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

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Irradiation-induced increase in the low-temperature specific heat has been measured in the temperature range of 1.9–43 K in graphite neutron-irradiated to 1.4×10^{20} n/cm^2 ($E>1$ MeV) around 333 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 of $V(\varphi)=(V_0/2)(1+\cos 2\varphi)$, where φ is the angle of rotation and V_0 is 0.040 eV. The first-excited rotational level is 0.0058 eV above the ground state and 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. It is in marked contrast with the result of recent first-principles theoretical calculations that interstitial atoms form strong covalent bonds with atoms in the graphite layers. The concentration of C_2 molecules is estimated to be $f=1.16\%$. The hole concentration, deduced from the electronic specific heat and the SWMcC band model, suggests that one single vacancy creates one hole and the single vacancy concentration is $2f$. Since the measurement of the lattice specific heat gave the concentration of the defects directly, we could evaluate some physical properties for a unit concentration of the defects. The volume changes by a single interstitial atom, an interstitial C_2 molecule, and a single vacancy are deduced to be 2.6 ± 0.3, 9.3 ± 1.4, and -0.46 ± 0.07 atomic volumes, respectively. The formation energy of a Frenkel pair is estimated to be 12.6 ± 2.5 eV. The phonon scattering with a reciprocal relaxation time proportional to $\omega^{1.5}$, where ω is the angular frequency of phonons, is attributed to the scattering of phonons by the disklike strain around interstitial C_2 molecule clusters. A broad dip in the a-axis thermal conductivity observed below room temperature is attributed to the resonance scattering of phonons by the hindered rotation of interstitial C_2 molecules as well as by the vibration of these molecules as rigid units. The positron lifetime of 350 ps is suggested to be the lifetime of positrons trapped in an open space on the periphery of the interstitial clusters of C_2 molecules. The well-known Wigner energy is stored mainly as interstitial C_2 molecules and single vacancies.

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I. INTRODUCTION

Irradiation of energetic particles to solids produces a cascade of atomic displacements in the crystal lattice. As a result, interstitial atoms, vacancies, and their complexes are formed. In particular, single interstitial atoms are produced by irradiation with electrons of ~1 MeV and reactor neutrons at low temperatures so that the produced interstitial atoms can be frozen in some isolated states and therefore they cannot migrate in the crystal lattice nor react with other defects.

In order to obtain information on single interstitial atoms in graphite, many electron or neutron irradiations have been performed at liquid helium and nitrogen temperatures, where the concentration of produced defects is low, usually less than 100 ppm. Changes in the various physical properties have been measured during irradiation at low temperatures and during thermal annealing after irradiation, such as electrical resistivity,[1–8] Hall effect,[2] thermal resistivity,[9,10] stored energy release,[11,12] and c-axis expansion.[13,14] 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.[5–7,11,15,16] Then, the volume expansion by an interstitial atom is estimated to be about 3 atomic volume.[14,16]

Two models have been proposed for describing an interstitial atom in graphite. One is the noncovalent bond model.[17–22] The model assumes that the interstitial atom does not form covalent bonds with atoms in the adjacent graphite layers and that their interaction potential consists of a repulsive term and an attractive van der Waals term. Semiempirical calculations on this model estimate that the migration energy of single interstitial atom is 0.02 ± 0.01 eV.[18–22] 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 recoveries are caused by the interaction of migrating interstitials with other interstitials and vacancies. Then, the calculations show the large outward expansion of adjacent layers around the interstitial atoms.[18–22] The calculated volume expansion by an interstitial atom is about 3.3 atomic volume,[21,22] which agrees with the above experimental one.

Second is the covalent bond model, which assumes that the interstitial atom forms covalent bonds with atoms in the adjacent graphite layers.[23–31] In particular, recent first-principles theoretical calculations give strong support to the model.[28–31] The calculated migration energies are >1.5 eV (Ref. 30) and 1.0 eV,[31] which show that the single interstitial atoms cannot migrate at low temperatures below room temperature. The covalent bond model considers that local defect rearrangements and/or basal dislocation motion could be responsible for the observed low-temperature annealing processes.[31] Then, first-principles calculations estimate that the volume change by the interstitial atom (in spiro-configuration) is actually negative.[30,31] However, Telling and Heggie suggested the possibility that a shear force associated with the spiro-interstitial atom would, if allowed to act in concert with other interstitials, generate areas of stacking fault that would locally increase the *c*-axis lattice spacing.[31]

Concerning whether the interstitials form covalent bonds with atoms in the layers or not, we notice the energy release around 473 K in neutron-irradiated graphite, known as the Wigner energy release.[32] It is practically important because the Windscale reactor accident in 1957 has been considered to be due to the sudden release of the stored energy in the moderator graphite. On the noncovalent bond model, we proposed an interpretation[19] such that (i) loose clusters of interstitial C_2 molecules, $(C_2)_n$, are formed during irradiation around room temperature, in which the stability of the clusters increases with the number n of molecules, and (ii) the energy release is triggered by the breakup of interstitial C_2 clusters into component C_2 molecules and their subsequent recombination with immobile vacancies. The energy release around 473 K can be described by the first-order kinetics with the activation energy of 1.34 eV.[33] An empirical calculation shows that the energy required to break up $(C_2)_2$ clusters is about 1.3 eV,[19] which agrees with the experimental value of 1.34 eV. On the other hand, on the covalent bond model, the first-principles calculation gives 1.3 eV as the energy required for the recombination of close interstitial-vacancy (I-V) pair (termed the intimate Frenkel pair):[29] this result also agrees with the above experimental value of 1.34 eV. Thus, on the covalent bond model, the energy release is attributed to the recombination of the intimate I-V pairs, which are formed during irradiation at the ambient temperature.

The mechanisms for the low-temperature annealing recoveries, the volume expansion, and the Wigner energy release have been studied for long on the two models.[31,34] However, there is still no direct experimental evidence to judge between the two models, that is, to judge whether interstitial atoms and their aggregates form covalent bonds with atoms in the adjacent layers or not.

In the infrared and Raman spectra of polyatomic molecules, the bond-stretching vibrations and the bond-bending vibrations of carbon-carbon covalent bonds are usually observed in the region of the wave numbers above 200 cm^{-1}, i.e., the vibrational frequencies above $6 \times 10^{12}\ \text{s}^{-1}$ (Ref. 35). These vibrations can hardly be excited at low temperatures below 30 K, where the fraction of excited vibrations which can contribute to the specific heat is less than 1%, so that their contribution to the specific heat is negligibly small there. Therefore, if the increase in the specific heat is observed at such low temperatures in irradiated graphite, there is a possibility that some defects produced by irradiation form weak noncovalent bonds with other atoms.

The increase in the specific heat of neutron-irradiated graphite had been found 5 decades ago in the temperature ranges from 13 to 300 K,[36] from 20 to 80 K,[37] and from 1.7 to 16 K.[38] Samples were polycrystalline graphite of the reactor grade. The increase was supposed as due to low-frequency vibrations of interstitial atoms and/or clusters of atoms such as C_2 molecules: it is implicitly assumed that interstitial atoms and clusters do not form covalent bonds with atoms in the adjacent layers. The increase in the specific heat at low temperatures favors the noncovalent bond model, however, further quantitative analyses have not yet been made.

In this paper, we report a detailed measurement of the specific heat in neutron-irradiated graphite in the temperature range from 1.9 to 43 K. The observed increase of the lattice specific heat is well explained by assuming the hindered rotation of interstitial C_2 molecules in a periodic potential with a height of 0.040 eV, in which the first-excited rotational state is 5.8 meV above the ground state and gives the rotational frequency of $1.39 \times 10^{12}\ \text{s}^{-1}$. This result strongly suggests that C_2 molecules exist and they do not form covalent bonds with atoms in the adjacent layers. Then, a further analysis suggests that C_2 molecules have gathered into clusters in which C_2 molecules are loosely coupled with each other and are performing a weakly coupled rotation.

The electronic specific heat also is increased by irradiation: it is considered to be due to irradiation-produced vacancies. From the electronic specific heat and using a model of the band structure, we obtain the hole concentration, which is compared to the estimated concentration of single vacancies. It is suggested that one single vacancy creates one hole.

Measurement of the lattice specific heat gives directly the concentration of vibrating defects. Accordingly, if we measure other physical properties on the present sample, we can discuss the physical properties for a unit concentration of defects. We have measured the dimensional changes, stored energy release, thermal conductivity, and so on. From these and using other available data, we deduce (i) the volume changes by a single interstitial atom, an interstitial C_2 molecule, and a single vacancy, (ii) the formation energy of a Frenkel pair, and (iii) information on the phonon scattering by interstitial C_2 molecules.

