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

Tadao Iwata
Nuclear Professional School, School of Engineering, The University of Tokyo, Tokai-mura, Naka-gun, Ibaraki-ken 319-1188, Japan and Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

Mitsuo Watanabe
Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken 319-1195, Japan

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In a recent paper [T. Iwata and M. Watanabe, Phys. Rev. B **81**, 014105 (2010)], we have interpreted the irradiation-induced increase in the low-temperature specific heat of neutron-irradiated graphite as due to the hindered rotation of interstitial C_2 molecules with a rotational frequency of 1.39×10^{12} s^{-1} in the periodic potential with a height of 0.040 eV, and concluded that the C_2 molecules do not form covalent bonds with atoms in the adjacent graphite layers. In their Comment [preceding paper, C. D. Latham *et al.*, Phys. Rev. B **82**, 056101 (2010)] on this paper, based on the recent first-principles theoretical calculations and related experiments, Latham *et al.* assert that self-interstitial atoms cannot exist as clusters of nearly free C_2 molecules. In this Reply, based on the experiments, we address the issues raised by Latham *et al.* in their Comment.

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In Ref. 1, the irradiation-induced increase in the low-temperature specific heat has been measured in neutron-irradiated graphite in the temperature range of 1.9–43 K. The increase of the lattice specific heat is interpreted as due to the hindered rotation of interstitial C_2 molecules in the periodic potential with a height of 0.040 eV, in which the rotational frequency is 1.39×10^{12} s^{-1}. This result shows that C_2 molecules do not form covalent bonds with atoms in the surrounding graphite layers. The reason is that, if C_2 molecules form covalent bonds with the surrounding atoms, their vibrations cannot be excited at the low temperatures of 1.9–43 K.

Latham *et al.*[2] argue that self-interstitial atoms cannot exist as clusters of nearly free C_2 molecules on the basis of the recent first-principles theoretical calculations.[3–7] They emphasize the validity of the first-principles calculations and refer to the results of the first-principles calculations which demonstrate that single interstitials and di-interstitials form strong covalent bonds with atoms in the graphite layers. As we are not familiar with the details of the first-principles calculations, we cannot judge whether the results of recent calculations on interstitials in graphite are valid or not. However, our assertion that interstitial atoms and C_2 molecules do not form covalent bonds with atoms in the layers is based on the low-temperature irradiation experiments as follows.[1]

Irradiation of energetic particles, in particular electron irradiation of ~1 MeV, to solids at low temperatures can produce isolated single interstitial atoms and single vacancies at low concentrations of less than 100 ppm. As stated in Ref. 1, changes in the various physical properties have been measured in graphite during irradiation at low temperatures and during annealing after irradiation, such as electrical resistivity, Hall effect, thermal resistivity, stored energy release, and *c*-axis expansion. There are several annealing stages below room temperature and about a half of the changes in the physical properties are recovered upon warming up to room temperature. For the annealing stages below 180 K, assigned are the activation energies ranging from 0.027 to 0.40 eV. Then, the volume expansion by an interstitial atom is estimated to be about 3 atomic volume. In order to explain these low-temperature annealing results and volume expansion, we assume that the interstitial atom does not form covalent bonds with atoms in the graphite layers and that their interaction potential consists of a repulsive term and an attractive van der Waals term; it is called the noncovalent bond model of interstitials. Semiempirical calculations on this model estimate that the migration energy of single interstitial atom is 0.02 ± 0.01 eV. Such a low migration energy suggests that single interstitial atoms can migrate at low temperatures far below room temperature and that the observed low-temperature annealing processes are caused by the interaction of migrating interstitials with other interstitials and immobile vacancies, although the details of defect reactions in the respective annealing stages are not clear. Then, the calculations show the large outward expansion of adjacent layers around the interstitial atoms. The volume expansion by an interstitial atom calculated on this model is about 3.3 atomic volume, which agrees with the above experimental one.

On the other hand, it seems that the first-principles calculations have not yet proposed a plausible and reasonable explanation on the low-temperature annealing processes and the volume expansion by interstitial atoms. It is suggested that local defect rearrangement and/or basal dislocation motion could be responsible for the observed low-temperature annealing processes[6] and that the buckling of the layers induced by basal dislocations and interstitial defects can account for the observed volume expansion.[7] However, the first-principles calculations have not yet been performed on these issues.

