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Metastable Frenkel Pair Defect in Graphite: Source of Wigner Energy?

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The atomic processes associated with energy storage and release in irradiated graphite have long been subject to untested speculation. We examine structures and recombination routes for interstitial-vacancy (I-V) pairs in graphite. Interaction results in the formation of a new metastable defect (an intimate I-V pair) or a Stone-Wales defect. The intimate I-V pair, although 2.9 eV more stable than its isolated constituents, still has a formation energy of 10.8 eV. The barrier to recombination to perfect graphite is calculated to be 1.3 eV, consistent with the experimental first Wigner energy release peak at 1.38 eV. We expect similar defects to form in carbon nanostructures such as nanotubes, nested fullerenes, and onions under irradiation.

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Sixty years ago, concerns raised by Wigner and Szilard for the behavior of moderators in the first nuclear reactors prompted research into radiation damage effects in graphite [1–3]. Today, understanding these effects continues to be an active area of research, and there is much crossover with the emerging interest in defect behavior and radiation-induced structural and electronic modification in carbon nanostructures [4]. Neutron collision damage in graphite results in the formation of structural defects, such as displaced atoms, vacancies, and higher-order aggregates that raise the internal energy. The subsequent interaction of these defects with each other and the surrounding lattice also causes dimensional distortion, and physical property changes (thermal, electrical, elastic). These effects in graphite are well characterized [2,3] but poorly understood at a basic level. New insights can be gained into the phenomenology of radiation damage using first principles calculation, enabling observed processes to be reconciled with actual defect behavior at the atomic level [5]. One such process about which little is currently known in terms of atomic rearrangements is the buildup and release of internal energy, which can potentially be a hazardous side effect of radiation damage [6]. This so-called Wigner energy is stored in a local defect structure and can be released either by defect rearrangement to configurations with lower energy or ultimately by the process of interstitial-vacancy recombination. Annealing measurements concerned with the removal of stored energy report specific temperatures at which energy releases occur, corresponding to different defect rearrangement processes. The characteristics of energy release vary depending on the dose, flux, and irradiation temperature, but generally a complex defect system develops with a wide range of length scales and energy barriers. Numerous defect schemes have been proposed to explain barrier mechanisms to energy release, for example, the breakup of loose aggregates of interstitial pairs into isolated interstitial pairs and their subsequent annihilation with di-vacancies [7], detrapping of interstitials from grain boundaries, dislocations, or impurities [8], and also recrystallization of irradiation-amorphized regions [9].

An energy release event known as the 200 °C release peak [8] has received particular attention due to its prominence in many irradiated graphite systems. It is associated with an activation barrier of 1.38 eV, and its nature has previously been open to speculation. This Letter examines in detail the recombination of an interstitial atom (I) with a vacancy (V) and finds a barrier to the process in line with this observed activation energy. It arises from the formation of a metastable mutually trapped I-V configuration as they approach one another, which we term an intimate Frenkel pair. The existence of such a defect in graphite has previously been indirectly inferred [10], but its structure has never before been studied nor has it been linked with Wigner energy release.

Various theoretical studies have been carried out on V and to a lesser extent I in graphite, mostly using parametrized approaches, e.g., Hückel-based linear combination of atomic orbitals [11–14], complete neglect of differential overlap theory level [15], extended modified Hückel with valence-effective Hamiltonian [16], and tight-binding interatomic potential model [17]. In addition, density functional studies have been performed [18,19] as well as molecular dynamics simulations of defects on graphite surfaces [20]. Unfortunately there is often significant discrepancy between the different groups on properties such as defect formation energy, and to date there has been no first principles examination of the recombination process between I and V.

We adopt a first principles approach with AIMPRO, a code using the local density functional formalism [21], and apply this to a 64 atom supercell of graphite containing the defect. Two *d*- and three *p*-like atom centered

Gaussian functions are used as a basis, performing a Bloch sum over lattice vectors. Matrix elements of the kinetic energy and the pseudopotentials are found in real space while the Hartree and exchange-correlation energies and potentials are found from a Fourier expansion of the charge density. Brillouin zone sampling is performed using the *k*-point generation scheme of Monkhorst and Pack [22] and minima in the total energy are found using a conjugate gradient algorithm.

