*J. Chem. Eng. Data* **2010,** *55,* 871–875 **871**

# Heat Capacity and Standard Thermodynamic Functions of a Fullerene Complex, $((CH_3)_3Si)_{12}C_{60}$, over the Range from $T \rightarrow 0$ K to $T = 350$ K

**Alexey V. Markin,*,[†] Vitaly A. Ruchenin,[†] Natalia N. Smirnova,[†] Elena A. Gorina,[‡] Sophia N. Titova,[‡] and Georgy A. Domrachev[‡]**

Chemistry Institute, Nizhny Novgorod State University, Gagarin Pr. 23/5, 603950, Nizhny Novgorod, Russian Federation, and G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinin Str. 49, 603950, Nizhny Novgorod, Russian Federation

Low-temperature heat capacities of the crystalline fullerene complex $((CH_3)_3Si)_{12}C_{60}$ have been measured by a precision adiabatic calorimeter over the temperature range from $T = (6.5 \text{ to } 350)$ K for the first time. The experimental results have been used to calculate the standard ($p^o = 0.1$ MPa) thermodynamic functions: molar heat capacities, $C^o_{p,\mathrm{m}}$, enthalpy, $H^o(T) - H^o(0)$, entropy, $S^o(T)$, and Gibbs energy, $G^o(T) - H^o(0)$, of $((CH_3)_3Si)_{12}C_{60}$(cr) over the range from $T \rightarrow 0$ K to $T = 350$ K. The low-temperature ($T < 50$ K) dependence of the heat capacity was analyzed on the basis of Debye's heat capacity theory of solids and its fractal variant. Following that analysis, the characteristic temperatures as well as the fractal dimension were determined, and some conclusions about the structure topology were made. The standard entropy of formation at $T = 298.15$ K of $((CH_3)_3Si)_{12}C_{60}$(cr) was calculated. The standard thermodynamic properties of tested fullerene complex and previously studied $C_{60}$ fullerite/fullerene complex $(t\text{-Bu})_{12}C_{60}$ were compared.

## Introduction

The electronic structure of a fullerene $C_{60}$ molecule with its 30 double bonds and the tension due to the pyramidalization of $\sigma$-bonds of carbon facilitate the reactions via the mechanism of [2 + 2] cycloaddition.[1] It was shown by us earlier[2] that the interaction of the sodium derivative of fullerene $Na_{12}C_{60}(THF)_x$ with trimethylchlorosilane ($Me_3SiCl$) in toluene solution leads to the formation of the monomeric complex $((CH_3)_3Si)_{12}C_{60}$. This compound was for the first time prepared and characterized by IR, NMR, and mass spectrometry methods.[3]

The thermodynamic properties of fullerene complexes containing trimethylsilyl groups, $[((CH_3)_3Si)_nC_{60}]_2$, $n = 3$ and 7, were studied by us earlier[4,5] in a wide temperature range. Thermodynamic properties of the monomeric complex $((CH_3)_3Si)_{12}C_{60}$ have not yet been studied. These properties are, however, necessary to detect the influence of trimethylsilyl groups on the thermodynamic characteristics and the thermal stability of the above compound. These data are necessary as the fundamental data for new functional derivatives of $C_{60}$. Knowledge of these functions at various temperatures will allow an assessment of different chemical processes with $((CH_3)_3Si)_{12}C_{60}$ under specified conditions.

The purpose of the present study is to measure the low-temperature heat capacities by adiabatic calorimetry over the temperature range $T = (6.5 \text{ to } 350)$ K of the crystalline fullerene complex $((CH_3)_3Si)_{12}C_{60}$, to calculate the standard thermodynamic functions: $C^o_{p,\mathrm{m}}$, $H^o(T) - H^o(0)$, $S^o(T)$, and $G^o(T) - H^o(0)$ of $((CH_3)_3Si)_{12}C_{60}$(cr) over the range from $T \rightarrow 0$ K to $T = 350$ K, to determine the characteristic temperatures and fractal dimension $D$, to establish the structure topology, to calculate the standard entropy of formation at $T = 298.15$ K of $((CH_3)_3Si)_{12}C_{60}$(cr), and to compare the thermodynamic characteristics of the fullerene complex under study, $C_{60}$[6] and $(t\text{-Bu})_{12}C_{60}$.[7]

## Experimental Section

***Synthesis and Characterization of the Fullerene Complex $((CH_3)_3Si)_{12}C_{60}$.*** The twice-sublimated fine-crystalline powder of fullerite (with not more than 0.0002 mass fraction of impurities) produced by the Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod, was used as the starting material. The sample of the fullerene complex $((CH_3)_3Si)_{12}C_{60}$ was synthesized by the procedure described earlier.[3] The fullerene complex $((CH_3)_3Si)_{12}C_{60}$ resulting from the reaction of $Na_{12}C_{60}(THF)_x$ with $Me_3SiCl$ was identified by IR spectroscopy, NMR spectroscopy, and also desorption chemical ionization (DCI) negative and electron spin ionization (ESI) negative mass spectroscopy.[3] The solubility of the complex in toluene and aliphatic solvents points to its nonionic structure.

