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The formation of heavier atoms (Sb,Te)-incorporated fullerenes has been investigated by using radionuclides produced by nuclear reactions. From the trace of radioactivities of ^{120}Sb (^{122}Sb) or ^{121}Te after high-performance liquid chromatography, it was found that the formation of endohedral fullerenes or heterofullerenes in atoms of Sb or Te is possible by a recoil process following the nuclear reactions. To confirm the produced materials, *ab initio* molecular-dynamics simulations based on an all-electron mixed-basis approach were carried out. We present the possibility of the formation of endohedral fullerenes or substitutional heterofullerenes incorporated with Sb or Te atoms.

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INTRODUCTION

Chemical interaction between C_{60} and a variety of atoms is becoming a very new field of cluster research. So far, numerous experimental studies for endohedrally doped[1–10] or exohedrally doped[11–13] 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 (B),[14,15] nitrogen (N),[16,17] and silicon (Si),[18,19] have been reported. In our previous studies, we have studied not only the endohedral doping of Be,[20] Kr, and Xe,[21] but also the substitutional doping of ^{11}C,[22] ^{13}N,[23] ^{69}Ge, and ^{72}As (Ref. 24) by a recoil-implantation process following nuclear reactions. 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 important and intriguing to synthesize new complexes, such as several foreign-atom incorporated fullerenes, and their properties should be investigated due to acquirement of the knowledge for producing a large amount of the complexes.

In this paper, we show evidence of Sb (or Te) atom-incorporated fullerenes on the collision between a C_{60} cage and an Sb (Te) atom, which was generated from a recoil process following nuclear reactions. We performed *ab initio* molecular-dynamics (MD) simulations: whether the Sb (Te) atom can be incorporated in the fullerene with endohedral doping, Sb@C_{60} (Te@C_{60}), or substitutional doping, SbC_{59} (TeC_{59}).

Furthermore, the chemical nature of the Sb (Te) atom in a fullerene is compared with that of an As atom.

EXPERIMENTAL PROCEDURE

According to the source nuclide used, high-energy bremsstrahlung or charged particle irradiation was used. In Table I, the nuclide produced, characteristic γ-ray, half-life, and reaction are listed for each material used here. About 10 mg of C_{60} fullerene powder was mixed homogeneously with 10 mg of an antimony oxide (Sb_2O_3), and used to the target material.

(1) For the production of ^{120}Sb- (^{122}Sb-) doping fullerene, the samples were irradiated with bremsstrahlung of $E_{max}=50$ MeV which originated from the bombardment of a Pt plate of 2 mm in thickness with an electron beam at a 300 MeV electron linac, Laboratory of Nuclear Science, Tohoku University. Two kinds of radioisotopes of ^{120}Sb and ^{122}Sb can be produced by photonuclear reaction, (γ,n) reactions, by irradiation on natural Sb. The irradiation time was set to about 8 h and the average beam current was typically

TABLE I. Nuclear data and experimental condition for atom-incorporated fullerene.

Nuclide produced	γ-ray[a]	Half-life	Reaction	Material[b] and abundance (%)
^{120}Sb	197 keV	5.76 d	^{121}Sb$(\gamma,n)^{120}$Sb	^{121}Sb, 57.4
^{122}Sb	564 keV	2.70 d	^{123}Sb$(\gamma,n)^{122}$Sb	^{123}Sb, 42.6
^{121}Te	573 keV	16.80 d	^{121}Sb$(d,2n)^{121}$Te	^{121}Sb, 57.4

[a]γ-ray used for the analysis.
[b]Irradiated material as a target (both for the case of Sb and Te): Sb$_2$O$_3$.

120 μA. The sample was cooled with water bath during the irradiation.

(2) For the production of ^{121}Te-doping fullerene, deuteron irradiation with beam energy of 16 MeV was performed at the Cyclotron Radio-Isotope Center (CYRIC), Tohoku University. A Radioisotope of ^{121}Te can be produced by a $(d,2n)$ reaction by irradiation on natural Sb. The beam current was typically 5 μA and the irradiation time was about 1 h. The sample was cooled with He gas during irradiation.

After the irradiation, the samples were left for 1 day to cool down the several kinds of short-lived radioactivities of by-products. After the 1-day cooling, radioactivities, such as ^{11}C or ^{13}N (e.g., ^{11}C decays to ^{11}B with $T_{1/2}=20$ min) and the radioactivities of ^{120}Sb (^{122}Sb) or ^{121}Te could be measured with its characteristic γ rays (see Table I).