We have considered two vacancy structures and three different types of interstitials. The vacancy can exist on either α sites, V_α (vacant site lies directly between atom sites on the planes adjacent to the plane of the vacancy), or β sites, V_β (vacant site lies between centers of hexagonal voids on the planes adjacent to the plane of the vacancy). The interstitial has several possible geometries which are close in energy including the "spiro" (bonded to 4 C atoms, two in each sheet, so-called because of its resemblance to the core of the molecule spiro-pentane) [23], the "Y-lid" interstitial (two bonds to one sheet, one bond to the other, so-called because of the Y-arranged bonds of the interstitial with an intact C-C bond above) [5] and the "grafted" (bonded to two C atoms in the same sheet) [23].

The first two form cross-links between neighboring graphite sheets, and in sheared or faulted graphite the spiro form is the most stable. In perfect *AB* stacked graphite all three have approximately the same energy. Since the migration barrier for I is an order of magnitude lower than that of V [24], we have assumed a stationary V and placed an I at various sites around it. Note that although V undergoes a Jahn Teller relaxation to shorten one C-C bond, the barrier to rotation is only 0.13 eV [25], and hence at room temperature and above, V can be considered trigonally symmetric in terms of approach routes for I. For both V_α and V_β we placed each different interstitial type in all the nearby symmetrically irreducible sites before fully relaxing the defect in each case. In all these calculations the spiro interstitials switch to the Y-lid structure.

All of the structures examined spontaneously relax into either a new metastable I-V complex shown in Fig. 1, perfect graphite, or a Stone-Wales (SW) defect (this is the replacement of four hexagons in the graphitic sheet with two pentagons and two heptagons, normally achieved through a 90° bond rotation of the central C-C bond). The new metastable I-V complex (referred to hereafter as an intimate I-V pair) consists of a C atom bonded below one of the three C atoms neighboring the V. It also forms covalent bonds with two C atoms in the sheet below. The two other C atoms neighboring the V form a weakly reconstructed bond. Bond lengths and angles are shown in Fig. 1. As can be seen from the short shared bond length, the interstitial and the two coordinate vacancy neighbor form a distorted double bond which accounts for the stability of this complex compared to other variants examined.

Which structure is adopted depends on the nature of the I atom. If the I forms cross-links between the sheets (the spiro or Y-lid), the I and V interact to form the intimate I-V pair. The cross-linked structures are the most stable forms of I, and hence this represents the most likely outcome. If I is a grafted two coordinate atom, then it interacts with V to form a SW defect (see Fig. 2). If a cross-linked I could reach sites within one bond length of V_α, they would recombine to form perfect graphite (not the case for V_β). However, before it can reach this position the I passes through sites where it spontaneously forms the intimate I-V pair. Equally the grafted I would