The synthesis and separation of $((CH_3)_3Si)_{12}C_{60}$ were conducted in evacuated ampules. The IR spectrum and DCI negative and ESI negative mass spectra were recorded on an IR Fourier spectrometer (FSM 1201) and Finnigan MAT 8200 instrument, respectively. The corresponding spectra, their interpretation, and the data on the structure and composition of the complex are cited elsewhere.[3] The high intensity of bands corresponding to $Me_3Si$ groups and the practically full disappearance of bands for $C_{60}$ are typical for an IR spectrum of $(Me_3Si)_{12}C_{60}$.[3]

The $((CH_3)_3Si)_{12}C_{60}$ was treated by gaseous HCl in argon to prove that a fullerene fragment was saved. The resulting $C_{60}$ was identified by IR spectroscopy and high-performance liquid chromatography.

The tested sample is relatively unstable in the air; it is easily hydrolyzed through a $Si-C_{60}$ bond, and therefore all operations related to its preparation for calorimetric measurements were conducted in a chamber in a flow of high-purity argon.

---

* To whom correspondence may be addressed. Fax: +7-831-4345056. E-mail: markin@calorimetry-center.ru.

[†] Nizhny Novgorod State University.

[‡] Russian Academy of Sciences.

10.1021/je900489g CCC: $40.75

***Adiabatic Calorimetry.*** A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range of $6.5 \leq (T/\mathrm{K}) \leq 350$. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[8,9] All of the measurements were performed with a computer-controlled measuring system comprised of an analog-to-digital converter, a digital-to-analog converter, and a switch. The calorimetric cell is a thin-walled cylindrical vessel made from titanium with a volume of $1.5 \cdot 10^{-6}$ m$^3$. Its mass is (2.040 ± 0.005) g. A miniature iron−rhodium resistance thermometer (with the nominal resistance of 100 Ω) was used to measure the temperature of the sample. The thermometer was calibrated on the basis of IST-90 by the Russian Metrology Research Institute, Moscow region, Russia. The difference in temperature between the ampule and an adiabatic shield was controlled by a four-junction copper−iron−chromel thermocouple. The sensitivity of the thermometric circuit was $1 \cdot 10^{-3}$ K, with the analog-to-digital converter pf 0.1 $\mu$V. The energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded and processed online by a computer. The speed of the computer-controlled measuring system was 10 measurements per second.

To verify the accuracy of the calorimeter, the heat capacities of the reference standard materials (K-2 benzoic acid and $\alpha$-$Al_2O_3$)[10,11] prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation were measured over the temperature range of $6.5 \leq (T/\mathrm{K}) \leq 350$. The sample masses were (0.768 and 1.500) g, respectively. It was established that the apparatus and the measurement technique enable the determination of the heat capacities of substances with an error not exceeding ± 2 % over the temperature range of $6.5 \leq (T/\mathrm{K}) \leq 15$, ± 0.5 % between $T = (15$ to $40)$ K, and ± 0.2 % over the temperature range of $40 \leq (T/\mathrm{K}) \leq 350$. The uncertainty of the phase transition temperatures is within about ± 0.01 K, and that of the enthalpies of transitions is ± 0.2 %.

Heat capacity measurements were continuously and automatically carried out by means of the standard method of intermittently heating the sample and alternately measuring the temperature. The heating rate and temperature increments were controlled at 0.01 K$\cdot$s$^{-1}$ and (0.5 to 2) K. The heating duration was about 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period were always kept within 0.01 K$\cdot$s$^{-1}$ during the acquisition of all heat capacity results. Liquid helium and nitrogen were used as coolants. The ampule with the substance was filled with dry helium as a heat exchange gas to the pressure of 4 kPa at room temperature. The sample mass used for calorimetric measurement was 0.3156 g, which was equivalent to 0.000197 mol in terms of its molar mass, $M = 1598.94$ g$\cdot$mol$^{-1}$. The molar mass of the object under study was calculated from the IUPAC table of atomic weights.[12] The experimental values of $C^{\circ}_{p,\mathrm{m}}$ (160 points) were obtained in two series reflecting the sequence of experiments. The first series of measurements was completed over the temperature range of $6.5 \leq (T/\mathrm{K}) \leq 86$. The second series of $C^{\circ}_{p,\mathrm{m}}$ measurements was carried out between $T = (83$ and $350)$ K. The heat capacity of the sample was between (15 and 30) % of the overall heat capacity of the calorimetric ampule with the substance under temperature change from (6.5 to 350) K.

