Formation of As- and Ge-doped heterofullerenes

Tsutomu Ohtsuki

Laboratory of Nuclear Science, Tohoku University, Mikamine, Taihaku, Sendai 982-0826, Japan

Kaoru Ohno, Keiichiro Shiga, and Yoshiyuki Kawazoe

Institute for Materials Research, Tohoku University, Katahira, Sendai 980-8577, Japan

Yutaka Maruyama

National Industrial Research Institute of Nagoya (NIRIN), 1-1 Hirate-cho, Kita-ku, Nagoya 462-8510, Japan

Kazuyoshi Masumoto

Radiation Science Center, High Energy Accelerator Research Organization, Tanashi, Tokyo 188-8501, Japan

Radioactive heterofullerenes As^*C_{59}, $As^*C_{69}(As^* = {}^{71}As, {}^{72}As, {}^{74}As)$, ${}^{69}GeC_{59}$, and their polymers are detected by using radiochemical and radiochromatographic techniques. This result suggests that a carbon atom in fullerene molecule can easily be substituted with As or Ge by a recoil process following nuclear reactions. Using *ab initio* molecular-dynamics simulations based on the all-electron mixed-basis approach, we confirmed that the formation of a substitutionally doped heterofullerene with a single As atom is really possible. [S0163-1829(99)03024-6]

Since the discovery of fullerenes[1] and the synthesis of large amounts of fullerenes,[2] numerous experimental studies for endohedrally doped[3–12] or exohedrally doped[13–15] fullerenes with foreign atoms have been undertaken by resorting to arc-desorption or laser vaporization techniques. On the other hand, it has become possible to synthesize the heterofullerenes, where the foreign atom is incorporated into the carbon cage. Experimentally, heterofullerenes doped with foreign atoms, such as boron[16,17] and nitrogen,[18,19] have been reported. In our previous studies, we have confirmed the substitutional doping of ${}^{11}C$ (Refs. 20 and 21) and ${}^{13}N$ (Ref. 22) by a recoil implantation process following nuclear reactions. Recently, Pellarin *et al.* have succeeded to synthesize silicon (Si) doped heterofullerenes[23,24] by means of laser vaporization technique. In spite of the intense research, only partial facts for the formation process and the produced materials have been unveiled on the nature of the chemical interaction between a foreign atom and a fullerene cage. Therefore, it is very important and intriguing to synthesize new plastic materials such as several atom-doped fullerenes, and their properties should be intensively and extensively investigated.

In this paper, we present evidence of arsenic(As)- and germanium(Ge)-heterofullerenes, i.e., As^*C_{59} ($As^* = {}^{71}As$, ${}^{72}As$, ${}^{74}As$), $Ge^*C_{59}(Ge^* = {}^{69}Ge)$, and their polymers, in a nuclear recoil reaction. We proved the presence of such heterofullerenes in the final product with radiochemical and radiochromatographic techniques. This suggests that one carbon atom in the C_{60} or C_{70} cages can be substituted directly by the radioactive ${}^{72}As({}^{71}As, {}^{74}As)$ or ${}^{69}Ge$ atom by using the recoil process following nuclear reactions. Carrying out *ab initio* molecular-dynamics simulations of $As + C_{60}$ and AsC_{59} using the all-electron mixed-basis approach,[25,26] we confirmed that such a heterofullerene may exist stably under realistic conditions.

In order to produce As- and Ge-doped heterofullerenes, natural Ge and Ga were used in experiment. Several radioisotopes of As can be produced by (d,n) or $(d,2n)$ reactions by a bombardment on a natural Ge, as shown in Table I. We paid attention to the radioactivity of ${}^{72}As$, ${}^{71}As$, and ${}^{74}As$, because of the appropriate half lives and the abundant β^+ decay rate when counting the 511 keV annihilation γ ray. The radioactive nuclide ${}^{69}Ge$ was produced by means of a bombardment of Ga (see Table I). About 10 mg of C_{60}

TABLE I. Radioactivity produced by naturally abundant materials in Ga and Ge.