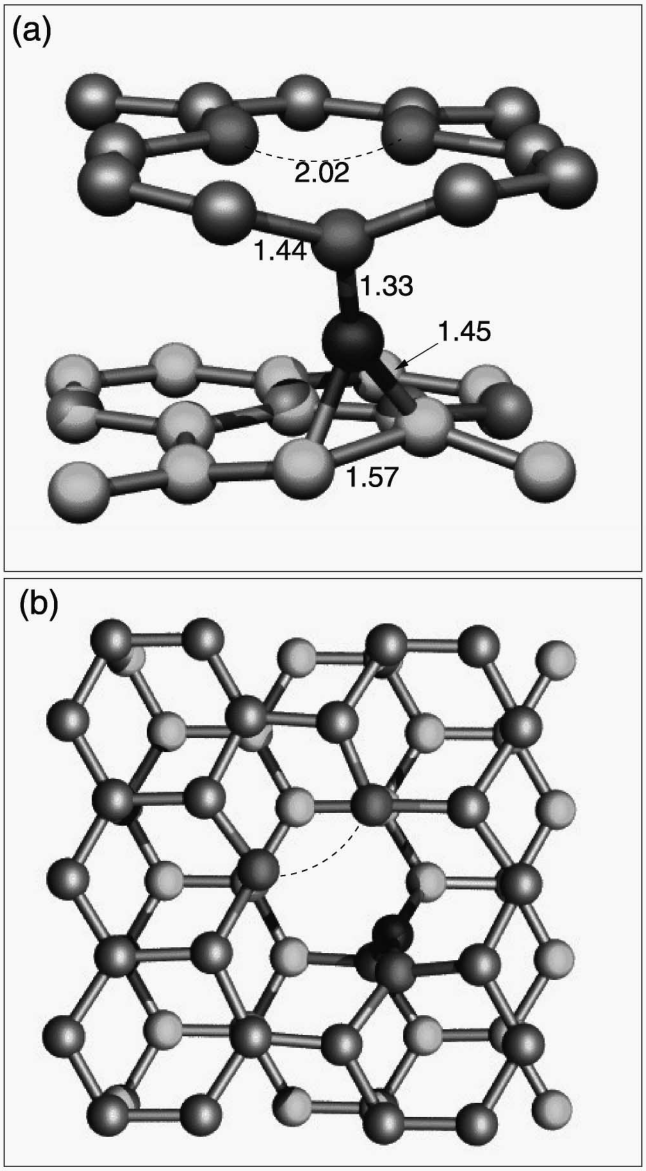

FIG. 1. The intimate I-V pair in graphite (a) side view and (b) from above. Interstitial atom is shown in black; atoms in the sheet below are lighter. All bond lengths are in Å. The example shown here involves V_β. Dotted line marks the weakly reconstructed vacancy bond.

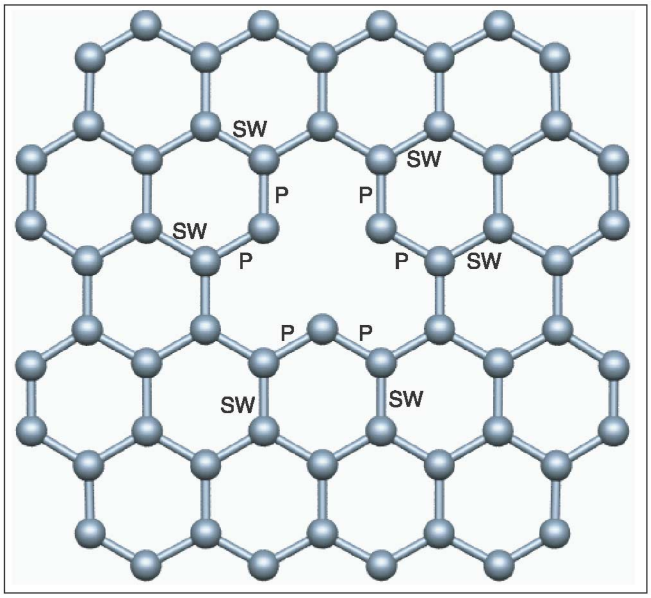

FIG. 2 (color online). Initial configuration of graphite vacancy. A twofold coordinated "grafted" interstitial (I) is then inserted into different sites above bond centers around the vacancy and all atoms relaxed. The system spontaneously forms either perfect graphite (P) or a Stone-Wales (SW) defect depending on the initial location of I. Initial bond centered sites for the I are labeled to show the resultant relaxed structure (P/SW). There is no barrier to recombination in any of these cases.

recombine with the V to form perfect graphite if it could reach bonds immediately neighboring the V, but it first passes through sites that spontaneously relax into SW defects.

It is unclear whether SW defects form in this way, whether they will remain, or whether they will revert to perfect graphite. The 7.6 eV energy release on formation of a SW patch from an isolated Frenkel pair may be sufficient to overcome the 5.6 eV barrier to graphite reformation [26] if the reaction coordinate and lattice vibrations can strongly couple. Another I atom will lower this 5.6 eV barrier to just 0.7 eV [26], and hence in the presence of mobile interstitials the SW patch will be only a short-lived species.

We calculate the energy of a widely separated Frenkel pair to be 13.7 eV compared to perfect graphite, in good agreement with experimental values which are reviewed in [24] and given as 14 ± 1.0 eV. The intimate I-V pair described here is 2.9 eV lower in energy than a separated Frenkel pair (both in unsheared AB stacked graphite) and hence metastable. On transformation to perfect graphite the defect yields a further 10.8 eV, a major energy release once the recombination barrier is overcome.

In a 64 atom supercell the intimate I-V pair spontaneously shears one graphite layer with respect to the other by half a C-C bond length along $\langle 1\bar{1}00 \rangle$. This allows the I atom to sit symmetrically between two C neighbors in the sheet below, lowering the system energy by 0.2 eV. The stacking fault cost associated with this shear (3.1 meV Å^{-2}), calculated in a perfect 64 atom cell totals 0.5 eV. This suggests a net 0.7 eV drop in energy if the I-V pair moves to or forms in a preexisting sheared site. In this situation the defect is 3.6 eV more stable than an isolated Frenkel pair. This shear is the same as that in the core of a basal partial dislocation and we expect the intimate I-V pair to be more stable in regions of sheared crystal. We have proposed in a separate paper that, in concert, such defects may be able to attract and bind shear in graphite planes [5]. The shear makes the local structure of the α and β vacancy forms of the defect equivalent.

