find $E_f \approx 7.0 \pm 0.5 \text{ eV}$ [46]) theory consistently predicts a very much smaller activation energy for vacancy migration (table 1) than is usually attributed to this process by experimental measurements ($E_a = 3.1 \pm 0.2 \text{ eV}$ [46]). Measurements of vacancy concentrations in single-crystal graphite irradiated with neutrons and carbon ions at different temperatures were an early exception to this, where it was found that the results of the experiments are inconsistent with the notion of a high activation energy for vacancy migration [40]. Unfortunately, the data did not allow an estimate for the activation energy to be made, and it was not possible to determine whether the mechanism involved single vacancies or pairs. Later, direct observations by scanning tunnelling microscopy (STM) of vacancy migration on the surface of graphite crystals gave an activation energy in much better agreement with theory ($E_a \approx 1 \text{ eV}$ [108]). This suggests, on balance, that the lower values are closer to the truth, and reinterpretation of the 3.1-eV figure is needed. According to the present work, $E_a \approx 1.1 \text{ eV}$ for vacancy migration. The structure at the transition state is shown in figure 3(b).

It is informative to apply the molar Arrhenius formula $k = A \exp(-E_a/RT)$ to estimate the temperature at which vacancy migration begins to occur at a significant rate. If the prefactor for the exponential is assumed to be the same order of magnitude as the Debye frequency of graphite ($A \sim 10^{13}\text{--}10^{14} \text{ Hz}$) then, for this range of frequencies and $E_a = 1.1 \text{ eV}$, onset of vacancy migration in graphite is predicted to occur at a rate $k \sim 1 \text{ s}^{-1}$ when the temperature reaches $T = 396\text{--}411 \text{ K}$, approximately. Within the accuracy of the calculation, this is consistent with the observed peak in energy released from electron irradiated graphite that occurs at about 475 K, which is attributed to the annihilation of Frenkel defects [24]. Later work, involving Raman scattering observations of HOPG irradiated with 3-keV He^+ ions measured the barrier to annihilation of Frenkel defects to be $E_a = 0.89 \pm 0.10 \text{ eV}$ [109], which was subsequently revised upwards slightly to $E_a = 0.98 \pm 0.10 \text{ eV}$, and found to follow second-order kinetics [110].

Table 1: Summary of calculated formation energies E_f , activation energies for migration E_a , magnetic moments M , length of reconstruction bond R , and out-of-plane displacement of the unpaired atom Δz of graphene monovacancies. The AIMPRO method finds $\Delta z = 0$ when $M \neq 0$.

Graphite	$6 \times 3 \times 2$ orthorhombic		$6 \times 6 \times 2$ hexagonal	
AIMPRO	LDA	GGA	LDA	GGA
$E_f(\alpha)$ (eV)	7.95	7.33	7.99	7.38
$E_f(\beta)$ (eV)	7.93	7.31	7.96	7.35
$E_a(\alpha \rightarrow \beta)$ (eV)	1.08	1.11	1.07	1.15
$M(\alpha)$ (μ_B)	1.00	1.01	1.15	1.13
$M(\beta)$ (μ_B)	1.45	1.48	1.25	1.25
$R(\alpha)$ (Å)	1.83	1.80	1.86	1.82
$R(\beta)$ (Å)	1.87	1.82	1.89	1.86
Graphene	6×3 orthorhombic		12×6 orthorhombic	
AIMPRO	LDA	GGA	LDA	GGA
E_f (eV)	8.07	7.45	7.91	7.36
E_a (eV)	1.32	1.26	1.24	1.25
M (μ_B)	1.26	1.38	1.31	1.32
R (Å)	1.89	1.85	1.83	1.80
Graphene	Reference [102]	References [103, 106]	Reference [107]	Reference [45]
Other work	LDA	GGA	LDA	GGA
E_f (eV)	7.4	7.7	7.65	7.85
E_a (eV)	1.7	1.3		1.37
M (μ_B)	0	1.04		
R (Å)	2.1 ± 0.1	2.02	2.15	2.37
Δz (Å)	0.47	0.18	0.43	0.29

Monovacancies in graphite and graphene are also predicted to possess a magnetic moment in their ground state of about 1.0–1.5 μ_B , according to the present and previous calculations [103–105, 111, 112]. Direct observations of vacancies on graphite surfaces by STM [113] have demonstrated that they possess localized magnetic moments, deduced from their effect on the local density of states, in accord with a tight-binding model [114]. The magnitude of the moment, and nature of the magnetic ordering is sensitive to the arrangement of vacancies in two [111, 115, 116] and three dimensions [117], as well as their identity [113, 114] (table 1). Further, we find that the magnetic moment of a monovacancy is quenched when the unpaired atom is displaced away from the basal plane. If the magnetic moment is forced to be zero, then displacement of the unpaired atom occurs spontaneously, according to our calculations. This supports the results of DFT calculations by Paz *et al.*, who show that the ground state of a monovacancy in graphene is planar, but that metastable states exist where the unpaired atom is displaced out of plane, depending on the net magnetic moment of the defect [118]. In the purely two dimensional case of graphene, a tight-binding study [116] has shown how magnetic moments induced in the π -electron system by *nonmagnetic* defects is determined by Lieb’s theorem [119]. Accordingly, when two vacancies occupy the same sublattice of graphene, the ground state is triplet; when each lies on the two different sublattices, the ground state is singlet. It is also found that the magnitude of the local moment for each vacancy increases with increasing separation between the vacancies [115, 116].