Latham *et al.*[2] have stated that there is longstanding empirical evidence against mobile C_2 units and referred to two papers of Brown *et al.*[8] and Reynolds and Thrower.[9] Kelly and Mayer irradiated boron-doped graphite crystals with reactor neutrons at 650 or 900 °C and studied the number and size of the interstitial loops by electron microscopy as a function of boron content.[10] Brown *et al.* proposed a model of nucleation and growth of these interstitial loops, in which they assumed that di-interstitials (i.e., C_2 units) are immobile as loop nuclei.[8] The model predicts that the loop density is proportional to the square root of boron concentration and that the loop radius is inversely proportional to the sixth root of boron concentration. In their model, however, the statement that di-interstitials are immobile is not a result of the model analysis but an assumption of the model. On the other hand, Reynolds and Thrower also studied the sizes and densities of the defects in graphite neutron-irradiated between 150 and 1200 °C by electron microscopy.[9] They developed a radiation damage model, in which there are small mobile groups of interstitials with an activation energy of motion of 1.2 eV in the presence of the radiation. This is inconsistent with the immobile di-interstitial model of Brown *et al.* Further, in these models, nothing has been stated on the bonding among atoms in the interstitial loops or small groups of interstitials. In spite of these longstanding extensive electron microscopic studies, the mechanism of radiation damage above room temperature is not clear.

Based on the first-principles calculations, Ewels *et al.*[4] proposed a model that Wigner energy release around 200 °C is caused by recombination of close Frenkel pairs (termed intimate Frenkel pairs): It is implicitly assumed that the majority of defects produced by neutron irradiation around room temperature are close Frenkel pairs. However, if we consider the formation of Frenkel pairs on the covalent bond model of interstitials, the proportion of close Frenkel pairs in all the defects produced by irradiation may not be so large: the reason is as follows. We infer the dynamic displacement of atoms at the end of displacement cascades from a static event in the energy diagram (Fig. 3 of Ref. 4) calculated by the first principles. Then, a close Frenkel pair is formed only when the kinetic energy of a displaced atom is between 12.1 (=10.8+1.3) eV and 13.7 eV (i.e., formation energy of a separated Frenkel pair): When the energy is between 13.7 eV and 25.8 (=13.7+12.1) eV, a separated Frenkel pair is formed. As atomic collisions in these energy range are isotropic, the concentration ratio of close Frenkel pairs to separated Frenkel pairs produced at the ends of atomic displacement cascades is (13.7−12.1) to (25.8−13.7)=1.6 to 12.1. Further, in the whole of atomic displacements caused by neutron irradiation the proportion of close Frenkel pairs may be much smaller, probably less than several percent. If single interstitial atoms are mobile around room temperature, they can migrate toward single vacancies to form close Frenkel pairs. However, the first-principles calculations estimate the migration energy of single interstitial atom to be >1.5 eV (Ref. 5) and 1.0 eV,[6] which means that single interstitial atoms cannot migrate to form closed Frenkel pairs around room temperature.

We also have proposed a model of radiation damage in graphite on the noncovalent bond model of interstitials as follows.[11] (i) Single interstitial atoms and interstitial C_2 molecules are mobile below room temperature, while single vacancies become mobile above 1000 °C. (ii) Single vacancies and loose clusters of interstitial C_2 molecules, $(C_2)_n$, are formed during irradiation around room temperature, in which the thermal stability of the clusters increases with the number n of molecules. These things are supported by the low-temperature annealing experiments, the increase in the lattice and electronic specific heat, volume changes, stored energy release, changes in the thermal conductivity, positron lifetimes, etc.[1] (iii) Wigner energy release around 200 °C and above is triggered by the breakup of interstitial $(C_2)_n$ clusters into component C_2 molecules and their subsequent recombination with immobile single vacancies,

$$(C_2)_n \rightarrow (C_2)_{n-1} + C_2 \quad (n = 2,3,4,\ldots), \tag{1}$$

$$C_2 + 2V \rightarrow \mathit{annihilation}, \tag{2}$$

where V means vacancy. The description of energy release is generally formulated using the Arrhenius equation,

$$\frac{dN(T,t)}{dt} = -fN(T,t)^{\gamma}\exp\left(-\frac{E}{kT}\right), \tag{3}$$

where $N(T,t)$ represents the defect concentration at the temperature T and the time t, f is the frequency factor, γ is the order of the reaction, E is the activation energy, and k is the Boltzmann constant. Examples of Wigner energy release are shown in Fig. 1 of Ref. 1. The curve for the neutron fluence of 3×10^{19} n/cm^2 has a well-known peak of energy release around 200 °C. However, the peak is too broad to be described by Eq. (3). In the case of the low-fluence irradiation of 4×10^{17} n/cm^2, we found that the peak consists of three subpeaks.[12] A kinetic analysis of the subpeaks gives γ=1. Then,

$$\text{for} \quad \gamma = 1, \quad \text{we put} \quad f = \frac{\nu}{n_j}, \tag{4}$$