Nuclide produced	γ-ray (decay rate by β^+)	Half-life	Reaction	Material and abundance
${}^{70}As$	511 keV(β^+, 90%)	53 m	${}^{70}Ge(d,2n){}^{70}As$	${}^{70}Ge$, 20.5%
${}^{71}As$	511 keV(β^+, 29.5%)	64 h	${}^{71}Ge(d,n){}^{71}As$	${}^{70}Ge$, 20.5%
${}^{72}As$	511 keV(β^+, 87.7%)	26 h	${}^{72}Ge(d,2n){}^{72}As$	${}^{72}Ge$, 27.4%
${}^{74}As$	511 keV(β^+, 29%)	17.8 d	${}^{74}Ge(d,2n){}^{74}As$	${}^{74}Ge$, 36.5%
${}^{69}Ge$	511 keV(β^+, 23.6%)	39.1 h	${}^{69}Ga(d,2n){}^{69}Ge$	${}^{69}Ga$, 60.1%

Other radioisotopes, such as ${}^{73}As$, ${}^{76}As$, ${}^{77}As$, and ${}^{71}Ge$, can also be produced by (d,n) or $(d,2n)$ reactions. Only the β^+ nuclei are listed here (Ref. 23).
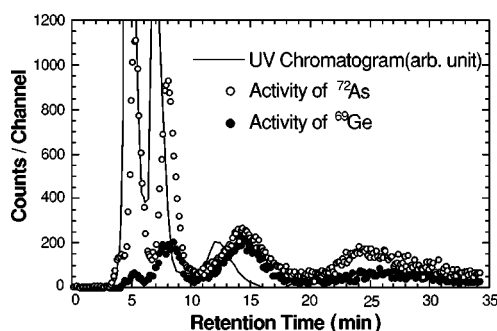
FIG. 1. HPLC elution curves of the soluble portion of the crude extracted in the deuteron-irradiated sample of C_{60} mixed with GeO or Ga_2O_3. The horizontal axis indicates retention time, while the vertical axis represents the counting rate of the radioactivities of ^{72}As (^{71}As, ^{74}As, indicating open circles) and ^{69}Ge (closed circles), measured with a BGO-detector and the absorbance of a UV chromatogram of C_{60} (solid line). (In the figure, only ^{72}As is indicated due to the abundance of its activity; see Table I.)

and/or C_{70} fullerene powder was mixed homogeneously with 10 mg of germanium oxide (GeO) or gallium oxide (Ga_2O_3). The samples were irradiated with deuterons, at the Cyclotron Radioisotope Center of Tohoku University using a beam energy of 16 MeV. Irradiation time was set to about 1 h and the average beam current was typically 5 μA. The sample was cooled with water and low-temperature He gas during the irradiation.

After the irradiation, the samples were left for one day to cool down the several kinds of short-lived radioactivities of byproducts. After the one day cooling, radioactivities, such as ^{13}N [$T_{1/2} = 10$ min, which is produced by a $^{12}C(d,n)^{13}N$ reaction], ^{70}As ($T_{1/2} = 53$ min), have decayed to negligible levels and the radioactivities of ^{72}As, ^{71}As and ^{74}As, or ^{69}Ge could be measured with the 511 keV annihilation γ ray.

The fullerene samples were dissolved in o-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size$=0.45$ μm). The soluble fraction was injected into a high-pressure liquid chromatograph (HPLC) equipped with a 5PBB (silica-bonded with the pentabromobenzyl-group) column of 10 mm (inner diameter)$\times 250$ mm (length), at a flow rate of 4 ml/min. The eluted solution was passed through a UV detector, the wavelength of which was adjusted to 290 nm in order to measure the amount of fullerenes and their derivatives. Downstream of the UV detector, two γ ray detectors consisting of a bismuth germanate scintillator and a photomultiplier (BGO-PM) were installed in order to count the 511 keV annihilation γ ray from β^+ decay of ^{72}As, ^{71}As, and ^{74}As, or ^{69}Ge in coincidence. Data of the radiochromatogram were accumulated with a multichannel scaler system (MCS), using a personal computer. The fraction was collected at 30 sec intervals, and the γ ray activities of each fraction were measured with a Ge-detector coupled to the 4096-channel pulse-height analyzer whose conversion gain was set to 0.5 keV per channel. Therefore, the existence of ^{72}As, ^{71}As, and ^{74}As, or ^{69}Ge could be confirmed by their characteristic γ rays.[27]