The present results are consistent with the noncovalent bond model of interstitial atoms and C_2 molecules. The well-known Wigner energy is stored mainly as interstitial C_2 molecules and single vacancies.

II. EXPERIMENT

Samples used for the specific heat measurement are pyrolytic graphite heat-treated at 3273 K for 4 h in Freon gas. The samples have high crystallinity as compared to those used in the previous reports.[36–38] Neutron irradiation was performed up to the fluence of $1.4 \times 10^{20}\ \text{n/cm}^2$ ($E > 1$ MeV) at about 333 K in the JAERI JRR-2 reactor at Tokai. The displacement per atom (DPA) is estimated to be 0.12.[39]

The stored energy release of this sample is shown in Fig. 1. The released energy integrated between 373 and 873 K amounts to about 450 J/g. The stored energy release for the lower fluence irradiations[33] and the specific heat for unirradiated sample[40] are also shown in Fig. 1 for reference. In the case of $4 \times 10^{17}\ \text{n/cm}^2$, the 473 K peak consists of three subpeaks and the activation energies of the respective subpeaks are 1.34, 1.50, and 1.78 eV.[33]

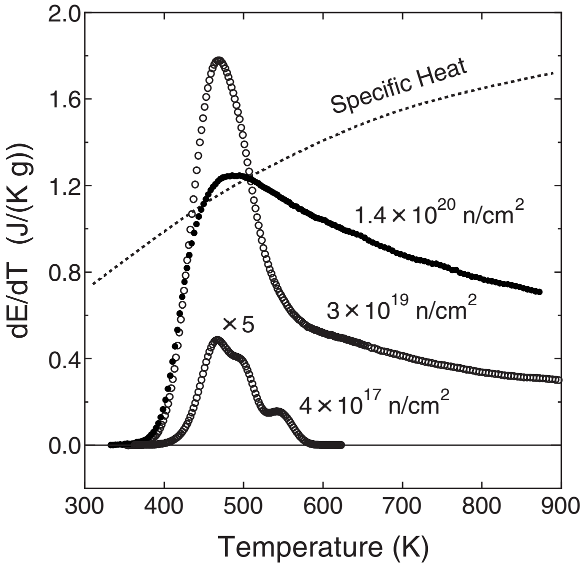


FIG. 1. Stored energy release in graphite neutron-irradiated at around 333 K. The heating rate is 5 K/min. The curve for 4×10^{17} n/cm^2 has been magnified by a factor of 5. The specific heat of unirradiated graphite is shown for comparison in the same unit.

The specific heat measurements between 1.9 and 43 K have been carried out by a standard adiabatic method. Unirradiated samples are three pieces of $19.5 \times 19.5 \times 8.5$ or 11.5 mm^3, 27.01 g in total weight, and irradiated samples are two pieces of $19.3 \times 19.3 \times 12.8$ mm^3, 19.62 g in total weight. Samples are stuck on a thin sapphire plate equipped with thermometers and a heater. The cryostat is the same as used in our previous experiments: it has a thermal switch and is prevented from entering of mechanical vibrations.[41]

Two types of highly oriented pyrolytic graphite (HOPG) samples, i.e., ZYA-grade [mosaic spread (full width at half maximum, FWHM): about 0.4°] and ZYH-grade [mosaic spread (FWHM): about 3.5°], were simultaneously irradiated with neutrons together with the above pyrolytic graphite samples under the same condition. The first HOPG samples were used to measure the thermal conductivity,[42] optical reflectivity and photoemission,[43] and positron lifetimes.[44–47] The thermal conductivity is reduced by 3 orders of magnitude below 100 K and by 2 orders of magnitude at 300 K.[42] Optical reflectivity measurements show that a small absorption band is produced around 3 eV, which is ascribed to single vacancies.[43] The positron lifetime is increased up to 350 ps.[44] Then, the second HOPG samples were used to measure the dimensional changes. The dimensional changes are on the average about 12% expansion along the *c* direction and about 1% shrinkage along the *a* direction.

TABLE I. Polynomial fitting of experimental ΔC_p data in J/(K mol). $\Delta C_p = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5 + a_6 T^6 + a_7 T^7$, where T is the temperature in K and coefficients a_i are given below.

T (K)	1.9–4.7	4.7–15.8	15.8–43
a_0	2.2970421×10^{-3}	2.3786586×10^{-3}	4.7988310×10^{-2}
a_1	1.9866223×10^{-3}	$-7.8447282 \times 10^{-5}$	$-1.2904128 \times 10^{-2}$
a_2	$-2.6255937 \times 10^{-3}$	3.6863447×10^{-5}	1.5222641×10^{-3}
a_3	1.5099026×10^{-3}	2.4967082×10^{-5}	$-7.3659318 \times 10^{-5}$
a_4	$-4.5358249 \times 10^{-4}$	$-3.0095422 \times 10^{-6}$	1.9977123×10^{-6}
a_5	7.8177120×10^{-5}	2.0017771×10^{-7}	$-3.1729248 \times 10^{-8}$
a_6	$-7.2763567 \times 10^{-6}$	$-7.3787927 \times 10^{-9}$	$2.7810199 \times 10^{-10}$
a_7	2.8438336×10^{-7}	$1.1120702 \times 10^{-10}$	$-1.0447414 \times 10^{-12}$

III. RESULTS

Figure 2 shows the specific heat C_p of the irradiated and the unirradiated graphite samples plotted as a function of temperature T. Data for the unirradiated samples agree with the previously evaluated specific heat data for single-crystal graphite within 1%.[40] The difference in C_p between the irradiated and the unirradiated samples, $\Delta C_p = C_p(irr) - C_p(unirr)$, has been fitted by a curve of polynomials: the result is given in Table I.

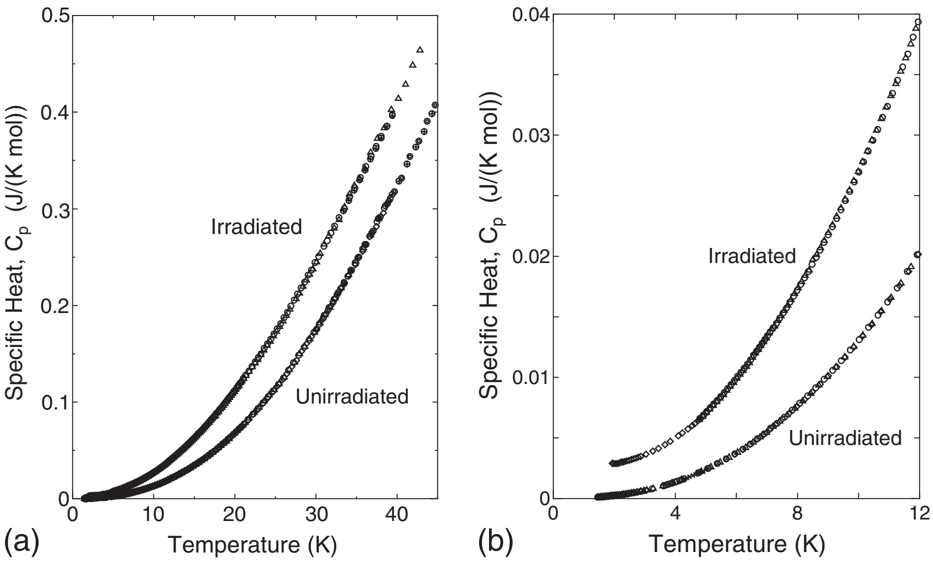


FIG. 2. Specific heat of irradiated and unirradiated graphite below 45 K. Neutrons were irradiated at around 333 K to 1.4×10^{20} n/cm^2($E > 1$ MeV). (b) is an enlarged figure of (a) below 12 K.

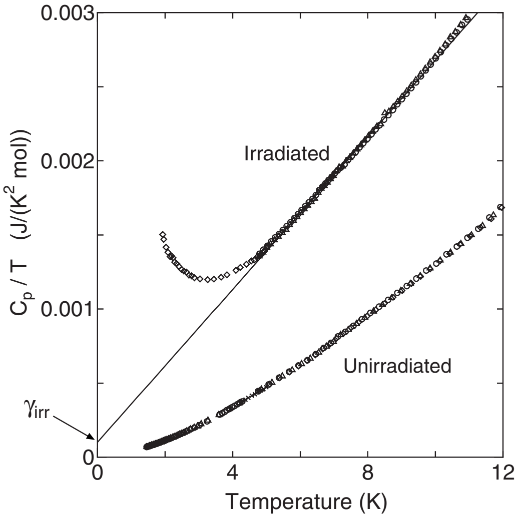


FIG. 3. C_p/T vs T for irradiated and unirradiated graphite. $\gamma_{irr}T$ is assumed to be the electronic specific heat.