Since shear has a "per area" energetic stacking fault cost to be offset against the 0.7 eV energy saving for the I-V defect center, we do not expect spontaneous shearing to be observed in larger supercell calculations where the area of graphite to be sheared is too great (i.e., for cells with more than ~90 atoms). Variations in the shear environment thus give a range of formation energies of the I-V pair of up to 0.7 eV, consistent with the spread observed in experiment. Such different environments range from perfect graphite (where the shear effect is smallest) to the core of a basal dislocation (where the shear effect is largest and the defect is most stable), and also include stacking faults and turbostratic graphite. We have not attempted to further quantify this energy spread since the calculation sizes required would be prohibitive. In addition, the error bars in experimental measurement and the indirect nature of the estimation of this spread deduced from stored energy release curves make comparison with experiment difficult.

We next examine the barrier to recombination for the intimate I-V pair. In this case the I atom is moved a fixed distance along a vector between its current site and its position in ideal graphite. It is then allowed to relax constrained to a plane perpendicular to this vector, while allowing five neighbors (three C atoms neighboring the vacancy and two C neighbors in the sheet below) to freely relax. A plot of this trajectory against system energy is shown in Fig. 3. At 1.3 eV, the barrier is in excellent agreement with the experimentally observed Wigner energy release at 1.38 eV, and indeed, once the defect overcomes this barrier the energy release is substantial. It should be noted that the experimental value is determined indirectly from differential-scanning calorimetric data [7] and can vary somewhat depending on the exact choice of prefactor to first order kinetics of release. The peak is relatively broad with a spread of ~0.4 eV [8], which is commensurate with our energy saving when the defect sits in regions of sheared crystal. Hence the peak width may be due to the varying local environment of the intimate I-V pairs.

Deeper traps form with prolonged irradiation or higher temperatures, and are likely to be interstitial and vacancy

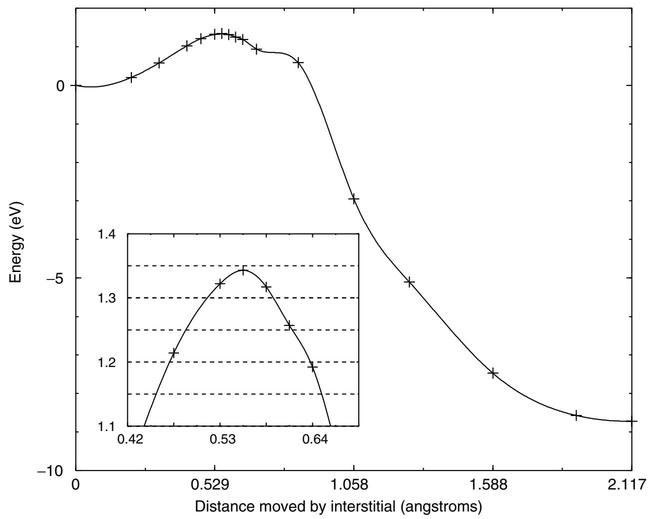

FIG. 3. The barrier for the intimate I-V pair of Fig. 1 to recombine giving perfect graphite. Distance moved by interstitial in Å (0 = intimate IV pair, 2.20 = perfect graphite). Inset is magnified section of the main peak. Solid line is a fit to guide the eye.

traps such as defect clusters. Both I and V should trap at prismatic dislocation loops, and it is possible that defect structures similar to the intimate I-V pair will form around the edge of such loops. However, under conditions of heavy irradiation, the primary capture species for mobile I atoms will be vacancies. In this case the intimate I-V pair described here represents the ultimate barrier to Frenkel pair recombination and must be overcome in every case.

It seems reasonable to expect similar metastable I-V defects to occur in other layered carbon systems such as nanotubes and carbon onions. I-V traps have been speculated to exist in other materials such as diamond and Si for some time and indeed concerted exchange centers [27] (tetrahedral equivalent of the Stone-Wales patch) have been identified in Si [28].

In summary, irradiation of graphite results in the production of I-V pairs. Depending on the structure of the interstitial, these interact to form either an intimate I-V pair or a Stone-Wales defect. The intimate I-V pair can recombine into perfect graphite with a barrier of 1.3 eV, releasing 10.1–10.8 eV in the process. For the majority of cases this defect represents a final barrier to recombination which must be overcome, and we suggest this complex to be the cause of the major 200 °C Wigner energy release peak in graphite.

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