Table 2: Binding energies (eV) of divacancy defects relative to two isolated monovacancies calculated for graphite with the AIMPRO program package ($6 \times 3 \times 2$ orthorhombic supercells), and for graphene by Lee *et al.* [105] with the VASP code.

	AIMPRO		VASP	
	LDA	GGA	LDA	GGA
$E_b(V_2^{cis})$	1.95	1.38		
$E_b(V_2^{trans})$	2.73	2.38	2.76	
$E_b(V_2^{\alpha\beta})$	7.99	7.69	7.59	7.71
$E_b(V_2^{haeckel.})$	8.91	8.68	8.50	8.61

3.3 Lattice vacancy coalescence

If monovacancies in graphite are mobile at temperatures above about 200 C, then it is anticipated that they will coalesce as pairs and higher complexes when they encounter one another, because this reduces the number of broken bonds [101]. A simple calculation shows that the energy gained by forming a pair must be of similar magnitude the cohesive energy of graphite [120]. The present calculations examine four structures where pairing occurs on the same graphene sheet. These structures are illustrated in figure 4; their binding energies are given in table 2.

The nearest-neighbour $\alpha\beta$ divacancy and haeckelite structure divacancy are predicted to be more stable than isolated monovacancies; hence, the concentration of divacancies will be higher than the concentration of

Figure 4: Lattice vacancy pairs in graphite: (a) cis third-neighbour divacancy; (b) trans third-neighbour divacancy; (c) $\alpha\beta$ divacancy; (d) haeckelite structure divacancy.

monovacancies when the system is at thermal equilibrium. The trans third-neighbour divacancy is more stable than the cis third-neighbour divacancy, owing to the $\text{C}\equiv\text{C}$ bond spanning the centre of the defect. This bond is calculated to have a high-frequency stretching mode at 2211 cm^{-1} . Long chain carbynes, which contain $-\text{C}\equiv\text{C}-$ units, exhibit a similar high-frequency mode at about 2000 cm^{-1} in Raman-scattering experiments [121], and the infrared spectrum of PPDO (a polymer with $-\text{C}\equiv\text{C}-$ units) has a strong absorption line at 2200 cm^{-1} [122]. The potential experienced by the central $-\text{C}\equiv\text{C}-$ unit of the trans third-neighbour divacancy has three local minima: one lies in the plane of the host graphene sheet containing the defect, and there are two equivalent locations offset from the plane by about $0.39\text{ \AA}$. All three minima have nearly the same energy. Therefore, the structure will certainly have complex very low-frequency behaviour; however, it is not possible to quantify this at present. Nevertheless, it is likely that modes with very low frequency from this defect contribute to an anomaly observed for the specific heat of radiation damaged graphite at low temperatures [123], and that the earlier explanation for this phenomenon is probably incorrect [51].

The onset of vacancy coalescence for two vacancies on the same graphene sheet begins at fourth neighbour separation. Beyond this there is negligible interaction. When two fourth neighbour vacancies lie along a $[10\bar{1}0]$ direction, the activation energy to form a cis third-neighbour divacancy is 0.29 eV , while it is only 0.25 eV to create a trans third-neighbour divacancy. When two vacancies lie along a $[11\bar{2}0]$ direction, the fourth neighbour divacancy is unstable, and spontaneous collapse to a trans third-neighbour divacancy occurs. Therefore, vacancy migration is much less likely to

produce cis third-neighbour divacancies than trans ones.

Cis third-neighbour divacancies face a barrier of about 0.82 eV to collapse to a nearest neighbour $\alpha\beta$ divacancy. Trans third-neighbour divacancies are significantly more stable, having an activation energy of 2.14 eV to form an $\alpha\beta$ divacancy, according to the present calculations. Previous estimates for the activation energy of this step of divacancy coalescence in a graphene sheet are $E_a = 2.17\text{ eV}$ by Zhang *et al.* [45], calculated using the Perdew-Wang (PW91) variant of the GGA, and $E_a = 1.52\text{ eV}$ by Lee *et al.* [105] using the LDA.

Raman scattering observations of HOPG exposed to 3-keV He^+ ions, attribute a process with $E_a = 1.8 \pm 0.3\text{ eV}$ as being one involving vacancy coalescence [109]. This value is consistent with the three theoretical estimates of E_a for the collapse of a trans third-neighbour divacancy given in the previous paragraph. However, the prevailing belief at the time when the experiments were performed was that the barrier to vacancy migration was much higher, which made this result difficult to understand, in spite of being confirmed in later work by the same group [110, 124].

When observed by STM, nearest neighbour divacancies in graphene are predicted to exhibit a characteristic pattern, aligned along the principal crystallographic directions [125, 126]. The experimental fingerprint of this defect for graphene on a $\text{SiC}(000\bar{1})$ substrate, and few-layer exfoliated HOPG appears to be a good match [126].

The final stage in the process, transforming an $\alpha\beta$ divacancy into a haeckelite divacancy, has a barrier of 5.14 eV . This is close to the result found by Lee *et al.* for a graphene sheet using the LDA, who found $E_a = 5.17\text{ eV}$ [105]. Figure 5 provides a summary of our results in a graphical form.