The fullerene samples were dissolved in o-dichlorobenzene after being filtrated to remove insoluble materials through a membrane filter (pore size$=0.45$ μm and/or 0.2 μm). The soluble fraction was injected into a high-performance liquid chromatograph (HPLC) equipped with a 5PBB (silica bonded with the pentabromobenzyl group) column of 10 mm (inner diameter)$\times250$ mm (length), at a flow rate of 3 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.

The fraction was collected at 30-s 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 ^{120}Sb (^{122}Sb) or ^{121}Te could be confirmed by their characteristic γ-rays.[25]

RESULTS AND DISCUSSION

Figure 1 shows three elution curves of the C$_{60}$ sample irradiated by bremsstrahlung of $E_{max}=50$ MeV. The horizontal axis indicates the retention time after injection into the HPLC; the vertical one indicates the absorbances monitored continuously by a UV detector (solid line) and the γ-counting rate of the ^{120}Sb or ^{122}Sb radioactivities measured with a Ge detector. Open circles are for ^{120}Sb and solid circles for ^{122}Sb radioactivities, respectively.

A strong absorption peak was observed at the retention time of 6.5–7 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 irradia-

tion. Following the first peak, two peaks at around 9–9.5 min and 13–16 min were consecutively observed in the UV chromatogram. For characterization of the components, the fraction corresponding to the second peak in Fig. 1 was collected and examined with MALDI TOF (matrix-assisted laser-desorption ionization time-of-flight) mass spectrometry. The mass spectrum of the fraction exhibited a series of peaks at m/z, $1440-24n$ ($n=1$–4), corresponding to the molecular ion peak of C$_{120}$-nC$_2$ in addition to the peak for C$_{60}$ as a base peak. 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 γ-rays or produced charged particles.

Three peaks appeared in the curve of the radioactivities ^{120}Sb (^{122}Sb) in the radiochromatogram. Aside from a slight delay, the first peak (7 min) corresponds to the UV absorption peak of C$_{60}$. The second and the relatively broad third peaks were observed at a retention time of 9–11 min and of 14–20 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. The elution curves shown by the solid line and solid circles in Fig. 2 indicate the absorbance monitored continuously by a UV detector and the γ-counting rate of ^{121}Te measured by a Ge detector, respectively. The horizontal and the vertical axes are also the same as in Fig. 1. From the mass measurements, three components in the UV chromatogram can be also attributed to C$_{60}$ monomers, their dimers, and their tri-
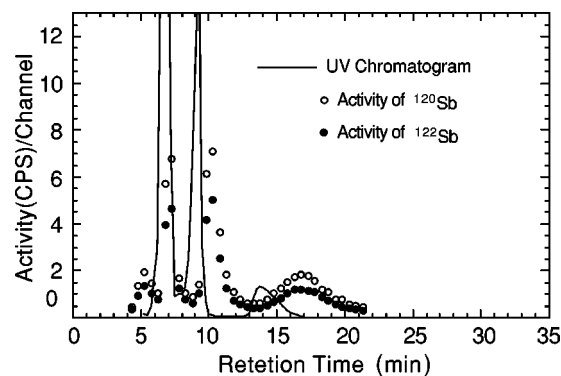

FIG. 1. HPLC elution curves of the soluble portion of the crude extracted in the γ-ray-irradiated sample of C$_{60}$ mixed with Sb$_2$O$_3$. The horizontal axis indicates retention time, while the vertical axis represents the counting rate of the radioactivities of ^{122}Sb (^{120}Sb) measured with a Ge detector and the absorbance of a UV chromatogram of C$_{60}$ (solid line).
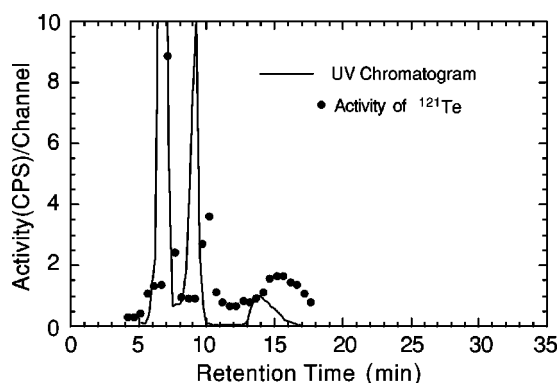
FIG. 2. HPLC elution curves of the soluble portion of the crude extracted in the deuteron-irradiated sample of C_{60} mixed with Sb_2O_3. The horizontal and vertical axis are the same as in Fig. 1, but for ^{121}Te.