**Table 1. Experimental Molar Heat Capacities of the Crystalline $((CH_3)_3Si)_{12}C_{60}$ Fullerene Complex ($M = 1598.94$ g$\cdot$mol$^{-1}$)**

| $T$/K | $C^{\circ}_{p,\mathrm{m}}$/J$\cdot$K$^{-1}\cdot$mol$^{-1}$ | $T$/K | $C^{\circ}_{p,\mathrm{m}}$/J$\cdot$K$^{-1}\cdot$mol$^{-1}$ | $T$/K | $C^{\circ}_{p,\mathrm{m}}$/J$\cdot$K$^{-1}\cdot$mol$^{-1}$ |
|---|---|---|---|---|---|
| Series 1 | | | | | |
| 6.48 | 6.34 | 9.02 | 18.1 | 38.09 | 212.5 |
| 6.71 | 7.20 | 9.21 | 19.2 | 41.17 | 232.1 |
| 6.93 | 8.20 | 9.41 | 20.3 | 43.22 | 245.0 |
| 7.05 | 8.50 | 9.64 | 21.7 | 45.77 | 259.6 |
| 7.13 | 8.94 | 9.90 | 23.2 | 48.32 | 274.9 |
| 7.27 | 9.51 | 10.17 | 25.3 | 50.86 | 290.4 |
| 7.39 | 10.1 | 10.48 | 27.2 | 53.61 | 305.1 |
| 7.47 | 10.5 | 10.81 | 29.2 | 55.93 | 318.2 |
| 7.55 | 10.8 | 11.18 | 32.3 | 58.47 | 331.1 |
| 7.65 | 11.2 | 11.59 | 35.5 | 61.02 | 346.1 |
| 7.74 | 11.7 | 12.07 | 39.1 | 63.19 | 359.0 |
| 7.84 | 12.1 | 13.20 | 47.3 | 66.18 | 376.1 |
| 7.94 | 12.8 | 14.69 | 59.28 | 68.69 | 392.4 |
| 8.04 | 13.1 | 16.23 | 68.70 | 71.63 | 412.0 |
| 8.15 | 13.7 | 17.84 | 80.00 | 73.74 | 425.0 |
| 8.19 | 13.8 | 19.52 | 91.30 | 76.27 | 437.9 |
| 8.34 | 14.6 | 22.36 | 108.7 | 78.79 | 450.3 |
| 8.38 | 14.8 | 25.09 | 125.7 | 81.32 | 464.2 |
| 8.47 | 15.3 | 27.72 | 142.6 | 84.07 | 477.8 |
| 8.59 | 15.8 | 30.36 | 159.1 | 85.53 | 483.2 |
| 8.71 | 16.7 | 32.95 | 175.8 | 86.36 | 490.0 |
| 8.85 | 17.1 | 35.53 | 193.6 | | |
| Series 2 | | | | | |
| 83.85 | 477.4 | 180.25 | 991.3 | 278.59 | 1607 |
| 87.20 | 492.5 | 183.27 | 1011 | 281.41 | 1628 |
| 88.88 | 502.9 | 186.27 | 1028 | 284.20 | 1645 |
| 90.56 | 509.7 | 189.31 | 1047 | 286.90 | 1658 |
| 91.40 | 514.4 | 192.31 | 1065 | 289.68 | 1676 |
| 93.92 | 524.9 | 195.30 | 1080 | 292.45 | 1690 |
| 97.33 | 543.6 | 198.82 | 1103 | 294.90 | 1703 |
| 100.43 | 558.5 | 202.33 | 1121 | 297.95 | 1720 |
| 103.54 | 578.2 | 205.30 | 1144 | 300.67 | 1737 |
| 106.65 | 594.3 | 208.28 | 1159 | 303.37 | 1752 |
| 109.77 | 613.7 | 211.24 | 1180 | 306.01 | 1766 |
| 112.87 | 629.8 | 214.21 | 1192 | 308.63 | 1781 |
| 115.97 | 644.2 | 217.17 | 1213 | 311.22 | 1793 |
| 119.08 | 662.1 | 220.12 | 1233 | 313.77 | 1805 |
| 122.17 | 675.5 | 223.07 | 1254 | 316.26 | 1817 |
| 125.26 | 691.7 | 226.01 | 1271 | 318.73 | 1829 |
| 128.35 | 707.9 | 228.96 | 1289 | 321.17 | 1842 |
| 131.43 | 726.1 | 231.89 | 1308 | 323.53 | 1855 |
| 134.51 | 740.2 | 234.82 | 1327 | 325.89 | 1869 |
| 137.58 | 756.7 | 237.74 | 1345 | 327.80 | 1880 |
| 140.74 | 774.3 | 240.66 | 1364 | 330.08 | 1893 |
| 143.81 | 791.4 | 243.58 | 1380 | 332.31 | 1908 |
| 146.88 | 810.0 | 247.30 | 1405 | 334.54 | 1918 |
| 149.94 | 826.0 | 250.00 | 1426 | 336.78 | 1931 |
| 152.98 | 844.0 | 252.89 | 1442 | 339.23 | 1944 |
| 156.03 | 858.6 | 256.30 | 1468 | 341.66 | 1957 |
| 159.08 | 875.3 | 258.66 | 1484 | 344.00 | 1970 |
| 162.13 | 894.0 | 261.53 | 1499 | 346.34 | 1983 |
| 165.16 | 907.2 | 264.40 | 1518 | 348.79 | 1995 |
| 168.19 | 922.2 | 267.26 | 1539 | | |
| 171.21 | 939.6 | 270.10 | 1561 | | |
| 174.23 | 957.7 | 272.95 | 1575 | | |
| 177.25 | 976.4 | 275.78 | 1594 | | |