Figure 5: Vacancy coalescence: this begins with one vacancy at the point marked with a solid (pink) disk and a second vacancy located further than the fourth-neighbouring points where the pair starts to interact. The process ends at the haeckelite divacancy centred, in effect, on the same point as the first vacancy marked with a solid (pink) disk. (Red) disks with a white horizontal bar represent unstable structures. Energies in eV relative to the total energy of two isolated monovacancies are shown with an upright typeface; activation energies in eV for each step are given in a *slanted* typeface, with arrows showing the direction for net vacancy motion.

In terms of annealing temperature, fourth-neighbour divacancies are stable when $T \lesssim 90$ – 100 K, and cis third-neighbour divacancies can survive while $T \lesssim 295$ – 320 K. Since monovacancies are not mobile at these temperatures, fourth-neighbour and cis third-neighbour divacancies cannot be created by monovacancy migration. Trans third-neighbour divacancies are hardier species: they remain stable while $T \lesssim 770$ – 830 K, which is well above the threshold for monovacancy mobility. Thus, monovacancies can migrate and form trans third-neighbour divacancies in the range $T \approx 450$ – 800 K, or be annihilated by any interstitial atoms they encounter. At higher temperatures, trans third-neighbour divacancies coalesce into nearest neighbour $\alpha\beta$ divacancies. An annealing temperature in excess of 1800 – 2000 K is needed to transform $\alpha\beta$ divacancies into the haeckelite divacancy state.

Vacancies on separate, neighbouring graphene sheets in graphite can form bound pairs [127]. The earlier results of calculations using $4 \times 4 \times 1$ hexagonal supercells are confirmed by the present work using $6 \times 3 \times 2$ orthorhombic supercells, with the addition of two new structures. In all, there are four different forms of cross-layer divacancies which are bound: one $\alpha\beta$ pair with a single cross-linking bond between the layers ($V_{2,1}^{\alpha\beta}$), and three $\beta\beta$ pairings (figure 6). Two of the $\beta\beta$ pairs are at nearest neighbour separation with one ($V_{2,1}^{\beta\beta}$) or two cross-links ($V_{2,2}^{\beta\beta}$), and second neighbour separation with one cross-link ($V_{2,1}^{\beta\beta*}$). A summary of the results, including the point group symmetry for each defect, is given in table 3.

Table 3: Binding energies (eV) of cross-layer divacancies relative to isolated monovacancies calculated by the AIMPRO program package. The second subscript denotes the number of cross-links between the graphene layers; the ‘*’ superscript means that the vacancies are located on second nearest neighbouring sites. The point group symmetry for each defect is given in the second column.

Description	LDA	GGA	Reference [127]
$V_{2,1}^{\alpha\beta}$	C_s	1.53	1.22
$V_{2,1}^{\beta\beta}$	C_2	1.77	1.38
$V_{2,2}^{\beta\beta}$	C_{2h}	1.77	1.10
$V_{2,1}^{\beta\beta*}$	C_{2h}	3.25	2.88

Telling *et al.* suggested the reason for the observed activation energy for vacancy migration in graphite being 3.1 eV [46], and the then best theoretical estimate being only 1.7 eV [102], is that the process is inhibited by the trapping of monovacancies as cross-layer pairs [127]. Based on their results for cross-layer divacancy binding energies, they arrived at an overall activation energy for dissociation $E_a = 3.6$ eV. Applying the same reasoning to the present results gives $E_a = 3.0$ eV with the LDA and $E_a = 2.7$ eV with the GGA.

Positron annihilation experiments have identified the presence of single and multivacancy complexes in electron- and neutron-irradiated HOPG [69, 128]. Evidence of a $\langle 10\bar{1}0 \rangle$ vacancy line has also been seen in STM experiments on HOPG irradiated with carbon ions [38]. Calculations show that the stability of multivacancy complexes is controlled by two factors: the number of dangling bonds [128], and their ability to reconstruct [107, 129, 130]. Thus, it is found that V_4 and V_6 are particularly stable entities. The possibility that vacancies may coalesce into lines has been investigated using models based on DFT, where it was found that energy barriers to vacancy migration favour the formation of lines oriented in $\langle 10\bar{1}0 \rangle$ directions over those in $\langle 11\bar{2}0 \rangle$ directions [129].

3.4 Displacement defects

Two types of defects exist in graphite where atoms are displaced from lattice sites of the host without adding or removing atoms. These are Stone-Wales defects and Frenkel defects.

A Stone-Wales defect is generated by a pericyclic rearrangement of a graphene sheet, nanotube, or fullerene [131]. According to the AIMPRO method, the defect has a formation energy in graphite of 5.14 eV using the PW92-LDA, and $E_f = 5.26$ eV with the PBE96-GGA. Since creation or removal of a Stone-Wales defect involves the concerted exchange of two pairs of bonds, this reaction has a high activation energy. The calculated activation energy for removal of a Stone-Wales defect is $E_a = 4.54$ eV with the PW92-LDA, which implies that annealing of the defect requires a temperature above about 1640 – 1760 K. This is close to the temperature range where nearest neighbour divacancies can transform at an appreciable rate into the haeckelite structure, which occurs by a similar mechanism involving the concerted exchange of two pairs of bonds, meaning that both mechanisms will contribute to the release of Wigner energy when graphite

Figure 6: Cross-layer lattice vacancy pairs in graphite: (a) $\alpha\beta$ single reconstructed close cross divacancy $V_{2,1}^{\alpha\beta}$; (b) $\beta\beta$ single reconstructed close cross divacancy $V_{2,2}^{\beta\beta}$; (c) $\beta\beta$ double reconstructed close cross divacancy $V_{2,2}^{\beta\beta}$; (d) single reconstructed second neighbour cross divacancy $V_{2,1}^{\beta\beta*}$. Pairs of atoms forming cross-layer reconstruction bonds are coloured yellow.