Figure 1 shows three elution curves of the C_{60} sample irradiated by a deuteron of $E_d = 16$ MeV, which are coincidentally observed by two BGO detectors [open circles for

^{72}As (^{71}As, ^{74}As) and solid circles for ^{69}Ge radioactivities] and by a UV detector (solid line). The horizontal axis indicates the retention time after injection into the HPLC and the vertical one the counting rate of the ^{72}As (^{71}As, ^{74}As) and ^{69}Ge radioactivities. In the figure, the time delay of the BGO chromatogram to the UV was corrected by the flow rate and the capillary length between the UV and the BGO detectors.

A strong absorption peak was observed at the retention time of 5 min in the elution curve (solid line) which was measured by the UV detector. This peak position corresponds to the retention time of C_{60}, which was confirmed by the calibration run using the C_{60} sample before the irradiation. Following the first peak, two peaks at around 7 min and 11–15 min were consecutively observed in the UV chromatogram. This fact indicates that the second and smaller third peaks can be assigned to C_{60} dimers and C_{60} trimers, respectively. These materials can be produced by the interaction between C_{60}'s in coalescence reactions after ionization by incident deuterons or produced charged particles.[26,28]

Four peaks appeared in the curve of the radioactivities ^{72}As (^{71}As, ^{74}As) in the radiochromatogram. Aside from a light delay, the first peak corresponds to the C_{60} UV absorption peak. The second, as well as the relatively broad third and fourth peaks were observed at retention time of 8 min, of 12–17 min and of 21–30 min, respectively. Though there is a delay in the elution peaks of the radioactivities against that of the UV absorption peaks, it seems that the elution behavior is similar. This result indicates that the radioactive fullerene monomers and their polymers labeled with ^{72}As (^{71}As, ^{74}As) possibly exist in the fractions. A similar trend was observed in the elution curve of ^{69}Ge radioactivities though the first and second peaks were relatively smaller than those of the ^{72}As (^{71}As, ^{74}As).