## Results and Discussion

***Heat Capacity.*** All experimental results of the molar heat capacity of $((CH_3)_3Si)_{12}C_{60}$ over the range from $T = (6.5$ to $350)$ K are listed in Table 1 and plotted in Figure 1. The heat capacity $C^{\circ}_{p,\mathrm{m}}$ of $((CH_3)_3Si)_{12}C_{60}$ rises gradually with temperature increase. It was shown that the structure of the compound was stable over the temperature range between $T = (6.5$ and $350)$ K; that is, no phase change, association, or thermal decomposition occurred.

The experimental points of $C^{\circ}_{p,\mathrm{m}}$ in the temperature range between $T = (6$ and $350)$ K were fitted by means of the least-squares method, and the polynomial equations of the $C^{\circ}_{p,\mathrm{m}}$ versus temperature is the following: for the range from $T = (7$ to $22)$ K,

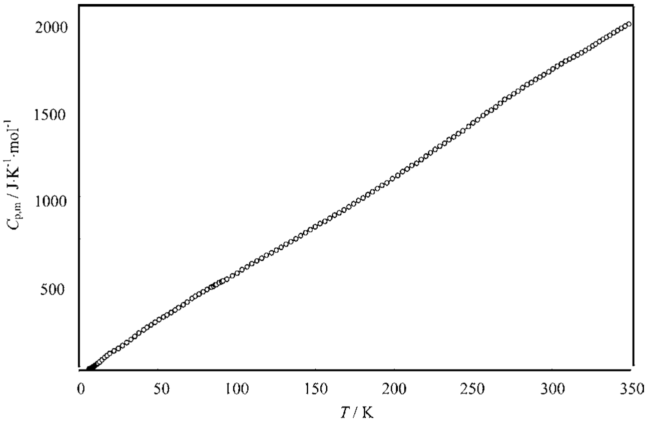

**Figure 1.** Curve of experimental molar heat capacities of $((CH_3)_3Si)_{12}C_{60}$ versus temperature ($T$).

**Table 2. Coefficients of Equations 1 and 2**

| | | $T$/K | | |
|---|---|---|---|---|
| | | 7 to 22 | 20 to 100 | 98 to 350 |
| coefficients·$10^{-3}$/ (J·K$^{-1}$·mol$^{-1}$) | $A$ | 0.03649929 | −0.727608 | −8.76358 |
| | $B$ | −1.052393 | 4.58564 | 11.492 |
| | $C$ | −5.063595 | −11.1 | −6.21314 |
| | $D$ | −11.25887 | 14.7563 | 1.89286 |
| | $E$ | −14.10511 | −11.4005 | −0.350551 |
| | $F$ | −10.06678 | 5.29108 | 0.0404033 |
| | $G$ | −3.805658 | −1.45319 | −0.00282877 |
| | $H$ | −0.5910049 | 0.217539 | 0.000110006 |
| | $I$ | | −0.0136743 | $-1.82079 \cdot 10^{-6}$ |

$$C^{o}_{p,m} = A + B\ln(T/30) + C(\ln(T/30))^2 + D(\ln(T/30))^3 + E(\ln(T/30))^4 + F(\ln(T/30))^5 + G(\ln(T/30))^6 + H(\ln(T/30))^7 + I(\ln(T/30))^8 \quad (1)$$

and for the ranges from $T = (20 \text{ to } 100)$ K and $T = (98 \text{ to } 350)$ K

$$C^{o}_{p,m} = A + B(T/30) + C(T/30)^2 + D(T/30)^3 + E(T/30)^4 + F(T/30)^5 + G(T/30)^6 + H(T/30)^7 + I(T/30)^8 \quad (2)$$

The corresponding coefficients ($A$, $B$, $C$, etc.) for eqs 1 and 2 are given in Table 2.