is annealed at these temperatures. Using the PBE96-GGA instead of the LDA predicts that the barrier to eliminate a Stone-Wales defect is slightly smaller, making the estimated temperature for onset of annealing lower by about 50 K than it is with the LDA. Previous studies have found broadly similar results [44, 132–138], with one exception [139]. The exception (Kaxiras and Pandey) uses a model based on rhombohedral graphite instead of a single graphene sheet, which all the others use, and gives significantly higher values for the formation and activation energies. Xu, Fu, and Pedraza suggest that may be a consequence of insufficient structural optimization [132]. Later work has also shown that, owing to long-ranged elastic effects, the formation energy for a Stone-Wales defect varies over a range $E_f = 4.20$ – 5.90 eV depending on the size of model and orientation of the defect within it [138]. Using graphene as the model, we find that $E_f = 5.13$ eV for a 6×3 orthorhombic supercell with the defect in the same orientation as it is for the graphite model, and $E_f = 4.84$ eV for a 12×6 supercell with the PW92-LDA. Using instead the PBE96-GGA gives $E_f = 5.27$ eV and 4.97 eV for the 72- and 288-atom supercells, respectively.

The lowest energy state for an isolated interstitial atom in graphite is a structure with C_2 symmetry, known as a spiro-interstitial [44, 52, 127, 140]. A self interstitial can also coexist in very close proximity to a lattice vacancy without mutual annihilation [141]. This is a metastable state, called an intimate Frenkel defect. It has a formation energy which is significantly lower than the sum of their individual formation energies. There are two forms of this defect, where either an

α - or a β -atom is displaced from its lattice site in the host to an interstitial location (figure 7). The interstitial atom is connected by one bond to the graphene sheet containing the vacancy, and makes two bonds to the adjacent graphene sheet. Both defects have no identifiable symmetry (C_1). Earlier calculations using the LDA estimated the formation energy of the defect in a 64-atom hexagonal supercell to be $E_f \approx 10.8$ eV, making it about 2.9 eV more stable than the total energy of an isolated monovacancy and a self interstitial in the spiro state [141]. Similar results for the structures and formation energies are found in the present work, using 288-atom orthorhombic supercells. The total energy of the α form of the defect is calculated to be 3.14 eV less than the sum of the formation energies of an α vacancy and a self-interstitial atom using the PW92-LDA, and 3.01 eV for the PBE96-GGA. For the β form of an intimate Frenkel defect, these energies are 3.19 eV using the PW92-LDA, and 3.04 eV for the PBE96-GGA.

In the earlier calculations [141], the activation energy to annihilate an intimate Frenkel defect was estimated to be $E_a \approx 1.4$ eV, suggesting this process likely to be the one which is responsible for the large release of Wigner energy that occurs when radiation damaged graphite is annealed at about 200 C. However, the present results predict that $V_a I$ has a nearly no barrier preventing its collapse, and $E_a(V_\beta I) \approx 0.76$ eV, implying that the onset of annealing would be observed at about 272–293 K. The annihilation of each intimate Frenkel defect removes scattering centres for conduction electrons from two graphene layers; hence, a large reduction in basal

Figure 7: Metastable intimate Frenkel defects in graphite. A carbon atom is displaced from either an α or β lattice site in the host crystal.

electrical resistivity is expected for this process. Experiments have shown that when graphite is irradiated with electrons or neutrons with energies over 1 MeV at temperatures below 80 K, its electrical resistivity increases [19, 142]. When the material is annealed, an abrupt rise in its electrical resistivity occurs over the temperature range 80–110 K, approximately. This phenomenon, known as *reverse annealing*, implies that new defects are created, which act as stronger scattering centres than their precursors. The resistivity continues to rise up to about 140 K, but then begins to decline, falling more rapidly above 160 K. At first glance, this temperature would appear to be too low for the annealing of intimate Frenkel defects. However, according to our calculations, the activation energy for intimate Frenkel defect removal is approximately halved when free relative translation of graphene sheets is allowed within a 128-atom, $4 \times 2 \times 2$ orthorhombic supercell. It is also reasonable to expect that the activation energy for this process in a twist boundary (where there is a relative rotation of the graphene layers) may be lower than in the ideal material. While this does not fully explain reverse annealing, it does provide a mechanism for the first stage of recovery above about 140 K. Further recovery of the electrical resistivity can occur at temperatures exceeding about 400 K, when vacancies are predicted to become mobile, allowing them to encounter interstitial atoms. A summary of formation energies, and activation energies for Stone-Wales and intimate Frenkel defect annealing are given in table 4.

Table 4: Formation and activation energies (eV) to remove a Stone-Wales defect (SW), and the α and β forms of intimate Frenkel defects in graphite (288-atom $6 \times 3 \times 2$ orthorhombic supercell).