where ν is the frequency of lattice vibrations dominant at T and n_j is the number of jumps required for the defect to cause the reaction. If we assume $\nu \approx 2\times kT/h \approx 4\times10^{10}T$ (s^{-1}) for graphite,[13,14] where h is the Planck constant, we have $n_j \approx 1$. The result of γ=1 and $n_j \approx 1$ suggests that the reaction of Eq. (1) is a rate-determining process and that the reaction of Eq. (2) is too fast to be detected in the experiments. The activation energies 1.34, 1.50, and 1.78 eV are deduced for the respective subpeaks and they are assumed to be the breakup energies of $(C_2)_n$ clusters in the reactions for n=2, 3, and 4 of Eq. (1), respectively. In the reaction of Eq. (2), both the migration energy of C_2 molecules and the barrier energy of recombination of C_2 molecules and vacancies may be much smaller than the energies for the reactions of Eq. (1). The reaction of each subpeak is not a single process with a unique activation energy but a process distributed in activation energy by the presence of the annealing defects themselves,[12] i.e., the disturbance is a function of the defect concentration. When the neutron fluence is increased, the defect concentration and the size of $(C_2)_n$ clusters are increased. Then, as the activation energy distributions become broad, several broadened subpeaks are merged into a large and broad peak around 200 °C as in the case of 3×10^{19} n/cm^2.

Latham *et al.*[2] note the recent first-principles calculations by Ma,[15] which confirm covalent bonding between the self-interstitials and atoms in the layers. However, we are rather astonished at Ma's calculations such that single interstitial atoms could migrate with the barrier energy less than 0.5 eV along the *a* axis, because it is very different from the result (>1.5 eV) calculated from the first principles by Li *et al.*[5] It seems that the present first-principles calculations on interstitials give different results depending on how to treat the van der Waals force, the size of model crystals, fixing of the lattice constants, fixing of atoms to block basal slip, selection of the migration path, etc.

Martin and Henson[16] measured the small angle neutron scattering (SANS) in neutron-irradiated graphite and analyzed the SANS result by taking account of the relaxation of the neighboring atoms around interstitial clusters: the relaxation was calculated on the noncovalent bond model of interstitials.[11,17] Latham *et al.*[2] disagree with this analysis and insist that the SANS result should be explained as due to local, long wavelength variations in the interlayer distance as might occur if the layers buckled or folded. We cannot judge which is better until the first-principles calculations can explain the SANS result quantitatively.

We stated in Ref. 1 that single vacancies are immobile below 1000 °C. Against this, Latham *et al.*,[2] citing two papers by Paredes *et al.*[18] and Lee *et al.*,[19] assert that single vacancies are mobile defects at room temperature. Through scanning tunneling microscopy observation of vacancy-decorated graphite surfaces, Paredes *et al.* deduced that the activation energy for migration of the single vacancy is $\sim 0.9-1.0$ eV.[18] Then, Lee *et al.* investigated vacancy defects in graphene layers by tight-binding molecular dynamics simulations and by first-principles calculations and found that the migration energy of single vacancy is 0.94–1.01 eV.[19] However, the vacancy migration in the graphite surfaces and graphene layers is not necessarily identical to that in the bulk of graphite. As shortly stated in Ref. 1, we found a positron lifetime of 245 ps in graphite samples neutron-irradiated around 60 °C and 800 °C, and identified it as the lifetime of positrons trapped at single vacancies on the basis of the considerations of vacancy production by irradiation and the first-principles calculations.[1,20,21] The 245 ps defects are annealed out between 1000 and 1400 °C by the isochronal annealing for 30 min at 100 °C intervals and divacancy formation is not observed there.[20] A preliminary kinetic analysis using Eqs. (3) and (4) gives that $\gamma=1$, $E=2.0\pm0.1$ eV, and $n_j\approx 1\times10^{10}$, if we assume $\nu=5\times10^{13}$ s^{-1}.[22] This means that single vacancies migrate to sinks with the migration energy of 2.0 eV and by $\approx 1\times10^{10}$ jumps. The sinks may be grain boundaries and interstitial loops. The energy of 2.0 eV agrees approximately with the calculated migration energy of single vacancy from the first principles, 1.7 eV.[23]