Their standard deviations from the smoothed $C^{o}_{p,m} = f(T)$ curve were listed in Figure 2.

As Figure 1 illustrates, an orientation phase transformation and glass-like transition of the $G$-type which are seen for the initial fullerite $C_{60}$ over the range from $T = (185 \text{ to } 275)$ K and $T = (81.0 \text{ to } 88.5)$ K are absent in the $C^{o}_{p,m} = f(T)$ plot of the tested fullerene complex.[6] The nature of these transitions is described sufficiently in ref 6. The above transformations were not apparent in the compound under study because of the absence of free fullerene fragments. So, in the range of low temperatures from $T = (100 \text{ to } 250)$ K this $C^{o}_{p,m}$ is linear with $T$.

In the fractal version of Debye's theory of the heat capacity of solids,[13−16] the exponent of $T$ in the expression for heat capacity is referred to as fractal dimension. The values of this key parameter denoted by $D$ were determined from experimental results on the heat capacity of $((CH_3)_3Si)_{12}C_{60}$ and literature data for $C_{60}$ fullerite[6] and $(t\text{-Bu})_{12}C_{60}$[7] (Table 3). The values of $D$ were estimated using the technique described, for example, in ref 16 with the use of eq 3

$$C_v = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\Theta_{max}) \quad (3)$$

where $N$ is the number of atoms in a molecule, $k$ is the Boltzmann constant, $\gamma(D+1)$ is the $\gamma$-function, $\xi(D+1)$ is the Riemann $\xi$-function, and $\Theta_{max}$ is the characteristic temperature.

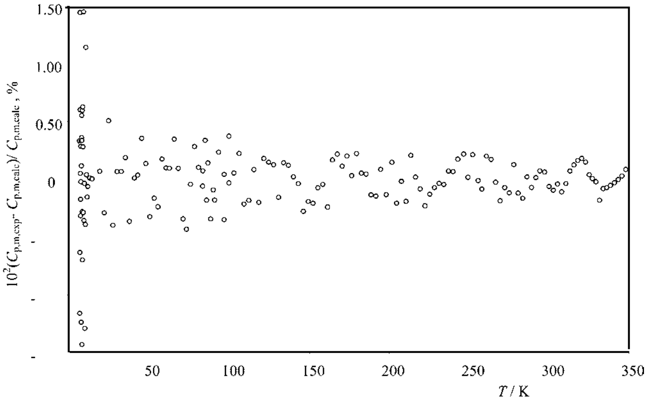

**Figure 2.** Deviations of experimental heat capacities $C^{o}_{p,m,exp}$ from values $C^{o}_{p,m,calc}$ calculated from eqs 1 and 2.

**Table 3. Fractal Dimensions and Characteristic Temperatures of $((CH_3)_3Si)_{12}C_{60}$, $C_{60}$, and $(t\text{-Bu})_{12}C_{60}$**

| substance | $\Delta T$/K | $D$ | $\Theta_{max}$/K | $\delta$/% |
|---|---|---|---|---|
| $((CH_3)_3Si)_{12}C_{60}$ | 20 to 50 | 1.3 | 261.6 | 0.9 |
| $C_{60}$[6] | 20 to 50 | 3.0 | 231.6 | 0.9 |
| $(t\text{-Bu})_{12}C_{60}$[7] | 20 to 50 | 1.5 | 264.0 | 0.4 |

To sufficient accuracy, it can be taken that isobaric and isochoric heat capacities are equal at temperatures below 50 K. Then, using eq 3, we find that, in the temperature range of $20 \le (T/K) \le 50$, $D = 1.3$ for $((CH_3)_3Si)_{12}C_{60}$, $D = 3$ for the $C_{60}$, and $D = 1.5$ for the $(t\text{-Bu})_{12}C_{60}$. According to refs 13 to 16, $D = 1$ corresponds to the solids with chain structure, $D = 2$ to those with a layered structure, and $D = 3$ to those with a spatial structure. Thus, it follows from the above that $((CH_3)_3Si)_{12}C_{60}$ as $(t\text{-Bu})_{12}C_{60}$ have a mixed, chain-layer structure topology, whereas $C_{60}$ has a spatial structure.

As can be seen from the comparison of the values of characteristic temperature $\Theta_{max}$ calculated in the temperature range of $20 \le (T/K) \le 50$, the $\Theta_{max}(C_{60}) < \Theta_{max}\{((CH_3)_3Si)_{12}C_{60}\}$ and $\Theta_{max}\{(t\text{-Bu})_{12}C_{60}\}$, while $\Theta_{max}\{((CH_3)_3Si)_{12}C_{60}\} \approx \Theta_{max}\{(t\text{-Bu})_{12}C_{60}\}$. Probably, it should be concluded that the examined derivatives of $C_{60}$ have a similar hardness for their crystalline structure.