In Fig. 3, the specific heat divided by temperature, C_p/T, of both samples is plotted as a function of temperature T. The C_p/T for the irradiated sample increases above an anticipated straight line with decreasing temperature below 4.5 K. Such an anomaly in the specific heat has been found in soft carbons and neutron-irradiated polycrystalline graphite below 4.5 K and considered as due to localized electronic spins.[48–51] This anomaly is not considered here.

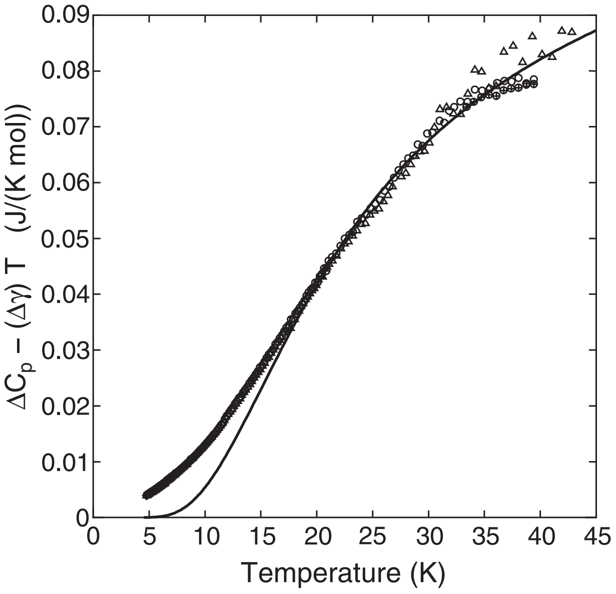


FIG. 4. Increased lattice specific heat as a function of temperature in neutron-irradiated graphite. The contribution of the electronic specific heat is subtracted. Solid line is the calculated specific heat caused by the hindered rotation of interstitial C_2 molecules.

The linear electronic term in the specific heat is due to the conduction electrons, which is γT. To estimate γ for the irradiated sample, γ_{irr}, we assume that the lattice specific heat is proportional to T^n, i.e., $C_p = \gamma T + \text{const} \times T^n$. Best fitting of this equation to the data between 5.5 and 9.5 K is given for $n=2.0$ and then we get

$$\gamma_{irr} = 100.6 \pm 8 \quad \mu\text{J}/(\text{K}^2\ \text{mol}). \tag{1}$$

This fitting is shown in Fig. 3. As stated later, the hole concentration deduced from the value of γ_{irr} is consistent with the single vacancy concentration deduced indirectly from the analysis of the lattice specific heat. The γ for the unirradiated sample has been given as $\gamma_{unirr} = 13.8 \quad \mu\text{J}/(\text{K}^2\ \text{mol})$.[52] Thus, we have

$$\Delta\gamma = \gamma_{irr} - \gamma_{unirr} = 86.8 \pm 8 \quad \mu\text{J}/(\text{K}^2\ \text{mol}). \tag{2}$$

The increase in the electronic specific heat, $(\Delta\gamma)T$, is subtracted from ΔC_p of Table I, so that we have the increase in the lattice specific heat

$$\Delta C_p - (\Delta\gamma)T = [C_p(irr) - C_p(unirr)] - (\Delta\gamma)T. \tag{3}$$

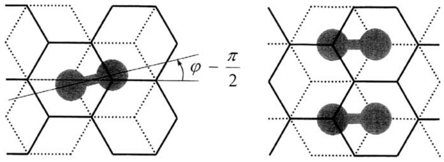
This increase is attributed to the oscillation of irradiation-produced defects. Figure 4 shows the experimental $\Delta C_p - (\Delta\gamma)T$ as a function of T.

If we assume that this increase in the lattice specific heat is caused by some kind of harmonic oscillators, the frequency of the oscillators is distributed around $1.45 \times 10^{12}\ \text{s}^{-1}$ and their concentration is about 1.2%. In the next section, we examine what type of defect oscillation can explain this frequency.

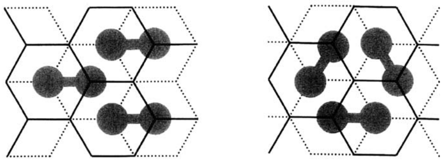
IV. ANALYSIS

Previous studies have shown that in graphite neutron-irradiated to such high fluences as in the present sample, $\sim 1 \times 10^{20}\ \text{n/cm}^2$, the disklike clusters of interstitial atoms are formed and in their surrounding neighborhood the interlayer spacing is expanded.[53–57] Bacon and Warren proposed this damage model based on the analysis of the asymmetric profile of the x-ray $(00l)$ lines.[53] The small-angle x-ray scattering by graphite irradiated at 423 K shows that the scattering centers are almost certainly interstitial clusters of disklike form, 5 to 15 Å in diameter.[54] The electron microscope observations show that the damage is visible as a dense fine speckling in material irradiated at 423 K and increases in size and separation at higher irradiation temperatures.[55,56] When the irradiation temperature is below 373 K, it is impossible to see individual defects as the whole field becomes too distorted. The relationship established between mean defect diameters and irradiation temperatures above 423 K suggests that the defect diameters for the present irradiation are distributed around 10 Å or less.[55] Then, the scattering of long-wavelength neutrons by a sample irradiated at 303 K has been measured and analyzed by taking account of the relaxation of the neighboring atoms around the interstitial clusters:[57] the relaxation is calculated on the noncovalent bond model.[18,19] It is suggested that the best estimate from the neutron-scattering experiment of the number of interstitials per cluster is 4 ± 2, with a remote possibility that this number could be as high as eight.[57] In the following, we discuss the oscillations of atoms in these interstitial clusters.

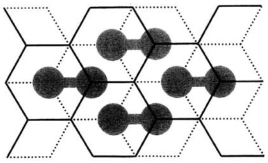
First, we assume that the interstitial cluster consists of nearly isolated atoms and that each atom vibrates in a potential of the form



Rotation of C_2 molecule (C$_2$)$_2$ cluster



(C$_2$)$_3$ cluster (1) (C$_2$)$_3$ cluster (2)



(C$_2$)$_4$ cluster

FIG. 5. Assumed configuration of interstitial C_2 molecules, $(C_2)_n$. The interatomic distance in graphite layers is 1.42 Å, while that of a C_2 molecule in free space is 1.24 Å. The graphite layers adjacent to interstitial C_2 molecules are deformed outward by the repulsive force from the C_2 molecules, while the C_2 molecules are held together by the deformed layers.

$$V(x) = \frac{V_0}{2}\left(1 - \cos\frac{\pi x}{a_0}\right), \tag{4}$$

where x is the coordinate of an interstitial atom, a_0 is the distance from the equilibrium point to the saddle point along the diffusion path, and V_0 is the potential height at the saddle point (for the diffusion path, see Refs. 18–21). When the energy of the atom is smaller than V_0, the potential can be regarded as parabolic in the neighborhood of the minimum and the energy levels will be those of a harmonic oscillator. Then, the vibrational frequency of the atom, ν, is given by

$$2\pi\nu = \sqrt{\frac{\pi^2 V_0}{2ma_0^2}}, \tag{5}$$

where m is the mass of C atom. If we put a_0=0.71 Å, we have V_0=0.0106 eV for $\nu = 1.45\times 10^{12}$ s^{-1}. The value of V_0 agrees with the calculated values of the migration energy of interstitial atom, 0.02 ± 0.01 eV, on the noncovalent bond model.[18–22] If the interstitial atom vibrates with this frequency in this potential, as V_0 is so low, it can easily climb over the potential at room temperature and migrate out of the cluster or combine with another atom to form a C_2 molecule in the cluster. Therefore, the single interstitial atoms are not relevant to the specific heat increase.

Second, we assume that the interstitial cluster consists of nearly isolated C_2 molecules and that each molecule vibrates as a single mass point of mass $2m$ in the potential of Eq. (4). If we substitute $2m$ into m of Eq. (5) and put a_0=0.71 Å, we obtain V_0=0.021 eV for $\nu = 1.45\times 10^{12}$ s^{-1}. This value of V_0 is compared to an estimation of the migration energy of interstitial C_2 molecule, i.e., 0.05 eV, on the noncovalent bond model.[19] In this case also, if the interstitial C_2 molecules vibrate as rigid units with this frequency, as V_0 is so low, they are not stable at room temperature and migrate out of the clusters.

