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Comment on "Increase in specific heat and possible hindered rotation of interstitial C_2 molecules in neutron-irradiated graphite"

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Iwata and Watanabe's model for the observed low-temperature specific heat of neutron-irradiated graphite [T. Iwata and M. Watanabe, Phys. Rev. B **81**, 014105 (2010)] assumes that self-interstitial atoms exist as clusters of nearly free C_2 molecules. We suggest that their hypothesis is not supported by other experiments and theory, including our own calculations. Not only is it inconsistent with the long-known kinetics of interstitial prismatic dislocation loop formation, density-functional theory shows that the di-interstitial is covalently bonded to the host crystal. In such calculations no prior assumptions are made about the nature of the bonding, covalent or otherwise.

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A recent study by Iwata and Watanabe[1] showed that neutron irradiation of graphite produces an enhancement of the material's low-temperature specific heat. They conclude from these measurements that the hindered rotation of interstitial C_2 molecules is responsible for this effect. These are elegant, precise experiments which provide important evidence about the nature of such materials. Nevertheless, we profoundly disagree with the analysis of results that they put forward because it contains unjustified assumptions which can be refuted in a number of different ways, particularly with regard to the C_2 entities invoked.

First, recent calculations reported by us, based on density-functional theory (DFT), using large supercells (with four graphite layers and up to 290 atoms) conclusively demonstrate that the binding energy between pairs of interstitial atoms to yield C_2 is large (3 eV), and hence their formation must be irreversible at the temperatures of irradiation cited by Iwata and Watanabe (333 K).[2] It is clear from the covalently bonded structures illustrated in Ref. 2 that any migration path for C_2 is unlikely to exist with as low an energy as suggested by Iwata and Watanabe or that any free rotation could occur. Isolated self-interstitial atoms also form covalent bonds with the host crystal, according to our calculations, and in agreement with others. Certainly, none of the structures obtained give rise to $c:a$ aspect ratios or formation volumes comparable with those inferred in their paper.

Our calculations were *not* based on the assumption of a model, either covalent or noncovalent. They are *only* conjugate-gradient geometry optimizations starting from various initial positions for two C atoms placed between perfect graphitic planes, as in Iwata and Watanabe's C_2 diagram in their Fig. 5. No special distortions or atomic displacements were applied before optimization. There is nothing to prevent the formation of freely floating C_2 units, if this is a valid outcome. The optimization algorithm cannot traverse any energy barrier it experiences; it only proceeds downhill. However, in every case the system spontaneously reorganized into fully covalently bonded structures, integrated with the host lattice, either in the same layer or between layers. Indeed, additional calculations confirm this behavior. Starting from exactly the structure illustrated in Fig. 5 of Ref. 1, the model system spontaneously relaxes into the stable, covalently cross-linked structure with C_{2h} symmetry shown in Fig. 3 of Ref. 2. The final, optimized configuration has about 5.8 eV lower energy than the initial one.

The calculations cited by Iwata *et al.*, used to support their view that interstitial atoms are responsible for dimensional change in irradiated graphite, employ a classical potential. The model also assumes that the interstitial atom is not bonded to the host crystal and generates an elastic deformation in the surrounding layers.[3,4] Thus, the model is constructed to yield the desired result, which Iwata *et al.* take to be evidence for its correctness.

Second, there is longstanding empirical evidence against mobile C_2 units. Interstitial prismatic dislocation loops (disks composed of interstitial atoms) were observed very early in studies of radiation damage, and this observation helped form the main focus of damage theories. For high temperatures of irradiation or annealing (1173 K or above), these loops were large and their growth could be studied quantitatively. The assumption made by Brown *et al.* was that radiation led to a homogeneous nucleation of a certain concentration of interstitials and vacancies which did not annihilate with one another.[5] Each one either met with another of its own kind, nucleating an aggregate, or met with the aggregate and grew it. For interstitials it was believed the aggregate was a disk and for vacancies a line.

In the experiments, the radii and mean separation of disks were measured in an electron microscope as a function of dose and temperature, giving an Arrhenius plot with activation energy $E_a = 1.25$ eV. At the time, the noncovalently bonded model was assumed, and hence migration energies were expected to be low ($\lesssim 0.1$ eV). In this context, Brown *et al.*[5] hypothesized the ability of boron to trap interstitial atoms during their migration. Thus, they arrived at a very convincing functional analysis of disk growth as a function of [B], arguing that the largest part of the migration energy was the B_i binding energy. They considered an alternative postulate (by Reynolds and Thrower[6]) that reconciled the activation energy with a low migration energy, by the formation of less mobile C_2 units. Brown *et al.*[5] explicitly ruled this out as incompatible with their observed kinetics. Telling and Heggie[7] pointed out that a much more natural assumption was that the measured activation energy was the effective migration energy and this is compatible with the covalently bonded model as discussed by Iwata *et al.*