mers, respectively. Three populations of ^{121}Te appear at retention times of 7 min, 10 min, and 14–18 min in Fig. 2. This result indicates that the radioactive fullerene monomers and their polymers (dimers and trimers) labeled with ^{120}Sb (^{122}Sb) possibly exist in the final fractions. In our previous study, a similar trend was also observed in the elution curve of Kr, Xe, and Ge, As cases.[21,24] The amount of Sb- (Te-) incorporated radioactive fullerenes produced here is estimated to be about 10^{10}–10^{11} molecules.

Here, it should be noted that no evidence of exohedral molecules has been presented so far by an extraction in the soluble portion. Such molecules can be removed during the solvation process if they are exohedral. Therefore, two possibilities should be considered in the present results: (1) endohedrally Sb (Te) atom-doped fullerenes $Sb@C_{60}$ ($Te@C_{60}$) and (2) substitutionally Sb (Te) atom-doped heterofullerenes as a part of the cage, SbC_{59} (TeC_{59}).

In order to understand the present experimental results, *ab initio* molecular-dynamics simulations were carried out. (In this and all the following studies, we used *ab initio* MD simulations instead of a more efficient technique for structural optimization, because we wanted to monitor the force acting on the Sb and C atoms along real trajectories at each time step.) The method, which is used here, is based on the all-electron mixed-basis approach[26–28] 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 core atomic orbitals are determined numerically by a standard atomic calculation based on the Herman-Skillman framework with logarithmic radial meshes. For the present system, we use 313 numerical AO's and 4169 PW's corresponding to a 7-Ry cutoff energy. For dynamics, we assume an 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 update of atomic positions. We do not impose any velocity control, so that the system is almost microcanonical with little energy dissipation from the SD algorithm.

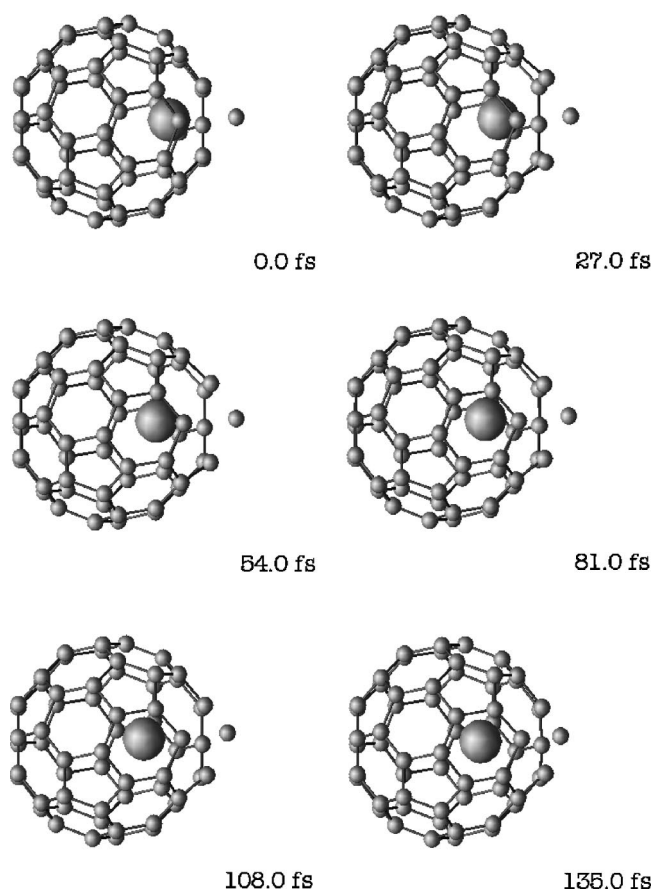We performed the following three types of simulations for

FIG. 3. Simulation of the structural stability of $Sb@C_{60}$ or SbC_{59}: change from an unstable innerside (Sb atom) and outer side (C atom) with an initial kinetic energy of 0 eV to a final stabilized configuration.

the As or Te cases: (A) insertion between one Sb atom and one C atom in the C_{60} cage, (B) structural stability of SbC_{59}, and (C) insertion of a Te atom through a six-membered ring of C_{60} (u-C_6).