On the basis of the present results, As- or Ge-doped heterofullerenes, as a part of the cage, can really exist in the final products. We present several reasons here for the formation of such atom-doped heterofullerenes: (1) To the best of our knowledge, 4B or 5B group elements (in the periodic table), such as Ge or As, respectively, prefer a covalent bond (an sp^3 like bonding). Recently, Pellarin et al. have presented evidence that a Si atom can remain in the fullerene skeleton stably even if the bond structure is sp^3.[23,24] (2) Previously, we reported results concerning the formation of other radioactive fullerenes, $^{11}CC_{59}$ and $^{13}NC_{59}$, using the recoil-implantation process following nuclear reactions. These results indicate that such an energetic ^{11}C or ^{13}N nuclide is successfully incorporated in fullerene cages to include the radioisotopes.[20,22] (3) Recently, we have confirmed formation of the endohedral fullerenes, namely $^7Be@C_{60}$, $^{79}Kr@C_{60}$, and $^{127}Xe@C_{60}$ (Refs. 26 and 29) and, furthermore, formation of the atom-doped fullerenes has also been tested in several radioisotopes (Na, Ca, Sc, V, Cr, Mn, Co, Ni, Zn, Ga), using the same method. It was also found that most of the elements could not be detected in the C_{60} portion against the produced amount of the endohedral fullerenes (here, $^{127}Xe@C_{60}$ was produced at most 10^{10} molecules). In the present study, however, it is noted that the amount of $^{72}As(^{71}As,^{74}As)$, which remains in the final fullerene portion, is estimated to be several tens of times greater than that of endohedral fullerenes (i.e., $^{127}Xe@C_{60}$). This amount is rather closer to the production rate of $^{11}CC_{59}$.[28] Therefore,
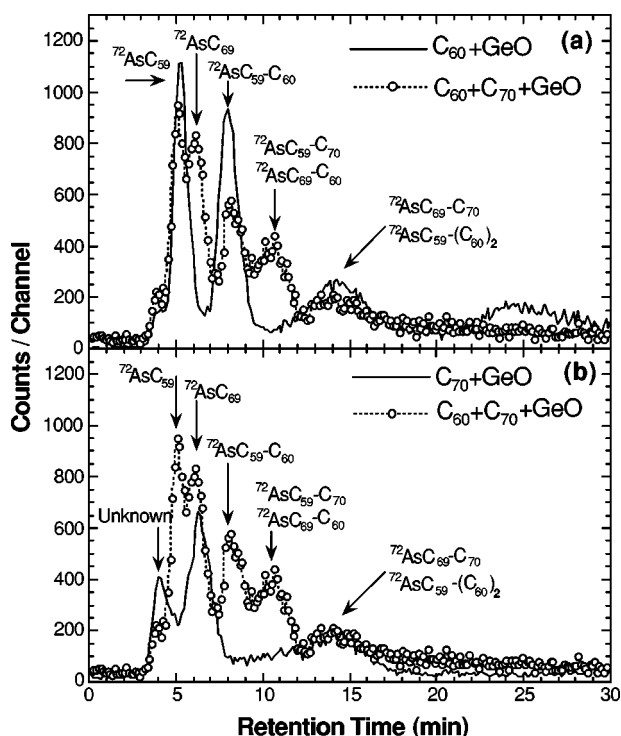
FIG. 2. (a) HPLC elution curves are the same as in Fig. 1, but for the samples of C_{60}:GeO=1:1 and of C_{60}:C_{70}:GeO=1:1:2. (b) HPLC elution curves are the same as in Fig. 1, but for the samples of C_{70}:GeO=1:1 and C_{60}:C_{70}:GeO=1:1:2. Vertical arrows indicate the position of ^{72}As(^{71}As, ^{74}As) radioactivities in retention time. (In the figures, only ^{72}As is indicated due to the abundance of its activity; see Table I.)

our observation may corroborate the formation of heterofullerenes with networked As* (Ge*) and their dimers (trimers and tetramers), namely, As*C_{59}(monomer) and As*C_{59}-C_{60}(dimer), As*C_{59}-$(C_{60})_2$ (trimer) and As*C_{59}-$(C_{60})_3$ (tetramer) for the sample of C_{60}, mixed with GeO (open circles), Ge*C_{59} and their polymers (dimer, trimer, tetramer) mixed with Ga_2O_3 (closed circles). Here, it should be noted that no evidence of exohedral molecules with a covalent nature have been presented so far by an extraction in the soluble portion. Such molecules can be removed out during the solvation process if they are exohedral.

Furthermore, C_{60} or C_{60}+C_{70} mixed samples were prepared with weight ratio, C_{70}:GeO=1:1 and C_{60}:C_{70}:GeO =1:1:2, and irradiated. Three peaks appeared in the radiochromatogram of the mixed sample (C_{70}:GeO=1:1), while five apparent peaks occurred in the radiochromatogram of the mixed sample (C_{60}:C_{70}:GeO=1:1:2). The same trend was observed in our previous study of radioactive fullerenes labeled with ^{11}C (Refs. 20 and 21) and with ^{127}Xe.[26] Therefore, these peaks can be assigned to the heterofullerenes, as indicated in Figs. 2(a) and 2(b).

Again, in Fig. 1, why does the delay occur in the retention time between the absorbance of the UV chromatogram and the counting rate of the radioactivities [^{72}As (^{71}As, ^{74}As), ^{69}Ge]. In these cases, it seems that the electron density of the heterofullerenes is strongly distorted by the atom trapped in the cage. The distorted electrons may change the magnitude of the interaction between the heterofullerene and the resin inside of column. It seems that the magnitude of the delay

observed in the present work is significantly greater than that which was noted in the case of endohedral fullerenes (^{127}Xe@C_{60} etc.),[26] since the electron field is more distorted by the hetero-atoms (As*, Ge*).