In Ref. 1 we explained the irradiation-induced increase in the specific heat as due to the hindered rotation of interstitial C_2 molecules. The first-excited rotational level is 5.8 meV above the ground state and the rotational frequency is 1.39×10^{12} s^{-1}. For explanation of the specific heat increase, Latham *et al.*[2] propose three other possibilities: (i) enhancement 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, (ii) bridging defects pinning two layers together, and (iii) reduction of the interlayer shear constant C_{44} by rotation and buckling of layers. In our experiment, the increase of specific heat at 12 K amounts to 100% of the specific heat of unirradiated graphite (Fig. 2 of Ref. 1). We consider the lattice vibrations of graphite in terms of the Komatsu-Nagamiya model.[14] First, the E_{2g} phonon mode belongs to the in-plane (transverse and longitudinal) modes. The contribution of the in-plane modes to the specific heat at 12 K is about 11% of the specific heat of unirradiated graphite. Therefore, in order to increase the specific heat at 12 K by 100%, it is necessary to multiply the phonon density of states of the in-plane modes about ten times. It is impossible. Second, we consider the vibrations of covalently bonded carbon atoms. In the infrared and Raman spectra of polyatomic molecules, the bond-stretching vibrations and the bond-bending vibrations of carbon-carbon covalent bonds have been observed in the region of the wave numbers above 200 cm^{-1}, i.e., the vibrational frequencies above 6×10^{12} s^{-1} (Ref. 24). These vibrations can hardly be excited at low temperatures below 30 K, so that their contribution to the specific heat is negligibly small there. Based on these experimental results, we judge that bridging defects as well as other interstitial models proposed from the first-principles calculations cannot cause the increase in the specific heat observed in our experiment. Third, we consider the change in C_{44} by neutron irradiation. The C_{44} value of unirradiated graphite has been deduced from analyses of the neutron scattering[22] and the specific heat[14] to be $0.46(\pm0.02)\times10^{11}$ and 0.425×10^{11} dyn/cm^2, respectively. The C_{44} has also been determined by ultrasonic, sonic resonance, and static test methods to be $0.018-0.035\times10^{11}$ dyn/cm^2 for the compression-annealed pyrolytic graphite (CAPG) (Ref. 25) and $0.04-0.17\times10^{11}$ dyn/cm^2 for the single crystals.[26] It is considered that the C_{44} deduced from the neutron scattering and the specific heat is intrinsic to graphite. The latter C_{44} determined from the mechanical methods has a spread in values and is much lower than the intrinsic C_{44}, which has generally been attributed to differences in the distribution of mobile basal dislocations. Actually, our specimens became difficult to cleave after irradiation, because the dislocations were pinned by irradiation-produced defects. Seldin and Nezbeda[26] irradiated CAPG and single-crystal specimens with neutrons up to the fluence of 7.1×10^{18} n/cm^2 at 50 °C. Then, the mechanical C_{44} increased rapidly with irradiation and approached a value equal to or greater than 0.40×10^{11} dyn/cm^2, i.e., the intrinsic C_{44}. The elastic compliances $1/S_{11}, S_{12}$, and S_{13} were essentially unchanged after irradiation. In contradiction to each other, C_{33} showed a slight decrease, and $1/S_{33}$ showed an apparent increase after irradiation. From Seldin and Nezbeda's experiments, we infer that in our specimens the intrinsic C_{44} related to the specific heat is not changed so much by irradiation, while the mechanical C_{44} is increased toward the intrinsic C_{44}. Even if the intrinsic C_{44} is decreased, the decrease may be as small as about 10%. When the intrinsic C_{44} is decreased by 10%, the calculated increase in the specific heat at 12 K by the Komatsu-Nagamiya model[14] is about 3% of the specific heat of unirradiated graphite. Further, even if we can put $C_{44}=0$ by neglecting the lattice being destroyed, the calculated increase at 12 K is about 43% of the specific heat of unirradiated graphite, which is less than the observed increase of 100%. Thus, the three possibilities proposed by Latham *et al.* cannot explain the present increase in the specific heat.

We discussed the formation energies of a Frenkel pair, a single interstitial atom, and a single vacancy in detail in Ref. 1. Then, we remarked that, if the formation energy of a single interstitial atom is 5.4 ± 0.1 eV as is given by first-principles calculations,[5,6] we can expect to detect the formation of single interstitial atoms at high temperatures around 3000 °C. However, we cannot find any sign of interstitial atoms in the measurement of specific heat up to 3650 °C (Ref. 27) and in the quenching experiment from 3100 °C.[28] For this statement, Latham *et al.*[2] pointed 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.[4] In radiation damage, interstitial atoms are produced together with vacancies by atomic collisions. In thermal equilibrium, however, the formation of interstitial atoms is independent of that of vacancies. The formation of single interstitial atoms in thermal equilibrium is governed not by the formation energy of a Frenkel pair but by that of a single interstitial atom.

At present, we believe that the irradiation-induced increase in the specific heat of graphite is caused by the hindered rotation of interstitial C_2 molecules, which do not form covalent bonds with atoms in the surrounding graphite layers. However, if the first-principles calculations can propose a more appropriate interpretation, we will admit it.

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