Here, we describe the results of the present simulations. (A) First, we shift one of the C atoms of C_{60} outward by 1.3 Å and put additionally one Sb atom on the same radial axis by 1.3 Å inward from the original C position (see Fig. 3). Then, starting the simulation with zero initial velocity, we found that there is a force acting on the Sb atom to move inward to encapsulate (~ 135 fs). On the other hand, the C atom of C_{60} placed outward by 1.3 Å induces a force acting to move inward as if the original shape of C_{60} is recovered. This result indicates the formation of $Sb@C_{60}$. (B) Second, one Sb atom is put at 1.3 Å outward from the cage sphere, instead of one C atom of u-C_6. Then, starting the simulation with zero initial velocity, we found that there is a slight moving force acting on the Sb atom against the cage, but still staying near by the initial position even after full relaxation($t = 500$ fs) with some rotational inertia in the system of SbC_{59} (see Fig. 4).

Therefore, it seems that the Sb atom, when put outside the cage, can be stable to create a heterofullerene such as SbC_{59}. It is interesting to note that the nature of the doping process of the Sb atom in the C_{60} cage can be compared with that of
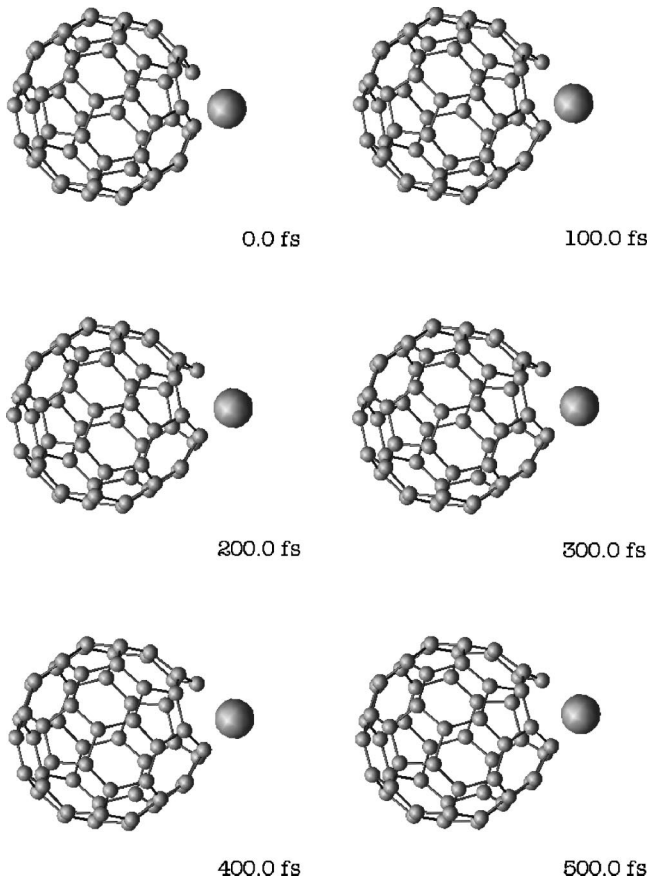
FIG. 4. Simulation of structural stability of SbC_{59}: change from an unstable outer side (0.13Å outward from the cage sphere) with a initial KE of 0 eV to a final stabilized configuration in SbC_{59}.

FIG. 5. Simulation of Te hitting the center of a six-membered ring of C_{60} with a kinetic energy of 40 eV. Here, the local skeleton disappears from the figure when the bond length is elongated to more than by 1.5 Å.

an As atom, because the As and Sb atoms are the same 5B group element. In our previous study, we also performed similar simulations in the case of As atoms.[24] From the simulations, the As atom put inside the cage is unstable and has a tendency to repel the closest C atom of C_{60} and, stabilized slightly outside the cage sphere, to create AsC_{59}, even if the As atom is initially put inside the cage as in case (A). Therefore, we confirmed that a heterofullerene, such as AsC_{59}, may exist stably under realistic conditions. In the present results, the Sb atom may also remain the local stable point around the cage sphere to create a heterofullerene (SbC_{59}). However, it seems that the formation of $Sb@C_{60}$ is rather more likely than the formation of SbC_{59} for the interaction between the Sb atom and the C_{60} cage.