We have considered on the noncovalent bond model that the interstitial clusters of C_2 molecules, $(C_2)_n$, are held together by the adjacent layers which are deformed outward, so that the clusters are stable at room temperature.[19] Then, the C_2 molecules may vibrate with a much higher frequency than the above ν value in the potential of a much higher V_0. The energy required to decompose a $(C_2)_2$ cluster to two C_2 molecules has been calculated to be about 1.3 eV.[19] Accordingly, we may suppose that V_0 is about 1.3 eV. If we assume that each C_2 molecule in the $(C_2)_n$ cluster vibrates as a single mass point in the potential of Eq. (4) with V_0=1.3 eV, its vibrational frequency is 1.14×10^{13} s^{-1} from Eq. (5). However, the vibration of this frequency can hardly be excited below 60 K. Therefore, if this description of $(C_2)_n$ clusters is valid, the vibration of C_2 molecules as rigid units may not be relevant to the present specific heat increase below 43 K. Of course, the contribution of the bond-stretching vibrations of C_2 molecules to the specific heat is negligibly small below room temperature.[58]

Lastly, the most favorable candidate responsible for the increase in the low-temperature lattice specific heat is the hindered rotation of interstitial C_2 molecules. Assumed configurations of $(C_2)_n$ clusters are shown in Fig. 5.

We assume that each C_2 molecule rotates as a rigid rotator independently from other C_2 molecules in a periodic potential of the form

$$V(\varphi) = \frac{V_0}{2}(1 + \cos 2\varphi), \tag{6}$$

where φ is the angle of rotation as shown in Fig. 5. The wave equation for this system is[59]

$$\frac{d^2\Psi(\varphi)}{d\varphi^2} + \frac{8\pi^2 I}{h^2}[E - V(\varphi)]\Psi(\varphi) = 0, \tag{7}$$

where h is the Planck constant, I is the moment of inertia of a C_2 molecule about the axis of rotation, $I=(m/2)r^2$, and r is the distance between two C atoms, 1.2425 Å.[58]

For $E \ll V_0$, Eq. (7) becomes the wave equation for a harmonic oscillator around $\varphi=\pi/2$. Then, the energy levels are given by

$$E \simeq \left(n + \frac{1}{2}\right)h\nu, \quad (n = 0,1,2,3,\ldots),$$

$$\nu \simeq \frac{1}{2\pi}\sqrt{\frac{2V_0}{I}}.$$

When $\nu = 1.45\times 10^{12}$ s^{-1}, we have $V_0 \simeq 0.04$ eV. This value of V_0 is physically acceptable for the rotation of a C_2 molecule in the interstitial $(C_2)_n$ clusters. Thus, we consider that the present specific heat increase is caused by the hindered rotation of C_2 molecules in the potential of Eq. (6) with V_0 of about 0.04 eV.

TABLE II. Energy eigenvalues, $E_a(i)$ and $E_b(j)$, of the wave equation Eq. (7) for the potential of Eq. (6) with V_0=0.040 eV, which are associated with the even and the odd Mathieu functions, respectively.

i	$E_a(i)$ (eV)	j	$E_b(j)$ (eV)
0	0.002941		
1	0.008702	1	0.002941
2	0.014215	2	0.008702
3	0.019459	3	0.014215
4	0.02441	4	0.019459
5	0.02902	5	0.02441
6	0.03320	6	0.02903
7	0.03672	7	0.03328
8	0.03935	8	0.03718
9	0.04176	9	0.04091
10	0.04499	10	0.04481
11	0.04916	11	0.04914
12	0.05400	12	0.05399
13	0.05938	13	0.05938
14	0.06527	14	0.06527
15	0.07166	15	0.07166

Next, we calculate the exact energy eigenvalues of Eq. (7). Making the substitution

$$\theta = \frac{2\pi^2 I V_0}{h^2} \quad \text{and} \quad a = \frac{8\pi^2 I}{h^2}\left(E - \frac{V_0}{2}\right), \tag{8}$$

Eq. (7) reduces to Mathieu's differential equation

$$\frac{d^2\Psi(\varphi)}{d\varphi^2} + (a - 2\theta \cos 2\varphi)\Psi(\varphi) = 0. \tag{9}$$

The eigenvalues a of the Mathieu equation are tabulated for values of θ in Ref. 60.

We have chosen V_0=0.040 eV (i.e., θ=44.22) so that the calculated values of the specific heat may be best fitted to the experimental values. The eigenvalues for θ=44.22 were calculated by the interpolation of the tabulated values. The energy levels thus obtained for V_0=0.040 eV are given in Table II. The first-excited rotational state is 5.76 meV above the ground state and gives the rotational frequency of 1.393×10^{12} s^{-1}.

The increase in the specific heat due to the rotational vibration, ΔC, is calculated as follows:

$$\Delta C = f N_A k T \frac{d^2}{dT^2}(T \ln Z), \tag{10}$$

$$Z = \sum_{i=0} \exp[-E_a(i)/kT] + \sum_{j=1} \exp[-E_b(j)/kT], \tag{11}$$

where N_A is the Avogadro number, f is the concentration of C_2 molecules, fN_A is the number of C_2 molecules per mol, and k is the Boltzmann constant. $E_a(i)$ and $E_b(j)$ are the energy levels and associated with the even and the odd Mathieu functions, respectively. The calculated ΔC for V_0 =0.040 eV and f=0.01164 is shown as a solid line in Fig. 4, which agrees well with the experimental $\Delta C_p-(\Delta\gamma)T$ data, although the latter is broader than the former.

Temperature dependence of the specific heat curve is characterized by its derivative with respect to temperature. In the present case, the temperature derivatives of the calculated and the experimental specific heat increase curves give curves with a single peak. The calculated $d(\Delta C)/dT$ vs. T curve has a peak at 15.1 K and its FWHM is 20.0 K. On the other hand, the experimental $d[\Delta C_p-(\Delta\gamma)T]/dT$ vs. T curve is obtained from Table I and $\Delta\gamma$ and it has a peak at 16.3 K and its FWHM is 28.8 K. The width of the experimental derivative curve is 1.44 times broader than that of the calculated one. The reason may be that the C_2 molecules in the interstitial clusters rotate not independently of but coupling with other C_2 molecules, which results in the broadening of the energy levels.

V. DISCUSSION

A. Increase in the lattice specific heat and bonding of interstitials

We have explained the increase in the lattice specific heat in neutron-irradiated graphite as due to the hindered rotation of the interstitial C_2 molecules in a periodic potential with a height of 0.040 eV, in which the rotational frequency is 1.39×10^{12} s^{-1}. As stated in Sec. I, if the vibrators form C-C covalent bonds with surrounding atoms, their vibrational frequencies are usually larger than 6×10^{12} s^{-1}.[35] Since the above rotational frequency is much smaller than this frequency, the present result shows that the C_2 molecules do not form strong covalent bonds with atoms in the adjacent atomic layers.

As stated in Sec. IV, the interstitial C_2 molecules are considered to form clusters $(C_2)_n$, the size of which is estimated to be about 10 Å or less, that is, $n \approx 2-10$. The C_2 molecules are loosely coupled with each other in the clusters and are performing a weakly coupled rotation. The total number of C_2 molecules contained in the present sample has been estimated as fN_A per mol, where f=0.011 64, that is, the concentration of C_2 molecules is 1.164%.

On the other hand, first-principles calculations show that interstitial atoms form strong covalent bonds with atoms in the adjacent layers.[28–31] Vibrational frequencies of such interstitial atoms may be larger than 6×10^{12} s^{-1}, so that they cannot contribute to the increase in the lattice specific heat at low temperatures below 30 K. We are concerned with what type of defects and their vibrations the first-principles calculations can propose for such a low-frequency excitation as 1.39×10^{12} s^{-1}.

B. Vacancies

In the irradiation of high-energy particles to solids, the mean free path for atomic collisions decreases at the end of the displacement cascade. We are concerned with whether vacancies produced during irradiation are single vacancies or whether the probability of divacancy production is high.

Kinchin and Pease calculated the defect production in the binary hard-sphere collisions.[61,62] In the modified Kinchin-Pease model which is currently adopted, only if the energy of moving atoms is larger than $2.5T_d$, where T_d is the average threshold energy for atomic displacements, they can produce additional vacancies.[63,64] In graphite, $T_d \sim 28$ eV at 5 K.[65] We estimate the mean free path of a knock-on atom with the energy of $2.5T_d(\sim 70$ eV) after Seitz and Koehler.[66] They assume the screened Coulomb interaction potential $V(r)=(Z^2e^2/r)\exp(-r/a)$ for an elastic collision between a moving atom and a lattice atom, where Z is the atomic number of carbon, e is the electric charge, r is the separation of the two atoms, and a is a screening constant for the pair. a is related to the Bohr radius a_H by the relation $a=a_H/(\sqrt{2}Z^{1/3})$. The mean free path for a knock-on atom of radius R undergoing hard-sphere collisions is given by $1/(\pi R^2 n_0)$, where $V(R)=2.5T_d$ and n_0 is the atomic density. Then, the mean free path of a moving atom of 70 eV in a random direction is calculated to be 9.6 Å, which gives the average separation of two vacancies at the end of the displacement cascade, i.e., the minimum of distances between neighboring vacancies. de Halas considered the effect of the anisotropy of graphite.[67] According to him, the mean free paths of an atom of 70 eV traveling in the (002) plane and in the (100) plane are 4.6 and 21 Å, respectively. Further, if we take account of the effect of the anisotropy and temperature on the threshold energy for atomic displacements, the minimum mean free path in the (002) plane at room temperature estimated after de Halas increases from 4.6 to 5.9 Å, as the corresponding threshold energy is 42 eV and $2.5T_d \sim 105$ eV.[65] From these considerations, we may conclude in graphite that the vacancies produced in a single displacement cascade consist of single vacancies, although these results depend on the assumed potential.