Description	PW92-LDA	PBE96-GGA
$E_f(SW)$	5.14	5.27
$E_f(V_\alpha I)$	10.67	10.61
$E_f(V_\beta I)$	10.59	10.55
$E_a(SW)$	4.54	4.42
$E_a(V_\alpha I)$	~ 0	~ 0
$E_a(V_\beta I)$	0.76	0.75

4 Summary and conclusions

Much of the information needed to explain the phenomena which occur when graphite is damaged by exposure to energetic radiation, such as dimensional change and reverse annealing, is available in the existing literature. However, in their interpretation of experimental results, most studies adhere to the conventional model in spite of its shortcomings described in the present work. One such shortcoming, central to the conventional model, is the assumption that interstitial carbon atoms do not form strong bonds with the host, contrary to chemical intuition, and the results of *ab initio* calculations. Another is the belief that lattice vacancies are relatively immobile species. The results of calculations reported here show, in agreement with previous work, that this is unlikely, and that vacancies rather than self-interstitials are the active entity responsible for the large release of Wigner energy at around 200 C.

The role of vacancies in annealing of radiation damage in graphite begins when the temperature is above about 140 K with the annihilation of intimate Frenkel defects in slip or twist boundaries, resulting in the sharp decrease of electrical resistivity observed by experiments. The removal of these defects cross-linking graphene layers also leads to the onset of recovery of both Young's modulus, and low-temperature dimensional change. Annealing continues with annihilation of the β -form of intimate Frenkel defects at about room temperature, then vacancies become fully mobile by 200 C. This means that they are free to consume any interstitial atoms they encounter, form trans third-neighbour or cross-layer divacancies, or disappear at surfaces, all of which will release large amounts of stored energy. More Wigner energy is released at temperatures above about 500 C when trans third-neighbour divacancies collapse to nearest neighbour divacancies. Aggregation into multivacancy complexes is likely to be an active process as well. All of these vacancy complexes (and Stone-Wales defects) require much higher temperatures to anneal out.

A summary of the findings of the present work is given in table 5. This should only be taken as a guide, since it relies on the assumptions and approximations described previously. In particular, the prefactor for the Arrhenius formula is an order-of-magnitude estimate, and the threshold frequency for the rates of reactions to become significant is assumed to

Table 5: Implications for annealing of radiation damage in graphite based on the results of the present work.

Temperature	Defect activity	Implied outcomes
100	Limit of stability for fourth-neighbour divacancies.	Vacancy coalescence commences.
140	Intimate Frenkel defects in twist or slip boundaries begin to collapse.	Onset of recovery for electrical and elastic parameters.
280	β intimate Frenkel defects vanish.	Recovery of electrical and elastic parameters accelerates; Wigner energy release grows.
310	Cis third-neighbour divacancies collapse.	Interstitial atoms are consumed; cross-layer and trans third-neighbour pairs form resulting in a large release of Wigner energy.
400	Monovacancies are mobile.	More Wigner energy is released by the formation of nearest-neighbour $\alpha\beta$ divacancies.
800	Limit of stability for trans third-neighbour divacancies.	Few interlayer cross-links remain; electrical and elastic parameters become close to their values in pristine graphite.
1400	Cross-layer divacancies dissociate.	Only haeckelite structure divacancies survive.
1700	Limit of stability for nearest-neighbour $\alpha\beta$ divacancies and Stone-Wales defects.	

be $\sim 1 \text{ s}^{-1}$. It is necessary, therefore, to take into account that fission reactors operate over timescales of decades, while laboratory measurements may be measured in seconds, when making comparisons with experimental observations. Only the contributions to annealing from specific vacancies and displacement defects are considered in the present work; other defects are ignored, or assumed to be bystanders. Further work is necessary to complete the picture.

Thus, in conclusion, reversing the role of vacancies and interstitials with respect to the conventional model is shown in this work to be more consistent with both experimental and theoretical evidence than is normally assumed in earlier studies.

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References

- [1] Kroto H W, Heath J R, O'Brien S C, Curl R F and Smalley R E 1985 *Nature* **318** 162–163
- [2] Bacon R 1960 *J. Appl. Phys.* **31** 283–290
- [3] Iijima S 1991 *Nature* **354** 56–58
- [4] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 *Science* **306** 666–669
- [5] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 *Proc. Nat. Acad. Sci., USA* **102** 10451–10453
- [6] Bernal J D 1924 *Proc. R. Soc. Lond., Ser. A* **106** 749–773
- [7] Benedek G, Milani P and Ralchenko V G (eds) 2001 *Nanostructured carbon for advanced applications* (NATO Science Series vol 24) (Dordrecht: Kluwer Academic Publishers)
- [8] Banhart F 2004 *Philos. Trans. R. Soc. Lond. A* **362** 2205–2222
- [9] Suarez-Martinez I, Grobert N and Ewels C P 2012 *Carbon* **50** 741–747
- [10] Kim K, Lee Z, Malone B D, Chan K T, Alemán B, Regan W, Gannett W, Crommie M F, Cohen M L and Zettl A 2011 *Phys. Rev. B* **83** 245433
- [11] Harris P J F 2012 *Carbon* **50** 3195–3199
- [12] Walker P L (ed) 1966 *Chemistry and Physics of Carbon* vol 2 (London: Edward Arnold)
- [13] Bacon G E and Warren B E 1956 *Acta Crystallogr.* **9** 1029–1035
- [14] Kelly B T 2000 *Dimensional changes in graphite and the thermal expansion coefficient* (TECDOC vol 1154) (Vienna: IAEA) chap 3, pp 49–84 http://www-pub.iaea.org/MTCD/Publications/PDF/te_1154_pn.pdf
- [15] Burton M and Neubert T J 1956 *J. Appl. Phys.* **27** 557–567
- [16] Bell J C, Bridge H, Cottrell A H, Greenough G B, Reynolds W N and Simmons J H W 1962 *Philos. Trans. R. Soc. Lond. A* **254** 361–395
- [17] Kelly B T 2000 *Stored Energy and the Thermo-Physical Properties of Graphite* (TECDOC vol 1154) (Vienna: IAEA) chap 4, pp 85–112 http://www-pub.iaea.org/MTCD/Publications/PDF/te_1154_pn.pdf
- [18] Kelly B T 1981 *Physics of graphite* (Barking and New Jersey: Applied Science Publishers)
- [19] Bochirol L and Bonjour E 1968 *Carbon* **6** 661–669 in French with English summary
- [20] Bonjour E, Bochirol L and Weil L 1962 *Comptes rendus* **254** 456–458 (in French)
- [21] Iwata T 1985 *J. Nucl. Mater.* **133–134** 361–364
- [22] Lexa D and Kropf A J 2006 *J. Nucl. Mater.* **348** 122–132
- [23] Lexa D and Dauke M 2009 *J. Nucl. Mater.* **384** 236–244
- [24] Mitchell E W J and Taylor M R 1965 *Nature* **208** 638–641
- [25] Agranovich V M and Semenov L P 1961 *Atomnaya Énergiya* **10** 572–576
Agranovich V M and Semenov L P 1962 *Atomic Energy* **10** 569–573 (English translation from Russian)