(C) Third, a Te atom with an initial kinetic energy (KE) of 40 eV can penetrate into the cage of C_{60} through the center of u-C_6 without difficulty. Figure 5 shows several snapshots (~ 150 fs) of the Te atom insertion with 40 eV KE. In the figure, after the Te atom first touches u-C_6, carbon atoms are pushed to open u-C_6 and go through. But the u-C_6 recovers soon its initial configuration. Finally the Te atom bounced at the other side and came back towards the center of the cage.

For a relatively low initial KE of the Te atom, C_{60} shows a tendency to recover its original shape within the simulation period. For higher initial KE over 100 eV, the Te atom goes out again from the opposite side of the cage. Further, for a
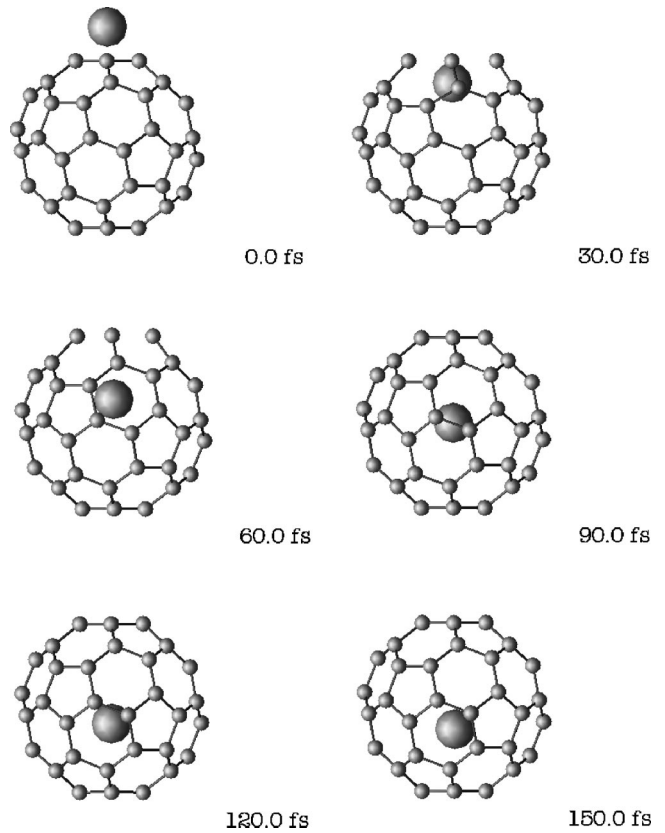
KE over 130 eV, six C_2 losses occur simultaneously from the upper side of C_{60}. The result of simulations changes of course according to the impact energy, impact point, and angle. If the Te atom is inserted toward off-center positions of a six- or a five-membered ring, the damage suffered to the C_{60} cage increases significantly. Similar simulations were also performed in the case of the Sb atom; we found that an Sb atom can penetrate into C_{60} with a relatively higher KE when its initial speed is greater than 70 eV. For an initial KE greater than 160 eV, an Sb atom goes out again from the opposite side of the cage. The results indicate that the insertion of the Te atom through u-C_6 seems to be rather easier than that of the Sb atom.

Consequently, Sb and Te atoms can penetrate into C_{60} through u-C_6 to create the endohedral fullerenes Sb-C_{60} or $Te@C_{60}$. There is, of course, another possibility for the Sb atom to replace one of the carbon atoms on the cage due to a local stable point around the cage sphere. The difference between the C atom and the Sb (Te) atom can be due mainly to the magnitude of the covalent bonding; it seems that the magnitude of the covalent bonding between the Te atom and the C_{60} cage is weaker than that in the case of As and the cage.

The results of analyses of the present work have to be further supported by some other experimental data such as direct mass measurements by a time-of-flight mass spectrom-

FIG. 6. Schematic view of a partial periodic table. In the figure, the formation of atom-doped C_{60}, which has been confirmed by using several techniques, is indicated by underbars. Elements shown by the gray area are investigated by the present method.

etry (TOFMAS), following another simple way to achieve the 40 eV initial kinetic energy for Sb ions by use of, for example, a pair of parallel flat electrodes with 40 eV bias voltage.