When the irradiation fluence is increased, there is some probability that divacancies are produced by subsequent displacement cascades. The probability may increase in proportion to the concentration of existing single vacancies. In the present sample, the irradiation was performed in the temperature range in which interstitial atoms are mobile but single vacancies are immobile, the DPA is about 0.12,[39] and the concentration of single vacancies surviving the thermal annealing during irradiation is about 0.0233 as mentioned below. Then, if we assume that the probability for single interstitial atoms to recombine with divacancies is 2 times larger than that for them to recombine with single vacancies, a simple estimation gives the result that the concentration of surviving divacancies is about 3% of that of single vacancies. Therefore, we may assume as a first approximation that most of the vacancies are produced as single vacancies during the present irradiation, although there are a few percent of divacancies produced.

We need to confirm that single vacancies are immobile at the irradiation temperature of about 333 K. The energy for migration of the single vacancy has recently been the subject of controversy. For many years, the accepted value from experiments has been 3.1 eV.[16] However, theoretical values for the migration energy obtained using first-principles quantum mechanics strongly suggest that it is of a lower value, 1.7 eV.[28,31,68,69] Even if the lower value of 1.7 eV is more appropriate for the single vacancy migration energy, it is almost impossible for single vacancies to migrate to form divacancies and small vacancy clusters at the irradiation temperature of about 333 K.

Positron lifetime measurements give information on vacancies. First, for the low fluence irradiations with neutrons and electrons at $333 \sim 353$ K, the positron lifetime data can be well explained by assuming that there are single vacancies only and the positron lifetime of 245 ps found is attributed to single vacancies.[44–47] As already mentioned, the optical absorption found around 3 eV also suggests that there are single vacancies in the present sample.[43] Then, we have irradiated a graphite sample with neutrons at about 1073 K to 1.6×10^{19} n/cm^2 (i.e., the DPA is about 0.014).[46] The concentration of existing single vacancies is estimated to be about 25 ppm from the changes in the concentrations of electrons and holes, which are obtained from the galvanomagnetic data at 4.2 K. In this case, as the concentration of single vacancies is low, the formation of divacancies during irradiation is negligible. The lifetime of 245 ps is found and the 245-ps defects are annealed out at about 1473 K.[46] Therefore, single vacancies are immobile below 1273 K. This is consistent with the result of previous other experiments.[16]

To sum up, the vacancies produced in the present sample by irradiation are mainly single vacancies. Although they are immobile at the irradiation temperature, about 80% $[\sim(\mathrm{DPA}-2f)/\mathrm{DPA}]$ of the produced single vacancies disappear by recombination with mobile interstitial atoms. Thus, the concentration of single vacancies which survived the recombination may be $2f$, i.e., 2.33%.

C. Electronic specific heat and hole concentration

In Sec. III, we have obtained $\gamma_{irr}=100.6\pm 8$ μJ/(K^2 mol) as the electronic specific heat. Using the relation $\gamma=(1/3)\pi^2k^2N(E_F)$,[70] where k is the Boltzmann constant and $N(E_F)$ is the density of electronic states at the Fermi energy E_F, the experimental value of γ_{irr} yields

$$N(E_F) = 0.0427 \pm 0.0034 \ \text{eV}^{-1}\ \text{atom}^{-1}. \qquad (12)$$

Expressions for the density of states have been obtained for the Slonczewski-Weiss-McClure (SWMcC) band model of graphite[71,72] by Boardman *et al.*[73] The expressions use four band parameters γ_0, γ_1, γ_2, and Δ (four parameter model) and neglect the other parameters, i.e., $\gamma_3=\gamma_4=\gamma_5=0$. When we adopt $\gamma_0=3.16$ eV, $\gamma_1=0.39$ eV, $\gamma_2=-0.019$ eV, and $\Delta=-0.008$ eV,[74] the above $N(E_F)$ gives $E_F=-1.17\pm 0.09$ eV from the top of the valence band and the hole concentration of 2.47 ± 0.2%.

Boardman *et al.*[73] calculated the change in the density of states due to defects. According to their calculation, the change ΔN in the unperturbed density of states $N(E)$ is $\Delta N/N(E)=5.7$% for the defect concentration of 2.3% if the excess valence of the defect is $Z=-1$. Taking account of this band deformation, the above $N(E_F)$ gives

$$E_F = -1.11 \pm 0.09 \ \text{eV} \quad \text{(from the top of the valence band)} \qquad (13)$$

and

$$\text{hole concentration} = 2.34 \pm 0.2\% . \tag{14}$$

We have not measured the Hall coefficient of the present sample, so we will estimate it from a similar measurement on HOPG samples. The Hall coefficient of the HOPG sample irradiated to 8×10^{19} n/cm^2 at 353 K at the JAERI JMTR reactor was 0.0049 ± 0.0003 cm^3/C between 4.2 K and room temperature for the magnetic field from 3 to 11 kOe. This gives the hole concentration of 1.12%. Then, we estimate the hole concentration for the present irradiation of 1.4×10^{20} n/cm^2 to be $1.96 \pm 0.2\%$. However, this value is not so accurate, as it has been deduced from the measurements for different reactor irradiations.

We assume that the hole concentration is increased by introduction of vacancies as follows:[75] A single vacancy acts as a repulsive potential to the electrons of π bands, i.e., the excess valence of a single vacancy is -1. It deforms the π bands.[43,73] The deformation appears, however, in the whole of π bands and it does not create discrete defect levels in the π bands, although the term "*acceptor level*" or "*electron trap*" has been often used.[2,75] The introduction of single vacancies does not change the total number of states of the π valence band, but decreases the number of π electrons by the number of single vacancies. Thus, we may assume that the introduction of one single vacancy removes one electron from the π valence band and therefore creates one hole.

The hole concentrations deduced from measurements of the electronic specific heat and the Hall coefficient, i.e., 2.34% and 1.96%, agree well with the single vacancy concentration estimated indirectly from measurement of the lattice specific heat, i.e., 2.33%. This result verifies the above assumption that one single vacancy creates one hole.

As to the interstitials such as single interstitial atoms and clusters of interstitial C_2 molecules, we consider their electronic states as follows. In the case of a single interstitial atom, it releases one electron into the π bands and acts as an attractive potential to the electrons of the π bands, where its excess valence is $+1$. Then, when a cluster of C_2 molecules, $(C_2)_n$, is formed, the number of released electrons to the π bands may be a fraction of the number of atoms, $2n$, constituting the cluster. The fractionally ionized cluster acts still as an attractive potential to the electrons of the π bands, but its excess valence is a fraction of $+2n$. Therefore, the number of released electrons by the clusters of C_2 molecules may be much smaller than that of removed electrons by the corresponding single vacancies. Here, we have neglected the effect of the clusters of interstitial C_2 molecules on the hole concentration.

Incidentally, it is well known that in semiconductors Si and Ge, substitutional impurity atoms of valence three, such as B and Al, and single vacancies form acceptor levels above the top of the valence band in the band gap.[76] When such an impurity atom of valence three or a single vacancy is introduced in the lattice, the number of the valence electrons is decreased by one. This defect acts as a repulsive potential to the valence electrons so that a discrete state is pushed out from the valence band to the band gap. This state is called an acceptor level. Then, the valence band is just filled by electrons at absolute zero. If the electrons are excited thermally from the filled valence band to the acceptor levels, holes are created in the valence band.

On the other hand, in semimetal graphite, the valence band overlaps slightly with the conduction band and there is no band gap. When an impurity atom of valence three or a single vacancy is introduced in the lattice, as discussed in the above, one electron is removed from the valence band, while the number of states of the valence band is not changed. As the result, this defect creates one hole at absolute zero. This concept on the hole creation is consistent with the measurements on the magnetic susceptibility, Hall effect, electrical conductivity and magnetoresistivity,[77] and the electronic heat capacity[78] of boron-doped graphite.