- [26] Iwata T and Suzuki H 1963 *Radiation damage in reactor materials - 1962 (Proceedings series vol 99)* (Vienna: International Atomic Energy Agency) pp 565–579
- [27] Coulson C A, Senent S, Herraez M A, Leal M and Santos E 1966 *Carbon* **3** 445–457
- [28] Thrower P A and Loader R T 1969 *Carbon* **7** 467–477
- [29] Maeta H Iwata T, and Okuda S 1975 *J. Phys. Soc. Jpn.* **39** 1558–1565
- [30] Kelly B T 1982 *Carbon* **20** 3–11
- [31] Gallego N and Burchell T D 2011 A review of stored energy release of irradiated graphite Tech. Rep. ORNL/TM-2011/378 Oak Ridge National Laboratory Oak Ridge, Tennessee <http://pbdupws.nrc.gov/docs/ML1131/ML113110373.pdf>
- [32] Niwase K 2002 *Philos. Mag. Lett.* **82** 401–408
- [33] Niwase K 2005 *Mater. Sci. Eng. A* **400–401** 101–104
- [34] Karthik C, Kane J, Butt D P, Windes W E and Ulic R 2011 *J. Nucl. Mater.* **412** 321–326
- [35] Amelinckx S and Delavignette P 1960 *Phys. Rev. Lett.* **5** 50–51
- [36] Thrower P A 1964 *Brit. J. Appl. Phys.* **15** 1153–1159
- [37] Thrower P A 1968 *Carbon* **6** 687–693
- [38] Annis B K, Pedraza D F and Withrow S P 1993 *J. Mater. Res.* **8** 2587–2599
- [39] Reynolds W N and Thrower P A 1965 *Philos. Mag.* **12** 573–593
- [40] Hinman G W, Haubold A, Gardner J O and Layton J K 1970 *Carbon* **8** 341–351
- [41] Iwata T, Fujita F E and Suzuki H 1961 *J. Phys. Soc. Jpn.* **16** 197–205
- [42] Kelly B T 1971 *Carbon* **9** 627–631
- [43] Abrahamson J and MacLagan R G A R 1984 *Carbon* **22** 291–295
- [44] Li L, Reich S and Robertson J 2005 *Phys. Rev. B* **72** 184109
- [45] Zhang H, Zhao M, Yang X, Xia H, Liu X and Xia Y 2010 *Diamond and Related Mater.* **19** 1240–1244
- [46] Thrower P A and Mayer R M 1978 *Phys. Status Solidi A* **47** 11–37
- [47] Niwase K 1995 *Phys. Rev. B* **52** 15785–15798
- [48] Niwase K 1997 *Phys. Rev. B* **56** 5685–5685
- [49] Ma Y 2007 *Phys. Rev. B* **76** 075419
- [50] Gulans A, Krasheninnikov A V, Puska M J and Nieminen R M 2011 *Phys. Rev. B* **84** 024114
- [51] Latham C D, Haffenden G L, Heggie M I, Suarez-Martinez I and Ewels C P 2010 *Phys. Rev. B* **82** 056101
- [52] Latham C D, Heggie M I, Gámez J A, Suárez-Martínez I, Ewels C P and Briddon P R 2008 *J. Phys.: Condens. Matter* **20** 395220
- [53] Tanabe T, Muto S and Niwase K 1992 *Appl. Phys. Lett.* **61** 1638–1640
- [54] Muto S and Tanabe T 1997 *Philos. Mag. A* **76** 679–690
- [55] Koike J and Pedraza D F 1994 *J. Mater. Res.* **9** 1899–1907
- [56] Tanabe T 1996 *Phys. Scr.* **T64** 7–16
- [57] Asthana A, Matsui Y, Yasuda M, Kimoto K, Iwata T and Ohshima K 2005 *J. Appl. Cryst.* **38** 361–367
- [58] Koike J and Pedraza D F 1992 *MRS Proc.* **279** 67–72
- [59] Tanabe T, Maruyama T, Iseki M, Niwase K and Atsumi H 1995 *Fusion Eng. and Design* **29** 428–434
- [60] Takeuchi M, Muto S, Tanabe T, Arai S and Kuroyanagi T 1997 *Philos. Mag. A* **76** 691–700
- [61] Muto S and Tanabe T 2000 *J. Nucl. Mater.* **283–287, Part 2** 917–921
- [62] Heggie M I, Suarez-Martinez I, Davidson C and Haffenden G 2011 *J. Nucl. Mater.* **413** 150–155
- [63] Jenkins G M and Jouquet G 1968 *Carbon* **6** 85–91