In order to understand the present experimental results, *ab initio* molecular-dynamics simulations were carried out. The method, which is used here, is based on the all-electron mixed-basis approach[25,26,29,30] using both plane waves (PW's) and atomic orbitals (AO's) as a basis set within the framework of the local-density approximation (LDA). In the present study, all the core atomic orbitals are determined numerically by a standard atomic calculation based on Herman-Skillman's framework with logarithmic radial meshes.[25] For the present system, we use 313 numerical AO's and 4,169 PW's corresponding to a 7 Ry cutoff energy. For dynamics, we assume the adiabatic approximation where the electronic structure is always in the ground state. We utilize a supercell composed of $64 \times 64 \times 64$ meshes, where one mesh corresponds to 0.196 Å. We set the basic time step as $\Delta t = 0.1$ fs and perform five steepest descent (SD) iterations after each updation of atomic positions. We do not impose any velocity control, so that the system is almost microcanonical with a little energy dissipation from the SD algorithm. We performed the following three types of simulations; (A) insertion of As atom through a six-membered ring of C_{60}, (B) insertion between one As atom and one C atom of C_{60}, and (C) structural stability of AsC_{59}.

Here, we describe the main results of the present simulations. First, in (A), the As atom with various kinetic energies hits vertically the center of a six-membered ring of C_{60}. Then, we find that the As atom can penetrate into C_{60} when its initial speed is greater than 70 eV. This threshold kinetic energy is comparable to that of noble gas atoms [80 eV for Kr and 130 eV for Xe (Ref. 26)] and is relatively lower than that of other atoms (150 eV for Cu; in the cases of K and V, they are hardly encapsulated even at 100 eV and 150 eV, respectively). Thus, we conclude that an As atom can penetrate into C_{60} easily with a relatively low-kinetic energy, just like noble-gas atoms.[26] This is due mainly to the covalent interaction between carbon and arsenic atoms shortranged and weak.

Second, in (B), we shift one of the C atoms of C_{60} outward by 1.3 Å (at radius 4.9 Å) and put additionally one As atom on the same radial axis by 1.3 Å inward from the original C position (at radius 2.2 Å). Then, starting the simulation with zero initial velocity, we find that there is a strong force acting on the As atom to accelerate it outward and, as a result, to repel the outward C atom still further outward. Surprisingly, this force exists even in the absence of the outer C atom. In fact, if we perform a similar simulation without the outer C atom [this is actually the simulation (C) we carried out], the inner As atom (initially put at 0.53 Å inward from the cage sphere) starts going outward as if it would leave the cage. (When we perform the same simulation with a negatively ionized initial condition, the As atom does not stop and actually leaves the cage.) In the neutral case, however, after 100 fs, at 0.73 Å from the cage sphere, it comes back again and stops finally (there is a little energy loss caused by the SD algorithm.) The final position of the As atom is at 0.50 Å from the cage sphere (at radius 4.06 Å). Figure 3 shows the structure of the As-doped heterofullerene,
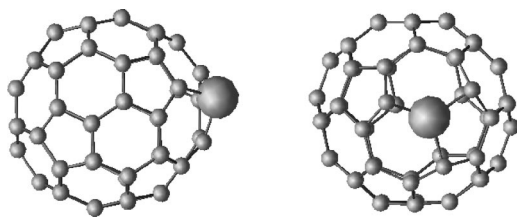
FIG. 3. Obtained stable structure of the As-doped hetrofullerene, as a front view (right) and a side view (left), after full relaxation.

front and side views after full relaxation ($t = 500$ fs). Thus we may conclude that the As atom put inside the cage is quite unstable and has a strong tendency to repel the closest C atom of C_{60} and is stabilized slightly outside the cage sphere after the removal of the closest C atom.