D. Dimensional changes

We have measured the dimensional change along the c direction, $\Delta L_c/L_c$, and that along the a direction, $\Delta L_a/L_a$, caused by neutron irradiation in the HOPG samples of ZYH grade, which were simultaneously irradiated together with the present specific heat samples. The result is as follows:

$$\frac{\Delta L_c}{L_c} = 11.8 \pm 0.4\% , \tag{15}$$

$$\frac{\Delta L_a}{L_a} = - 1.05 \pm 0.15\% . \tag{16}$$

Then, the volume change $\Delta V/V$ is given by

$$\frac{\Delta V}{V} = \left(1 + \frac{\Delta L_c}{L_c}\right)\left(1 + \frac{\Delta L_a}{L_a}\right)^2 - 1. \tag{17}$$

The dimensional changes of Eqs. (15) and (16) give the volume change $\Delta V/V$=9.5%. On the other hand, we have measured the density. It is decreased by $\Delta D/D$=−8.6%, which is equivalent to $\Delta V/V$=9.4%.

Using Eqs. (15)–(17), we estimate the dimensional changes and volume changes by a C_2 molecule and a single vacancy. In the present sample, C_2 molecules are not isolated but clustered and a few percent of vacancies may be divacancies. However, we assume as a first approximation that the dimensional changes are proportional to the concentrations of defects, whether the defects are isolated or clustered. It is equivalent to assume that C_2 molecules are isolated and vacancies are single vacancies only.

If n_i is the concentration of interstitial C_2 molecules and n_v is the concentration of single vacancies, the dimensional changes along the c and the a directions in graphite are given as follows:

$$\frac{\Delta L_c}{L_c} = K_i n_i + \frac{2S_{13}}{S_{11} + S_{12}} K_v n_v , \tag{18}$$

$$\frac{\Delta L_a}{L_a} = K_v n_v + \frac{S_{13}}{S_{33}} K_i n_i , \tag{19}$$

where K_i is the dimensional change along the c direction by a unit concentration of C_2 molecules and K_v is that along the a direction by a unit concentration of single vacancies. For the elastic compliances S_{ij}, we use the values of unirradiated graphite $S_{11}=0.975\pm0.03$, $S_{12}=-0.161\pm0.06$, $S_{13}=-0.335\pm0.08$, and $S_{33}=27.7\pm0.8$ in 10^{-13} $\mathrm{cm}^2/\mathrm{dyn}$.[34,40,79] Although they may be changed by irradiation,[80] if their changes are at similar rates toward the same direction, they may be canceled between numerators and denominators of Eqs. (18) and (19).

Putting $n_i=f=1.164\%$, $n_v=2f=2.33\%$, and Eqs. (15) and (16) into Eqs. (18) and (19), we have

$$K_i = 9.5 \pm 1.4 \quad \text{for a } C_2 \text{ molecule}, \tag{20}$$

$$K_v = -0.39 \pm 0.06 \quad \text{for a single vacancy}. \tag{21}$$

When $n_v=0$, the volume change by C_2 molecules is given by

$$\left(\frac{\Delta V}{V}\right)_{C_2} = (1+K_i n_i)\left(1+\frac{S_{13}}{S_{33}}K_i n_i\right)^2 - 1.$$

Since $(\Delta V/V)_{C_2}/n_i \to 9.3$ as $n_i \to 0$, we have

$$\text{volume change by a } C_2 \text{ molecule} = 9.3 \pm 1.4 \text{ atomic volume}. \tag{22}$$

Then, when $n_i=0$, the volume change by single vacancies is given by

$$\left(\frac{\Delta V}{V}\right)_v = \left(1+\frac{2S_{13}}{S_{11}+S_{12}}K_v n_v\right)(1+K_v n_v)^2 - 1.$$

Since $(\Delta V/V)_v/n_v \to -0.46$ as $n_v \to 0$, we have

$$\text{volume change by a single vacancy} = -0.46 \pm 0.07 \text{ atomic volume}. \tag{23}$$

Low-temperature irradiations can produce isolated single interstitial atoms and single vacancies in frozen states if their concentrations are not so high, namely, about 100 ppm or less. Previously, we irradiated HOPG (ZYA) samples at 5 K with fission neutrons in a fast converter in the LHTL (Liquid Helium Temperature Loop) of JAERI JRR-3 reactor and measured changes in the c-axis spacing, $\Delta c/c$.[14] Here we reanalyze the result. Electrical resistivity samples have also been irradiated at the same time to estimate the concentration of produced Frenkel defects. The electrical resistivity increase by a unit concentration of Frenkel pairs has been determined using the electron irradiation at 5 K. When the concentration is less than 3 ppm, it is 4.9 ± 0.2 Ω cm for a Frenkel pair.[7,65,81] Then, the fractional change in the c-axis spacing is such that $\Delta c/c=0.030\pm0.002\%$ for 100 ppm of Frenkel pairs.

When the produced defects are single interstitial atoms and single vacancies, we may assume $\Delta L_c/L_c=\Delta c/c$. We put $n_i=n_v=1.00\times10^{-4}$, $\Delta L_c/L_c=3.0\times10^{-4}$, and $K_v=-0.39$ in Eq. (18): in this case, n_i is the concentration of single interstitial atoms. Then, we have

$$K_i = 2.68 \pm 0.3 \quad \text{for a single interstitial atom}. \tag{24}$$

When $n_v=0$, we obtain $(\Delta V/V)_I$ for single interstitial atoms using Eqs. (17)–(19). Since $(\Delta V/V)_I/n_i \to 2.6$ as $n_i \to 0$, we have

$$\text{volume change by a single interstitial atom} = 2.6 \pm 0.3 \text{ atomic volume}. \tag{25}$$

The calculated volume expansion by a single interstitial atom on the noncovalent bond model is about 3.3 atomic volume,[21,22] which agrees approximately with the above experimental value.

If we assume that the vibrators causing the increase of the lattice specific heat are not C_2 molecules but single interstitial atoms, by putting $n_i=n_v=f=1.164\%$ and Eqs. (15) and (16) in Eqs. (17)–(19), we have the result that the volume change by a single interstitial atom is 9.3 atomic volume and the volume change by a single vacancy is −0.92 atomic volume. Both the values are much bigger than expected. In Sec. IV, we have concluded that, if their vibrational frequency is around 1.45×10^{12} s^{-1}, single interstitial atoms are not stable at room temperature and therefore cannot become the candidate for the present specific heat increase. In addition, consideration of dimensional changes also excludes the possibility that single interstitial atoms cause the observed specific heat increase of the present sample.

The positron lifetimes have been measured on HOPG (ZYA) samples of the present irradiation.[44] Only one defect-lifetime component of 350 ps has been found overwhelmingly. Then, by the first-principles calculation based on the two-component density-functional theory, we concluded that the lifetime of 350 ps should be attributed to the positrons trapped at planar V_6 vacancy rings. However, the discussion of Sec. V B shows that the vacancies produced by irradiations are mainly single vacancies. On the other hand, the large volume expansion by an interstitial C_2 molecule, i.e., 9.3 atomic volume, means that there is an open space on the periphery of the interstitial clusters of C_2 molecules. Thus, we suggest that the lifetime of 350 ps can be attributed to the positrons trapped in an open space around the clusters of C_2 molecules.

E. Stored energy and formation energy of a Frenkel pair

The stored energy is the number of defects times the formation energy of defects for each defect. If the number of defects is known and the stored energy is measured, then the formation energy of the defects is calculable.

In the present sample, the stored energy released between 373 and 873 K is 450 ± 30 J/g (Fig. 1). We estimate the stored energy released above 873 K by using the data of Woods *et al.*[32] They irradiated graphite with neutrons at 303 K to the total stored energy of 515 cal/g and measured the stored energy which remains after annealing with a combustion method as a function of annealing temperature up to 2273 K. The ratio of the energy released below 873 K to the energy released above 873 K is 1:2.48. Then the total stored energy of the present sample is estimated to be 1560 ± 280 J/g for C_2 molecules of 1.164% and single vacancies of 2.33%. The uncertainty is estimated by taking account of the differences in the irradiation fluence and temperature.[82] This corresponds to

$$\text{formation energy for a } C_2 \text{ molecule and two single vacancies} = 16.7 \pm 3.0 \text{ eV}. \tag{26}$$

When two single interstitial atoms combine to form an interstitial C_2 molecule, the sum of the difference between their respective self-energies and the binding energy of C_2 molecule is released. The self-energy of a single interstitial atom and that of an interstitial C_2 molecule are estimated to be 2.5 ± 0.5 eV (Refs. 16 and 18–21) and 2.85 eV (Ref. 19) on the noncovalent bond model, respectively: the difference of self-energies being $2.5 \times 2 - 2.85 = 2.15$ eV. The binding energy of C_2 molecule is given as 6.21 eV.[83] Then, the energy released when two single interstitial atoms form an interstitial C_2 molecule is estimated to be 8.4 ± 2.0 eV. Adding this value to Eq. (26), we have 25.1 ± 5.0 eV for the formation energy of two single interstitial atoms and two single vacancies. Namely, we have

$$\text{formation energy of a Frenkel pair} = 12.6 \pm 2.5 \text{ eV}$$
$$\text{(from the present experiment and related data)}. \tag{27}$$

In this calculation, we neglected the energy released when C_2 molecules gather to form clusters. If it is included, the value of Eq. (27) may be somewhat increased.