Note that, in recent times there have been high-quality DFT calculations by Ma, which are interpreted to give a relatively low migration energy of 0.4 eV for an isolated self-interstitial atom moving in the basal plane.[8] It is difficult to understand this interpretation, where Ma forces agreement with the historical view by invoking migration between metastable states (labeled B in her nomenclature), instead of the ground state (labeled A). When the migration is ground state to ground state, i.e., $A \rightarrow B \rightarrow A'$, $E_a = 1.2 - 1.7$ eV, the uncertainty arising from the application of van der Waals corrections or not. Using DFT, Li *et al.* also conclude that $E_a > 1.5$ eV (Ref. 9). Both results confirm covalent bonding in the self-interstitial, i.e., the spirostructure described in Refs. 10 and 11, which gives rise to negligible dimensional change.[2]

Thus, it is apparent that mobile and clustering C_2 units are unrealistic assumptions. Appealing to the completely inadequate theoretical models of interstitials and di-interstitials of 50 years ago is scant justification since these clearly do not reproduce the physics. The suggestion by Martin and Henson[12] that C_n units with $n = 4 \pm 2$ cause swelling of the interlayer spacing, as measured by small-angle neutron scattering (SANS), is based on the same models, and it was soon recognized that these clusters must not give rise to loops, else the nucleation density of loops would be wrong. Thus, they had to breakup (by a somewhat mysterious and unspecified mechanism). It is far more reasonable to allow that the SANS measured local, long-wavelength variations in the interlayer distance as might occur if the layers buckled or folded.

Furthermore, scanning tunneling microscopy of graphite surfaces provides direct evidence that the activation energy for migration of the isolated lattice vacancy in graphite is as low as 1 eV and may be lower.[13] Thus, contrary to Iwata and Watanabe's beliefs, vacancies are mobile defects at room temperature. This is also supported by theory, which predicts that it is energetically favorable for monovacancies to coalesce into divacancies in graphene.[14] These defects have been observed directly in graphene by high-resolution microscopy.[15,16] Finally, we note two important points about heat capacity.

The first is that Iwata and Watanabe *assume* freely rotating C_2 units with a rotational level of 5.8 meV in order to explain the augmentation of the very low-temperature specific heat in irradiated graphite and they dismiss any other irradiation-induced changes. It is, however, not difficult to see that any reduction of the E_{2g} phonon mode at 42 cm^{-1} (i.e., 5.2 meV), which arises from the shearing of one layer past another, by irradiation could be the cause. At least three possibilities arise for this: (1) bridging defects[10] pinning two layers together so that they vibrate as a rigid unit of double the mass (reducing frequency by $\sqrt{2}$); (2) rotation of layers so that the interlayer shear constant (C_{44}) approaches zero;[17] and (3) buckling of layers, increasing interlayer spacing and hence reducing C_{44} (Ref. 18).

Furthermore, these are not the only ways in which irradiation-induced changes might lead to an enhancement of the specific heat at low temperatures. In amorphous silicon, exchanged-coupled dangling bonds are known to be responsible for this effect,[19] and it is reasonable to suppose that irradiated graphite could contain similar dangling bonds.[20] Our own calculations ongoing at present suggest also that the existence of a floppy, low-frequency mode for the trans third neighbor divacancy could contribute to the low-temperature specific heat. The frequency of this mode is difficult to estimate; however, we find it to be $\lesssim 70$ cm^{-1}. Details of this work will be provided in a forthcoming article.

The second important point for heat capacity is the early inference discussed by the authors that the enormous jump at high temperatures is due to the reversible formation of vacancies.[21] If such vacancies can form and have a higher formation energy than the interstitial, as DFT results dictate, then interstitials should also be formed—and they are not. We point out that the reversible formation of Frenkel defects is indeed unlikely up to the melting temperature because it requires an activation energy in bulk of at least the Frenkel defect formation energy of some 14 eV (Refs. 22 and 23). Much more likely is that this peak arises from the reversible formation of the metastable state in direct exchange[24,25]—now known as Stone-Wales defects—which has a calculated formation energy and entropy at 3500 K of 5.1 eV and 7.6 k_B, respectively.[26] Previous estimates of the formation energy for this reaction in graphite include Li *et al.*[9] ($E_f = 4.8$ eV) and in graphene Ewels *et al.*[27] ($E_f = 3.4$ eV).

Thus, in conclusion, although we find the experimental results presented in the article of Iwata and Watanabe of great interest, we disagree with their interpretation based on free rotation of molecular C_2 units as being inconsistent with a range of theoretical and experimental results in the literature. While there may be refinements to be made to the covalent defect model, it remains the most consistent with the available data in the literature.

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