In Figure 3, the temperature dependence of the molar heat capacity $C^{o}_{p,m}$ for $((CH_3)_3Si)_{12}C_{60}$ (curve 1), $(t\text{-Bu})_{12}C_{60}$[7] (curve 2), and fullerite $C_{60}$[6](curve 3) are shown. As can be learned, the molar heat capacities of $((CH_3)_3Si)_{12}C_{60}$ and $(t\text{-Bu})_{12}C_{60}$

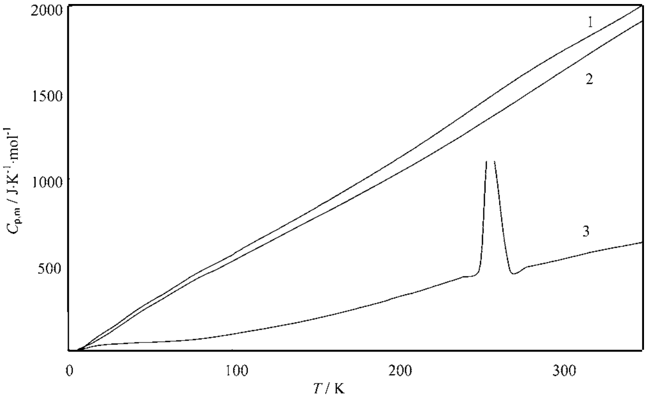

**Figure 3.** Curves of smoothed molar heat capacities of $((CH_3)_3Si)_{12}C_{60}$ (1), $(t\text{-Bu})_{12}C_{60}$[7] (2), and $C_{60}$[6] (3).

**Table 4. Smoothed Molar Heat Capacities and Thermodynamic Functions of the $((CH_3)_3Si)_{12}C_{60}$ Fullerene Complex ($M = 1598.94$ g·mol$^{-1}$, $p^o = 0.1$ MPa)**

| $T$ | $C^o_{p,m}$ | $H^o(T) - H^o(0)$ | $S^o(T)$ | $-[G^o(T) - H^o(0)]$ |
|---|---|---|---|---|
| K | J·K$^{-1}$·mol$^{-1}$ | kJ·mol$^{-1}$ | J·K$^{-1}$·mol$^{-1}$ | kJ·mol$^{-1}$ |
| 5 | 3.20 | 0.004 | 1.07 | 0.0013 |
| 10 | 23.9 | 0.0627 | 8.34 | 0.0207 |
| 15 | 60.7 | 0.2737 | 25.0 | 0.1009 |
| 20 | 94.49 | 0.6619 | 47.06 | 0.2794 |
| 30 | 155.5 | 1.908 | 96.79 | 0.996 |
| 40 | 224.5 | 3.809 | 151.0 | 2.231 |
| 50 | 284.6 | 6.364 | 207.8 | 4.024 |
| 60 | 340.5 | 9.488 | 264.6 | 6.386 |
| 80 | 457.9 | 17.49 | 378.9 | 12.82 |
| 90 | 506.5 | 22.32 | 435.7 | 16.89 |
| 100 | 556.5 | 27.64 | 491.6 | 21.53 |
| 110 | 613.6 | 33.50 | 547.4 | 26.72 |
| 120 | 665.5 | 39.89 | 603.1 | 32.48 |
| 130 | 717.4 | 46.81 | 658.4 | 38.78 |
| 140 | 770.5 | 54.24 | 713.5 | 45.64 |
| 150 | 824.8 | 62.22 | 768.5 | 53.05 |
| 160 | 880.0 | 70.74 | 823.5 | 61.01 |
| 170 | 935.8 | 79.82 | 878.5 | 69.52 |
| 180 | 992.4 | 89.46 | 933.6 | 78.58 |
| 190 | 1050 | 99.67 | 988.8 | 88.20 |
| 200 | 1109 | 110.5 | 1044 | 98.36 |
| 210 | 1169 | 121.8 | 1100 | 109.1 |
| 220 | 1231 | 133.8 | 1155 | 120.4 |
| 230 | 1295 | 146.5 | 1212 | 132.2 |
| 240 | 1360 | 159.8 | 1268 | 144.6 |
| 250 | 1426 | 173.7 | 1325 | 157.6 |
| 260 | 1492 | 188.3 | 1382 | 171.1 |
| 270 | 1556 | 203.5 | 1440 | 185.2 |
| 280 | 1617 | 219.4 | 1497 | 199.9 |
| 290 | 1676 | 235.9 | 1555 | 215.1 |
| 298.15 | 1722 | 249.7 | 1602 | 228.0 |
| 300 | 1732 | 252.9 | 1613 | 231.0 |
| 310 | 1786 | 270.5 | 1671 | 247.4 |
| 320 | 1839 | 288.6 | 1728 | 264.4 |
| 330 | 1892 | 307.3 | 1786 | 282.0 |
| 340 | 1947 | 326.5 | 1843 | 300.1 |
| 350 | 2004 | 346.2 | 1900 | 318.8 |

are higher than the heat capacity of $C_{60}$. Perhaps, the observed behavior is due to the contribution of 12 groups at $C_{60}$. The groups in the derivatives differ insignificantly and have similar values of the heat capacity. The different character in the increase of the heat capacity for the compounds being compared takes place in the ultralow temperature range and is caused by different crystalline packing.