Bochirol and Bonjour irradiated pyrolytic graphite samples with electrons at 20 K and with neutrons at 27 K and measured the stored energy release.[11] In these low-temperature irradiations, we can assume that the defects produced consist of isolated single interstitial atoms and single vacancies, where the concentrations of both defects are identical. We will reevaluate the concentration of defects produced in these irradiations to deduce the formation energy of a Frenkel pair.

For the electron irradiations with the energy of 2.1 MeV to 1.74×10^{18} e/cm^2, the stored energy release between 60 and 470 K was 1.09 cal/g. We expect from the extrapolation of their data that an additional energy of 0.10 ± 0.03 cal/g may be released between 470 and 570 K. When the 2.1 MeV electrons are irradiated along the c axis of pyrolytic graphite, the displacement cross section is 19.2 ± 1.3 b at 5 and 80 K.[65] If the sample is thin, the concentration of produced defects is 33.4 ± 2.3 ppm. However, if the sample is thick, when an initially monoenergetic and collimated electron beam traverses the sample, it loses energy, decreasing the defect production. At the same time, its path length is increased due to multiple scattering, increasing the defect production.[65] If the sample is 1 mm thick, the defect production decrease by the energy loss is 3.3% and the defect production increase by the path-length increase is 4.2%: the net increase is 0.9%. Then, if it is 2 mm thick, they are 6.8% decrease and 9.1% increase: the net increase is 2.3%. Here, we suppose that their sample was 2 mm thick.[84] Hence, the total stored energy is estimated to be 1.19 ± 0.03 cal/g for the defect concentration of 34.2 ± 2.4 ppm. Namely, we have

$$\text{formation energy of a Frenkel pair} = 18.1 \pm 1.7 \text{ eV}$$
$$\text{(from Bochirol and Bonjour's electron irradiation)}. \tag{28}$$

For the neutron irradiation to 4.96×10^{17} n/cm^2 ($E > 1$ MeV), the stored energy release between 60 and 600 K was 16.2 cal/g. If we assume the fission neutron spectrum and include the neutrons with $E < 1$ MeV, the total neutron fluence is estimated to be 7.39×10^{17} n/cm^2.[85] The directional average of the threshold energy for atomic displacements at 5 and 80 K is 28 ± 2 eV.[65] The spectral-averaged damage energy cross section for the fission spectrum is calculated to be 52.0 keV b, using the nuclear data file ENDF/B-V.[86] Then, based on the modified Kinchin-Pease model,[63,64,81] we have the displacement cross section of $7.43(\pm 0.6) \times 10^{-22}$ cm^2 for the fission spectrum and therefore the defect concentration is estimated to be about 549 ppm. Then, we have

$$\text{formation energy of a Frenkel pair} = 15.4 \pm 1.4 \text{ eV}$$
$$\text{(from Bochirol and Bonjour's neutron irradiation)}. \tag{29}$$

In the above estimation of the defect concentration for the neutron irradiation, we have assumed that neutrons have the fission neutron spectrum and the defect concentration can be estimated by the modified Kinchin-Pease model. In reality, however, there are deviations from these assumptions. First, in a reactor the neutrons are moderated and the proportion of neutrons with $E < 1$ MeV is increased over the fission spectrum[85] so that the increased neutron fluence for $E < 1$ MeV makes the defect concentration higher than the above estimate by the fission spectrum. Second, when the energy of primary knock-on atom (PKA) becomes high and the number of displacements produced by one PKA increases, as in the case of neutron irradiations, the spatial distribution of displacements becomes localized so that the recombination of unstable Frenkel pairs increases. These localized displacements are not taken into account in the modified Kinchin-Pease model. As a result, as the PKA energy increases, the defect concentration becomes lower than the above estimate by the modified Kinchin-Pease model.[64] The correction for the fission spectrum and that for the modified Kinchin-Pease model may cancel partly each other. However, owing to the uncertainties in these corrections of the defect concentration, the formation energy obtained from the neutron irradiation, Eq. (29), may be less reliable than that obtained from the electron irradiation, Eq. (28).

Based on the two measurements by Bochirol and Bonjour and the above analysis, we may conclude that the experimental formation energy of a Frenkel pair is 16.8 ± 3 eV, that is, the average of Eqs. (28) and (29). On the other hand, since the analysis of our measurement depends on some assumptions, our result of Eq. (27) is not so reliable as their results. However, it is consistent with their result from the neutron irradiation.

We will discuss the formation energy of a Frenkel pair. As to the single vacancy, Rasor and McClelland found a large and reversible increase in the specific heat between 3573 and 3923 K and showed that it is due to the thermally produced vacancies with a formation energy in the vicinity of 7.7 eV.[87,88] Hennig carried out the quenching of graphite *in vacuo* from 3373 K and the quenched-in vacancies were less than 10^{-10} vacancies per atom. This implies that the formation energy of a single vacancy is larger than 6.6 eV.[89] Then, recent first-principles calculations give 7.5 ± 0.1 eV for it.[30,31,68,69] From these, we may conclude that the formation energy of a single vacancy is 7.5 ± 0.2 eV.

As to the single interstitial atom, its self-energy is calculated semiempirically to be 2.5 ± 0.5 eV on the noncovalent bond model.[16,18–21] We assume that the formation energy of a single interstitial atom is given by the sum of the self-energy and the sublimation energy, i.e., 7.4 eV.[90,91] Then, we have 9.9 ± 0.5 eV for the formation energy of a single interstitial atom. Therefore, on the noncovalent bond model, the formation energy of a Frenkel pair is estimated to be 17.4 ± 0.7 eV, which agrees well with the experimental values by Bochirol and Bonjour.

On the other hand, first-principles calculations show that the interstitial atom is strongly covalent bonded to atoms in the adjacent layers and the formation energy of a single interstitial atom is 5.4 ± 0.1 eV.[30,31] Therefore, on the covalent bond model, the formation energy of a Frenkel pair is 12.9 ± 0.3 eV, although another calculation gives 13.7 eV to it.[29,31] These values are at variance with the experiment of Bochirol and Bonjour. However, the quantitative measurement of the formation energy of a Frenkel pair is so difficult that at present we cannot judge experimentally which model is valid for the single interstitial atom. Further deliberate experiments are needed. They are the production of separated Frenkel pairs by low-temperature irradiations and the subsequent measurements of both the total stored energy and the defect concentration.

By the way, if the formation energy of a single interstitial atom is 5.4 eV as is given by first-principles calculations,[30,31] we can expect to detect the formation of single interstitial atoms at high temperatures around 3273 K. However, we cannot find any sign of interstitial atoms in the measurement of specific heat up to 3923 K (Refs. 87 and 88) and in the quenching experiment from 3373 K.[89]

F. Phonon scattering by interstitials

We have measured the *a*-axis thermal conductivity of neutron-irradiated HOPG (ZYA) samples between 5 and 300 K, which were simultaneously irradiated together with the present sample.[42] The thermal conductivity is the sum of the lattice thermal conductivity K_L and the electronic thermal conductivity K_E. From the analysis of K_L, we deduce information on the phonon scattering by the interstitial C_2 molecules.

The lattice thermal conductivity along the *a* axis, $K_{L,a}$, is given by using the relaxation-time approximation as follows:

$$K_{L,a} = \frac{1}{8\pi^3}\sum_i \int d^3q\, S(\omega_{qi},T)\tau_{qi}[v_{qi}^x]^2, \qquad (30)$$

where ω_{qi} is the angular frequency of a phonon of wave number q in the ith phonon mode, $S(\omega_{qi},T)$ is the specific heat due to the phonon of angular frequency ω_{qi}, T is the absolute temperature, τ_{qi} is the relaxation time for the scattering of phonon q_i, and v_{qi}^x is the propagation velocity of phonon q_i perpendicular to the c axis. The relaxation time in Eq. (30) is given by

$$\tau^{-1} = \tau_{pure}^{-1} + \tau_{defect}^{-1}. \qquad (31)$$

The suffix qi is omitted for brevity. The first and second terms of the right-hand side contain all the information describing phonon scattering in the unirradiated and irradiated samples, respectively.