- [64] Jenkins G M 1973 *Chemistry and Physics of Carbon* vol 11 ed Walker P L (New York: Marcel Dekker) pp 189–242
- [65] Choudhary S K and Gupta A K 2007 *Jpn. J. Appl. Phys.* **46** 7450–7452
- [66] Eeles W T 1975 *Philos. Mag.* **32** 1273–1276
- [67] Eeles W T 1968 *Acta Crystallogr. A* **24** 688–689
- [68] Pregler S K, Hayakawa T, Yasumatsu H, Kondow T and Sinnott S B 2007 *Nucl. Instrum. Methods B* **262** 240–248
- [69] Onitsuka T, Ohkubo H, Takenaka M, Tsukuda N and Kuramoto E 2000 *J. Nucl. Mater.* **283–287, Part 2** 922–926
- [70] Banhart F 2002 *Fizika Tverdogo Tela* **44** 388–392 republished in Banhart F 2002 *Phys. Solid State* **44(3)** 399–404
- [71] Briddon P R and Jones R 2000 *Phys. Status Solidi B* **217** 131–171
- [72] Goss J P, Shaw M J and Briddon P R 2007 *Theory of defects in semiconductors (Topics Appl. Phys. vol 104)* ed Drabold D A and Estreicher S K (Berlin Heidelberg: Springer-Verlag) chap 3, pp 69–94
- [73] Rayson M J and Briddon P R 2008 *Computer Phys. Commun.* **178** 128–134
- [74] Rayson M J 2007 *Phys. Rev. E* **76** 026704
- [75] Perdew J P and Wang Y 1992 *Phys. Rev. B* **45** 13244–13249
- [76] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865–3868
- [77] Hartwigsen C, Goedecker S and Hutter J 1998 *Phys. Rev. B* **58** 3641–3662
- [78] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188–5192
- [79] Methfessel M and Paxton A T 1989 *Phys. Rev. B* **40** 3616–3621
- [80] Henkelman G, Uberuaga B P and Jónsson H 2000 *J. Chem. Phys.* **113** 9901–9904
- [81] Henkelman G and Jónsson H 2000 *J. Chem. Phys.* **113** 9978–9985
- [82] Schabel M C and Martins J L 1992 *Phys. Rev. B* **46** 7185–7188
- [83] Green J F and Spain I L 1975 *Phys. Rev. B* **11** 3935–3943
- [84] Weinert M, Wimmer E and Freeman A J 1982 *Phys. Rev. B* **26** 4571–4578
- [85] Brewer L 1975 Cohesive energies of the elements Technical report 3720 Lawrence Berkeley Lab. California Univ., Berkeley (USA)
- [86] Nieminen R M 2007 *Theory of defects in semiconductors (Topics Appl. Phys. vol 104)* ed Drabold D A and Estreicher S K (Berlin Heidelberg: Springer-Verlag) chap 2, pp 29–68
- [87] Charlier J, Gonze X and Michenaud J 1994 *Europhys. Lett.* **28** 403–408
- [88] Savini G, Dappe Y J, Öberg S, Charlier J C, Katsnelson M I and Fasolino A 2011 *Carbon* **49** 62–69
- [89] Dolling G and Brockhouse B N 1962 *Phys. Rev.* **128** 1120–1123
- [90] Kelly B T and Duff M J 1970 *Carbon* **8** 77–83
- [91] Nekovee M, Foulkes W M C and Needs R J 2003 *Phys. Rev. B* **68** 235108
- [92] Wu Q and Yang W 2002 *J. Chem. Phys.* **116** 515–524
- [93] Ortman F, Bechstedt F and Schmidt W G 2006 *Phys. Rev. B* **73** 205101
- [94] Teobaldi G, Ohnishi H, Tanimura K and Shluger A L 2010 *Carbon* **48** 4145–4161
- [95] Teobaldi G, Tanimura K and Shluger A L 2010 *Phys. Rev. B* **82** 174104
- [96] Dion M, Rydberg H, Schröder E, Langreth D C and Lundqvist B I 2004 *Phys. Rev. Lett.* **92** 246401
- [97] Gulans A, Puska M J and Nieminen R M 2009 *Phys. Rev. B* **79** 201105
- [98] Tsetseris L and Pantelides S T 2011 *Phys. Rev. B* **84** 195202