Consequently, we have the following scenario to finally realize the atom-doped heterofullerenes substituted by a foreign atom, such as As or Ge resulting from a collision against C_{60}: The As* or Ge* atoms are produced by a nuclear reaction and removed from their own material with kinetic energies of about a few hundred keV.[20,29] Then, the kinetic energy decreases in the sample to a magnitude, which is appropriate for the atomic collision. As* (or Ge*) atom penetrates into C_{60} through a six-membered ring, moving inside toward the opposite side of the cage, and then repelling one carbon atom there, and replacing it. There is, of course, another possiblity for As* (or Ge*) atoms to directly replace one of the carbon atoms on the cage from outside without first penetrating the inside of the C_{60}. This additional possibility would enhance the production rate of As*C_{59} or Ge*C_{59}. Further, the shock caused by collision most probably induces the cages to coalesce with neighboring cages.

Finally, it should be noted that the purified heterofullerenes produced in the present experiment seem to be more stable than a diverse, broad mixture of cluster fragments that are detected by mass-spectrometry, since unstable molecules can be removed out during the solvation process.

[1] H. Kroto *et al.*, Nature (London) **318**, 162 (1985).
[2] W. Krätschmer *et al.*, Nature (London) **347**, 354 (1990).
[3] Y. Chai *et al.*, J. Phys. Chem. **95**, 7564 (1991).
[4] R. D. Johnson *et al.*, Nature (London) **355**, 239 (1992).
[5] J. H. Weaver *et al.*, Chem. Phys. Lett. **190**, 460 (1992).
[6] H. Shinohara *et al.*, Nature (London) **357**, 52 (1992).
[7] M. Takata *et al.*, Nature (London) **377**, 46 (1995).
[8] W. Sato *et al.*, Phys. Rev. Lett. **80**, 133 (1998).
[9] M. Saunders *et al.*, Science **271**, 1693 (1996).
[10] T. Braun and H. Rausch, Chem. Phys. Lett. **288**, 179 (1998).
[11] T. Braun and H. Rausch, Chem. Phys. Lett. **237**, 443 (1995).
[12] G.E. Gadd *et al.*, J. Am. Chem. Soc. **120**, 10 322 (1998).
[13] L.M. Roth *et al.*, J. Am. Chem. Soc. **113**, 6298 (1991).
[14] Y. Huang and B.S. Freiser, J. Am. Chem. Soc. **113**, 9418 (1991).
[15] S.W. McElvany *et al.*, J. Phys. Chem. **96**, 4935 (1992).
[16] T. Guo *et al.*, J. Phys. Chem. **95**, 4948 (1991).
[17] H.J. Muhr *et al.*, Chem. Phys. Lett. **249**, 399 (1996).
[18] T. Pradeep *et al.*, J. Phys. Chem. **95**, 10 564 (1991).
[19] J.F. Christian *et al.*, J. Phys. Chem. **96**, 10 597 (1992).
[20] T. Ohtsuki *et al.*, J. Am. Chem. Soc. **117**, 12 869 (1995).
[21] T. Ohtsuki *et al.*, Mater. Sci. Eng., A **217/218**, 38 (1996).
[22] T. Ohtsuki *et al.*, J. Radioanal. Nucl. Chem. **239** 356 (1999).
[23] M. Pellarin *et al.*, Chem. Phys. Lett. **277**, 96 (1997).
[24] C. Ray *et al.*, Phys. Rev. Lett. **80**, 5365 (1998).
[25] K. Ohno *et al.*, Phys. Rev. B **56**, 1009 (1997).
[26] T. Ohtsuki *et al.*, Phys. Rev. Lett. **81**, 967 (1998).
[27] *Table of Isotopes*, 8th ed., edited by R.B. Firestone (Wiley, New York, 1996), Vol. I.
[28] T. Ohtsuki *et al.*, Chem. Phys. Lett. **300**, 667 (1999).
[29] T. Ohtsuki *et al.*, Phys. Rev. Lett. **77**, 3522 (1996).
[30] K. Ohno *et al.*, Phys. Rev. Lett. **76**, 3590 (1996).