***Standard Thermodynamic Functions of the Fullerene Complex $((CH_3)_3Si)_{12}C_{60}$.*** To calculate the standard thermodynamic functions in Table 4 of $((CH_3)_3Si)_{12}C_{60}$, their smoothed molar heat capacities $C^o_{p,m}$ were extrapolated from the temperature of the measurement beginning at approximately $T = 7$ K to $T \rightarrow 0$ K with the Debye law in the low-temperature limit:[17]

$$C^o_{p,m} = nD(\theta_D/T) \tag{4}$$

where $n = 30$ is the number of degrees of freedom, $D$ is the Debye function, $\theta_D = 91.9$ K refers to the Debye characteristic temperature. Using the above parameters,[17] eq 4 describes the $C^o_{p,m}$ values of the compound over the range of $7 \leq (T/K) \leq 12$ with the uncertainties of ± 1 %. In calculating the functions, it was assumed that eq 4 reproduced the $C^o_{p,m}$ values of $((CH_3)_3Si)_{12}C_{60}$ at $T \leq 7$ K with the same uncertainties.

The calculations of $[H^o(T) - H^o(0)]$ and $S^o(T)$ were made by numerical integration of the curves with respect to $T$ and ln $T$, respectively. The Gibbs energy $[G^o(T) - H^o(0)]$ was calculated from $[H^o(T) - H^o(0)]$ and $S^o(T)$ values at corresponding temperatures. The zero entropy of $((CH_3)_3Si)_{12}C_{60}$ was assumed to be zero. The calculation procedure was described in detail in ref 18. The uncertainties determined for the function values are ± 2 % at $T < 15$ K, ± 0.5 % from (15 to 40) K, and ± 0.3 % from $T = (40$ to $350)$ K.

Using the value of the absolute entropy of $((CH_3)_3Si)_{12}C_{60}$ in Table 3 and the elemental substances, namely, carbon,[19] hydrogen,[20] and silicon,[20] the standard entropy of formation at $T = 298.15$ K was estimated to be $\Delta_f S^o_m(298.15, ((CH_3)_3Si)_{12}C_{60}, \text{cr}) = -6231 \pm 11$ J·K$^{-1}$·mol$^{-1}$.

The values obtained fit the equation

$$96C(gr) + 54H_2(g) + 12Si(cr) \rightarrow ((CH_3)_3Si)_{12}C_{60}(cr) \tag{5}$$

where gr, cr, and g are graphite, crystal, and gas, respectively.

## Conclusions

This work reports low-temperature heat capacities measured by adiabatic calorimetry of the crystalline fullerene complex $((CH_3)_3Si)_{12}C_{60}$. Additionally, the standard thermodynamic functions of $((CH_3)_3Si)_{12}C_{60}(cr)$ over the range from $T \rightarrow 0$ K to $T = 350$ K and the standard entropy of formation at $T = 298.15$ K were derived from these experimental results.

The low-temperature ($T \leq 50$ K) dependence of the heat capacity was analyzed on the basis of the heat capacity theory of solids of Debye and the multifractal variant, and as a result, a chain-layer structure topology was established. The thermodynamic characteristics of $((CH_3)_3Si)_{12}C_{60}$ were compared with the corresponding data for $C_{60}$ and $(t\text{-Bu})_{12}C_{60}$.

## Literature Cited

(1) Rao, A. M.; Zhou, P.; Wang, K. A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W. T.; Be, X. X.; Eklund, P. S.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. Photoinduced polymerization of solid films. *Science* **1993**, *259*, 955–957.

(2) Titova, S. N.; Domrachev, G. A.; Gorina, E. A.; Kalakutskaya, L. V.; Ob'edkov, A. M.; Kaverin, B. S.; Ketkov, S. Yu.; Lopatin, M. A.; Markin, A. V.; Smirnova, N. N.; Zhogova, K. B. Interaction of sodium fullerene derivatives with trimethyl-chlorosilane. *Phys. Solid State* **2006**, *48*, 1000–1006.