In the calculation of Eq. (30), we followed the method developed by Dreyfus and Maynard.[92,93] It uses the dispersion relation $\omega(q_i)$ given by the Komatsu and Nagamiya theory,[40] in which the lattice vibrations of graphite consist of three kinds of modes: namely, the in-plane longitudinal mode, the in-plane transverse mode, and the out-of-plane mode. Previous calculations did not consider the contribution of the out-of-plane mode,[42,92,93] but the present calculation contains its contribution.

In pure, unirradiated graphite, the electronic thermal conductivity K_E has been observed below 10 K. Then, K_E is related to the electrical resistivity ρ by the Wiedemann-Franz law: $K_E = L_0 T/\rho$, where L_0 is the Lorenz number.[94,95] The relaxation time for the lattice thermal conductivity is assumed to be given as follows:

$$\tau_{pure}^{-1} = \frac{v}{L} + A\omega^3 + D\omega T^3, \qquad (32)$$

where the three terms of the right-hand side are, in order, the phonon scattering by grain boundary with grain size L, the phonon scattering by point defects such as C-13 isotopes, impurities, vacancies, etc., and the phonon-phonon scattering. The lattice thermal conductivity data are fitted by adjusting the constants L, A, and D. The result of fitting is as follows:

$$L = 18\ \mu\text{m},$$

$$A\omega^3 = 2.5 \times 10^{-32}\omega^3\ \text{s}^{-1},$$

$$D\omega T^3 = 1.8 \times 10^{-11}\omega T^3\ \text{s}^{-1}. \qquad (33)$$

In the present irradiated sample, the density of charge carriers (i.e., holes) does not change with temperature. The reciprocal mobility of charge carriers is more than 3 orders of magnitude larger than that of unirradiated graphite: it is due to the scattering of charge carriers by the irradiation-produced defects. Since the carrier scattering by the defects is elastic, we can estimate K_E from the electrical resistivity by using the Wiedemann-Franz law.[96] K_E amounts to 5～24% of the measured conductivity in the range of 5–300 K. For the lattice thermal conductivity, which is obtained by subtracting K_E from the measured thermal conductivity, the relaxation time for the phonon scattering by defects is assumed to be given as follows:

$$\tau_{defect}^{-1} = A'\omega^3 + B\omega^n + C\frac{\gamma\omega_0\omega^2}{(\omega_0^2-\omega^2)^2 + \gamma^2\omega_0^2\omega^2}. \qquad (34)$$

The first and second terms of the right-hand side mean the phonon scattering by vacancies and interstitials, respectively. The third term means the resonance scattering of phonons, which is needed to explain a broad dip in the lattice thermal conductivity below room temperature.[42] ω_0 is the resonance angular frequency and $\gamma\omega_0$ is the full width at half maximum of the resonance curve. The main contribution to the thermal conductivity comes from the second term by interstitials. The effect of the first term is negligibly small and cannot be extracted. The result of data fitting is as follows:

$$n = 1.5,$$

$$B\omega^{1.5} = 8.6 \times 10^{-9}\omega^{1.5}\ \text{s}^{-1},$$

$$C = 3.0 \times 10^{27}\ \text{s}^{-2},$$

$$\omega_0 = 2\pi\nu_0 = 1.5 \times 10^{13}\ \text{rad/s},$$

$$\gamma = 1.4 \times 10^{-2}. \tag{35}$$

As stated before, on the noncovalent bond model, interstitial C_2 molecules gather to form small clusters and the atoms in the adjacent layers around these C_2 clusters are displaced outwards, giving rise to the disklike strain. We consider that the phonon scattering proportional to $\omega^{1.5}$ is caused by the disklike strain around interstitial C_2 clusters.

For the resonance scattering, we obtain the resonance frequency of $\nu_0 = 2.4 \times 10^{12}\ \text{s}^{-1}$ and the Q value $(=1/\gamma)$ of about 70. The value of ν_0 is about 70% higher than the rotational frequency of C_2 molecules obtained from the specific heat measurement. We consider that the reason for the high ν_0 is as follows. While the specific heat has been measured below 43 K, the thermal conductivity was measured between 5 and 300 K. As discussed in Sec. IV, the vibration of C_2 molecules as rigid units may be excited above 60 K so that it can cause the resonance scattering of phonons there with a resonance frequency much higher than that obtained from the specific heat measurement below 43 K. The resonance scattering of phonons below room temperature is caused not only by the hindered rotation of C_2 molecules but also by the vibration of C_2 molecules as rigid units. However, it is difficult to extract two different types of resonance scattering from the present thermal conductivity data. Therefore, in effect, we have a higher resonance frequency in the thermal conductivity measurement than in the specific heat measurement.

Note to the experiment by DeSorbo and Tyler (Ref. 36)

DeSorbo and Tyler measured the specific heat of neutron-irradiated graphite in the temperature range from 13 to 300 K. The difference in C_p between the irradiated and the unirradiated graphite is plotted as a function of temperature in Fig. 3 of Ref. 36. They concluded that the plotted data could be fitted by two separate Einstein functions for vibrations of interstitials in directions parallel and perpendicular to the graphite planes. We followed their data analysis. Numerical data of the specific heat of the irradiated graphite have been tabulated in their Table I. We evaluated their specific heat data of the unirradiated graphite and fitted the data using polynomials.[40] Then we plotted the difference in C_p between their numerical data of the irradiated graphite and the evaluated polynomials of the unirradiated graphite. The plotted data were scattered more largely than those shown in their Fig. 3. We could not judge whether they should be fitted by one Einstein function or by two Einstein functions. However, their conclusion is very suggestive and leads to a prediction that the vibrations of C_2 molecules as rigid units may contribute to the specific heat increase above 60 K and the bond-stretching vibrations of C_2 molecules may contribute to it above room temperature, as discussed in Sec. IV.

VI. SUMMARY

Irradiation-induced increase in the specific heat has been measured in the temperature range of 1.9 to 43 K in pyrolytic graphite neutron-irradiated to $1.4 \times 10^{20}\ \text{n/cm}^2$ $(E > 1\ \text{MeV})$ around 333 K. Analysis shows that the increase in the lattice specific heat can be well explained as due to the hindered rotation of interstitial C_2 molecules in the periodic potential of $V(\varphi) = (V_0/2)(1 + \cos 2\varphi)$, where φ is the angle of rotation and V_0 is 0.040 eV. The first-excited rotational level is 0.0058 eV above the ground state and the rotational frequency is $1.39 \times 10^{12}\ \text{s}^{-1}$. The concentration of C_2 molecules is estimated to be $f = 1.16\%$. The interstitial C_2 molecules are considered to form clusters $(C_2)_n$, the size of which is estimated to be about 10 Å or less, roughly $n \approx 2-10$. The C_2 molecules are loosely coupled with each other in the clusters and are performing a weakly coupled rotation.

There is a controversy on whether interstitial atoms and C_2 molecules form strong covalent bonds with atoms in the adjacent layers or not. Recent first-principles calculations show that interstitials form strong covalent bonds. However, the present results insist that interstitial C_2 molecules do not form covalent bonds with atoms in the graphite layers.

From the increase in the electronic specific heat and using the SWMcC band model, the hole concentration has been deduced. The hole concentration suggests that one single vacancy creates one hole and the single vacancy concentration is $2f$.

Using the concentrations of C_2 molecules and single vacancies, we have evaluated the changes in physical properties for a unit concentration of defects, such as the dimensional changes, stored energy release, and changes in the a-axis thermal conductivity. Then, the volume changes by a single interstitial atom, an interstitial C_2 molecule, and a single vacancy are deduced to be 2.6 ± 0.3, 9.3 ± 1.4, and -0.46 ± 0.07 atomic volume, respectively. The formation energy of a Frenkel pair is estimated to be 12.6 ± 2.5 eV. The phonon scattering with a reciprocal relaxation time proportional to $\omega^{1.5}$, where ω is the angular frequency of phonons, is attributed to the scattering of phonons by the disklike strain around interstitial C_2 molecule clusters. A broad dip in the a-axis thermal conductivity observed below room temperature is attributed to the resonance scattering of phonons by the hindered rotation of interstitial C_2 molecules as well as by the vibration of these molecules as rigid units. It is suggested that the positron lifetime of 350 ps is the lifetime of positrons trapped in an open space on the periphery of the interstitial clusters of C_2 molecules.

We conclude that the present results favor the noncovalent bond model of interstitials. The well-known Wigner energy is stored mainly as interstitial C_2 molecules and single vacancies.

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