Finally, schematic view of a partial periodic table is shown in Fig. 6. In the figure, elements which are experimentally and theoretically confirmed as an incorporation in the fullerene cage are shown by an underbar (endohedral doping or substitutional doping). Elements shown by the gray area are investigated by the present method. We found that elements, which are experimentally and/or theoretically confirmed as an atom-incorporated fullerene, can be limited to (1) small atoms (like Li, Be), (2) noble-gas atoms ($\sim$ Kr, Xe), and (3) 4B–6B atoms in the periodic table (Ge, As, Se,

Sb, and Te). It is interesting to note that group elements such as 4B–6B, even in heavier elements like an Sb and Te atoms, can be possible for the formation of complex materials.

CONCLUSION

In this study, the formation of atom-incorporated fullerenes has been investigated by the traces of radioactivity of ^{120}Sb (or ^{122}Sb, ^{121}Te) produced by nuclear reactions. It was found that 5B–6B elements, like Sb or Te, remained in the final C_{60} portion after a HPLC process. This fact suggests that the formation of endohedral fullerenes Sb@C_{60} (Te@C_{60}) and their polymers or substituted heterofullerenes SbC$_{59}$ and their polymers can be possible by a recoil process following nuclear reactions. Carrying out *ab initio* molecular-dynamics simulations on the basis of the all-electron mixed-basis approach, we confirmed that endohedral fullerenes of Sb (Te) atoms inside the C_{60} cage can be possible. From the difference between the case of Sb (Te) and the case of As, the chemical nature of a doping atom seems to play an important role in the process of endohedrally doping or substitutionally doping in fullerenes.

[1] Y. Chai *et al.*, J. Phys. Chem. **95**, 7564 (1991).

[2] R.D. Johnson *et al.*, Nature (London) **355**, 239 (1992).

[3] J.H. Weaver *et al.*, Chem. Phys. Lett. **190**, 460 (1992).

[4] H. Shinohara *et al.*, Nature (London) **357**, 52 (1992).

[5] M. Takata *et al.*, Nature (London) **377**, 46 (1995).

[6] W. Sato *et al.*, Phys. Rev. Lett. **80**, 133 (1998).

[7] M. Saunders *et al.*, Science **271**, 1693 (1996).

[8] T. Braun and H. Rausch, Chem. Phys. Lett. **288**, 179 (1998).

[9] T. Braun and H. Rausch, Chem. Phys. Lett. **237**, 443 (1995).

[10] G.E. Gadd *et al.*, J. Am. Chem. Soc. **120**, 10 322 (1998).

[11] L.M. Roth *et al.*, J. Am. Chem. Soc. **113**, 6298 (1991).

[12] Y. Huang and B.S. Freiser, J. Am. Chem. Soc. **113**, 9418 (1991).

[13] S.W. McElvany *et al.*, J. Phys. Chem. **96**, 4935 (1992).

[14] T. Guo *et al.*, J. Phys. Chem. **95**, 4948 (1991).

[15] H.J. Muhr *et al.*, Chem. Phys. Lett. **249**, 399 (1996).

[16] T. Pradeep *et al.*, J. Phys. Chem. **95**, 10 564 (1991).

[17] J.F. Christian *et al.*, J. Phys. Chem. **96**, 10 597 (1992).

[18] M. Pellarin *et al.*, Chem. Phys. Lett. **277**, 96 (1997).

[19] C. Ray *et al.*, Phys. Rev. Lett. **80**, 5365 (1998).

[20] T. Ohtsuki *et al.*, Phys. Rev. Lett. **77**, 3522 (1996).

[21] T. Ohtsuki *et al.*, Phys. Rev. Lett. **81**, 967 (1998).

[22] T. Ohtsuki *et al.*, J. Am. Chem. Soc. **117**, 12 869 (1995).

[23] T. Ohtsuki *et al.*, J. Radioanal. Nucl. Chem. **239**, 365 (1999).

[24] T. Ohtsuki *et al.*, Phys. Rev. B **60**, 1531 (1999).

[25] *Table of Isotopes*, 8th ed., edited by R.B. Firestone *et al.* (Wiley, New York, 1996), Vol. I.

[26] K. Ohno *et al.*, Phys. Rev. Lett. **76**, 3590 (1996).

[27] K. Ohno *et al.*, Phys. Rev. B **56**, 1009 (1997).

[28] K. Shiga *et al.*, Modell. Simul. Mater. Sci. Eng. **7**, 621 (1999).