(3) Titova, S. N.; Domrachev, G. A.; Gorina, E. A.; Kalakutskaya, L. V.; Ob'edkov, A. M.; Kaverin, B. S.; Ketkov, S. Yu.; Lopatin, M. A.; Markin, A. V.; Smirnova, N. N.; Zhogova, K. B. Stoichiometric synthesis of fullerene compounds with lithium and sodium and analysis of their IR and EPR spectra. *Phys. Solid State* **2006**, *48*, 1323–1327.

(4) Smirnova, N. N.; Markin, A. V.; Ruchenin, V. A.; Titova, S. N.; Gorina, E. A.; Kalakutskaya, L. V.; Domrachev, G. A.; Ob'edkov, A. M.; Ketkov, S. Yu. Thermodynamic properties of fullerene complex $[(Me_3Si)_7C_{60}]_2$. *Russ. J. Phys. Chem.* **2007**, *81*, 854–860.

(5) Markin, A. V.; Smirnova, N. N.; Bykova, T. A.; Ruchenin, V. A.; Titova, S. N.; Gorina, E. A.; Kalakutskaya, L. V.; Ob'edkov, A. M.; Ketkov, S. Yu.; Domrachev, G. A. Thermodynamics of dimer fullerene complex $[(Me_3Si)_3C_{60}]_2$ in the range from $T \rightarrow 0$ to 480 K. *J. Chem. Thermodyn.* **2007**, *39*, 798–803.

(6) Lebedev, B. V.; Zhogova, K. B.; Kaverin, B. S.; Karnatsevich, V. L.; Lopatin, M. A. Thermodynamics $C_{60}$ fullerene in the range 0−340 K. *Russ. Chem. Bull.* **1996**, *45*, 2113–2117.

(7) Markin, A. V.; Ruchenin, V. A.; Smirnova, N. N.; Gorina, E. A.; Titova, S. N.; Kalakutskaya, L. V.; Domrachev, G. A. Thermodynamic functions of fullerene complex $(t\text{-Bu})_{12}C_{60}$ over temperature range from $T \rightarrow 0$ to 420 K. *Russ. J. Phys. Chem.* **2009**, *83*, 2032–2038.

(8) Varushchenko, R. M.; Druzhinina, A. I.; Sorkin, E. L. Low temperature heat capacity of 1-bromoperfluorooctane. *J. Chem. Thermodyn.* **1997**, *29*, 623–637.

(9) Malyshev, V. M.; Milner, G. A.; Sorkin, E. L.; Shibakin, V. F. An automatic and low-temperature calorimeter. *Prib. Tekh. Eksp.* **1985**, *6*, 195–197.

(10) Ginnings, D. C.; Furukawa, G. T. Heat capacity standards for the range 14 to 1200 K. *J. Am. Chem. Soc.* **1953**, *75*, 522–527.

(11) Gatta, G. D.; Richardson, M. J.; Sarge, S. M.; Stolen, S. Standards, calibration, and guidelines in microcalorimetry. Part 2. Calibration standards for differential calorimetry. *Pure Appl. Chem.* **2006**, *78*, 1455–1476.

(12) Coplen, T. B. Atomic weights of the elements 1999 (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 667–683.
(13) Yakubov, T. S. About heat capacity of solids having fractal character. *Dokl. Akad. Nauk SSSR* **1990**, *310*, 145–149.
(14) Izotov, A. D.; Shebershnyova, O. V.; Gavrichev, K. S. *Fractal model of low-temperature heat capacity*. Third All-Union Conference on Thermal Analysis and Calorimetry, Kazan, Russia, 1996.
(15) Lazarev, V. B.; Izotov, A. D.; Gavrichev, K. S.; Shebersheneva, O. V. Fractal model of heat capacity for substances with diamond-like structures. *Thermochim. Acta* **1995**, *269*, 109–1116.
(16) Lebedev, B. V.; Markin, A. V. Thermodynamics of $C_{60}$ Polyfullerites. *Phys. Solid State* **2002**, *44*, 434–436.
(17) Rabinovich, I. B.; Nistratov, V. P.; Telnoy, V. I.; Sheiman, M. S. *Thermochemical and thermodynamic properties of organometallic compounds*; Begell House: New York, 1999.
(18) McCullough, J. P.; Scott, D. W. *Calorimetry of Non-reacting Systems*; Butterworth: London, 1968.
(19) Cox, J. D.; Wagman, D. D.; Medvedev, V. A., *CODATA Key Values for Thermodynamics*; Hemisphere: New York, 1984; p 1.
(20) Chase, M. W., Jr. NIST-JANAF Thermochemical tables, Monograph 9. *J. Phys. Chem. Ref. Data* **1998**, 1−1951.

Received for review June 13, 2009. Accepted October 29, 2009. The work was performed with the financial support of the Russian Foundation of Basic Research (Project No. 08-03-00214a), Federation Agency for Science and Innovations (contract 02.513.11.0002), and the grant from the President of the Russian Federation (S.Sc.-1396.2008.3).

JE900489G