- [99] Tsetseris L and Pantelides S T 2009 *Carbon* **47** 901–908
- [100] Björkman T, Gulans A, Krasheninnikov A V and Nieminen R M 2012 *J. Phys.: Condens. Matter* **24** 424218
- [101] Coulson C A, Herraez M A, Leal M, Santos E and Senent S 1963 *Proc. R. Soc. Lond., Ser. A* **274** 461–479
- [102] El-Barbary A A, Telling R H, Ewels C P, Heggie M I and Briddon P R 2003 *Phys. Rev. B* **68** 144107
- [103] Ma and Y Lehtinen P O, Foster A S and Nieminen R M 2004 *New J. Phys.* **6** 68
- [104] Lehtinen P O, Foster A S, Ma Y, Krasheninnikov A V and Nieminen R M 2004 *Phys. Rev. Lett.* **93** 187202
- [105] Lee G D, Wang C Z, Yoon E, Hwang N M, Kim D Y and Ho K M 2005 *Phys. Rev. Lett.* **95** 205501
- [106] Krasheninnikov A V, Lehtinen P O, Foster A S and Nieminen R M 2006 *Chem. Phys. Lett.* **418** 132–136
- [107] Saito M, Yamashita K and Oda T 2007 *Jpn. J. Appl. Phys.* **46** L1185–L1187
- [108] Paredes J I, Solís-Fernández P, Martínez-Alonso A and Tascón J M D 2009 *J. Phys. Chem. C* **113** 10249–10255
- [109] Asari E, Kitajima M, Nakamura K G and Kawabe T 1993 *Phys. Rev. B* **47** 11143–11148
- [110] Asari E, Kitajima M and Nakamura K G 1998 *Carbon* **36** 1693–1696
- [111] Yazayev O V and Helm L 2007 *Phys. Rev. B* **75** 125408
- [112] Faccio R and Mombrú A W 2012 *J. Phys.: Condens. Matter* **24** 375304
- [113] Ugeda M M, Brihuega I, Guinea F and Gómez-Rodríguez J M 2010 *Phys. Rev. Lett.* **104** 096804
- [114] Castro E V, López-Sancho M P and Vozmediano M A H 2010 *Phys. Rev. Lett.* **104** 036802
- [115] Zhang Y, Talapatra S, Kar S, Vajtai R, Nayak S K and Ajayan P M 2007 *Phys. Rev. Lett.* **99**(10) 107201
- [116] Kumazaki H and Hirashima D S 2008 *Fiz. Nizk. Temp.* **34** 1025–1032
Kumazaki H and Hirashima D S 2008 *Low Temp. Phys.* **34** 805–811 (English translation from Russian)
- [117] Faccio R, Pardo H, Denis P A, Yoshikawa Oeiras R, Araújo-Moreira F M, Veríssimo-Alves M and Mombrú A W 2008 *Phys. Rev. B* **77** 035416
- [118] Paz W S, Scopel W L and Freitas J C C 2012 *arXiv: Cond. Matter* 1211.2695v1
- [119] Lieb E H 1989 *Phys. Rev. Lett.* **62** 1201–1204
- [120] Coulson C A and D P M 1964 *Carbon* **2** 275–279
- [121] Kastner J, Kuzmany H, Kavan L, Dousek F P and Kuerti J 1995 *Macromolecules* **28** 344–353
- [122] Lee H J and Shim S C 1993 *J. Chem. Soc., Chem. Commun.* **18** 1420–1422
- [123] Iwata T and Watanabe M 2010 *Phys. Rev. B* **81** 014105
- [124] Asari E, Nakamura K G, Kawabe T and Kitajima M 1997 *J. Nucl. Mater.* **244** 173–175
- [125] Amara H, Latil S, Meunier V, Lambin P and Charlier J C 2007 *Phys. Rev. B* **76** 115423
- [126] Ugeda M M, Brihuega I, Hiebel F, Mallet P, Veuillen J Y, Gómez-Rodríguez J M and Ynduráin F 2012 *Phys. Rev. B* **85** 121402
- [127] Telling R H, Ewels C P, El-Barbary A A and Heggie M I 2003 *Nature Mater.* **2** 333–337
- [128] Tang Z, Hasegawa M, Shimamura T, Nagai Y, Chiba T, Kawazoe Y, Takenaka M, Kuramoto E and Iwata T 1999 *Phys. Rev. Lett.* **82** 2532–2535
- [129] El-Barbary A A 2005 *First principles characterisation of defects in irradiated graphitic materials* Phd thesis School of Life Sciences University of Sussex
- [130] Oubal M, Picaud M, Rayez M T and Rayez J C 2012 *Computational and Theo. Chem.* **990** 159–166
- [131] Stone A J and Wales D J 1986 *Chem. Phys. Lett.* **128** 501–503
- [132] Xu C H, Fu C L and Pedraza D F 1993 *PR B* **48** 13273–13279
- [133] Zhou L G and Shi S Q 2003 *Appl. Phys. Lett.* **83** 1222–1224
- [134] Zhao Q, Nardelli M B and Bernholc J 2002 *Phys. Rev. B* **65** 144105
- [135] Jensen P, Gale J and Blase X 2002 *Phys. Rev. B* **66** 193403
- [136] Dumitrică T and Yakobson B I 2004 *Appl. Phys. Lett.* **84** 2775–2777
- [137] Ewels C P, Heggie M I and Briddon P R 2002 *Chem. Phys. Lett.* **351** 178–182
- [138] Ertekin E, Chrzan D C and Daw M S 2009 *Phys. Rev. B* **79** 155421
- [139] Kaxiras E and Pandey K C 1988 *Phys. Rev. Lett.* **61** 2693–2696
- [140] Heggie M I, Eggen B R, Ewels C P, Leary P, Ali S, Jungnickel G, Jones R and Briddon P R 1998 *Fullerenes: Chemistry, Physics, and New Directions (Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* vol 6) ed Kadish K M and Ruoff R S (Pennington, NJ: The Electrochemical Society) pp 60–67
- [141] Ewels C P, Telling R H, El-Barbary A A, Heggie M I and Briddon P R 2003 *Phys. Rev. Lett.* **91** 025505
- [142] Austerman S B and Hove J E 1955 *Phys. Rev.* **100** 1214–1215