Low-Temperature Heat Capacity and Standard Thermodynamic Functions of $Li_{12}C_{60}(THF)_{1.4}$ Fulleride[†]

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Low-temperature heat capacities of the crystalline coordination compound $Li_{12}C_{60}(THF)_{1.4}$ have been measured by a precision adiabatic calorimeter over the temperature range $T = 6$ K to $T = 350$ K and by a differential scanning calorimeter over the temperature range $T = 330$ K to $T = 520$ K for the first time. Using the obtained data, the temperature of the onset of $Li_{12}C_{60}(THF)_{1.4}$ destruction was determined to be 468 K. The experimental results have been used to calculate the standard ($p^o = 0.1$ MPa) thermodynamic functions: molar heat capacities $C^o_{p,m}$, enthalpy $H^o(T) - H^o(0)$, entropy $S^o(T)$, and Gibbs energy $G^o(T) - H^o(0)$ of $Li_{12}C_{60}(THF)_{1.4}$ (cr) over the range from $T \to 0$ K to $T = 468$ K. The low-temperature ($T < 50$ K) dependence of the heat capacity was analyzed based on Debye's heat capacity theory of solids and its fractal variant. As results, the characteristic temperatures as well as the fractal dimension were determined, and some conclusions about structure topology are given. The standard entropy of formation at $T = 298.15$ K of $Li_{12}C_{60}(THF)_{1.4}$ (cr) was calculated. The standard thermodynamic properties of tested fulleride and previously studied C_{60} fullerite and hydrofullerene $C_{60}H_{36}$ were compared.

Introduction

The discovery of the method for producing C_{60} fullerenes in macroquantities[1] has led to a new field of research. Because of extremely good prospects of the practical application of fullerenes and their derivatives, the intensity of studies of these materials is continuously increasing.

Lithium doping of fullerene has recently attracted special attention also because of subtle structural and charge transfer effects that take place in alkali metal doped fullerenes A_nC_{60} (A = alkali metal, n = 1,3,4,...) when the metal ion radius is much smaller than the typical size of the tetrahedral and octahedral voids of the pristine C_{60} pseudocubic structure.[2−5] This class of materials has commanded much interest because of its superconducting and magnetic properties.[4] In particular, lithium fulleride $Li_{12}C_{60}$ is of interest as a material used in the development of hydrogen storage cells.[6]

Many scientific groups have investigated the molecular and electronic structure of this compound as well as its phase transformations. On the basis of theoretical calculations, Kohanoff et al.[3] supposed that $Li_{12}C_{60}$ should be a stable highly symmetric "superfulleroid" where the 12 lithium atoms are located above each of the 12 pentagonal faces thus preserving the preferable icosahedral (I_h) symmetry.

This supposition was confirmed by the mass spectroscopy[7] of different lithium−fullerene clusters Li_nC_{60} prepared by the gas-phase method. The authors found an unusual stability of $Li_{12}C_{60}$ which was not decomposed even being doubly ionized. None of the other alkali metals form such a stable compound. It is the authors' opinion that the highly symmetrical arrangement of the atoms is responsible for the high stability of $Li_{12}C_{60}$, independent of the fullerene core charge, rather than a full occupation of low-lying vacant C_{60} molecular orbitals.

However, up to now, low-temperature heat capacities and standard thermodynamic functions of crystalline $Li_{12}C_{60}$ as the coordination complex $Li_{12}C_{60}(THF)_{1.4}$ (THF: tetrahydrofuran) have not been reported in the literature. These data are, however, necessary as the fundamental data for new functional derivatives of C_{60}. With regard to the foregoing, a thermodynamic study of one of the representatives of fullerides is actual and urgent.[8] Knowledge of these functions at various temperatures will allow an assessment of different chemical processes with $Li_{12}C_{60}(THF)_{1.4}$ under defined conditions.

The purpose of the present study is to measure the low-temperature heat capacities by adiabatic calorimetry and differential scanning calorimetry over the temperature range $T = 6$ K to $T = 520$ K of the crystalline coordination compound $Li_{12}C_{60}(THF)_{1.4}$, to estimate the onset of the temperature of destruction, to calculate the standard thermodynamic functions ($C^o_{p,m}$, $H^o(T) - H^o(0)$, $S^o(T)$, and $G^o(T) - H^o(0)$ of $Li_{12}C_{60}(THF)_{1.4}$ (cr) over the range from $T \to 0$ K to $T = 468$ 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 $Li_{12}C_{60}(THF)_{1.4}$ (cr), and to compare the thermodynamic characteristics of the fulleride under study, C_{60} and $C_{60}H_{36}$.

Experimental Section

Synthesis and Characterization of $Li_{12}C_{60}(THF)_{1.4}$ Fulleride. The twice sublimated fine-crystalline powder of fullerite (not more than 0.02 mass 0.01 of impurities) produced by the

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[†] Part of the special section "2008 European Conference on Thermophysical Properties".

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10.1021/je800765s CCC: $40.75

Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhny Novgorod, was used as the starting material. The solvents (toluene, tetrahydrofurane) were stored over sodium benzophenone ketyl and distilled into a reaction ampule immediately before use. The synthesis and isolation of $Li_{12}C_{60}(THF)_{1.4}$ were performed in a vacuum (10^{-2} Torr). The procedure of preparing $Li_{12}C_{60}(THF)_{1.4}$ has been described in detail earlier.[9]

A solution of lithium naphthalenide in THF [prepared from lithium (0.020 g, 2.86 mmol) and naphthalene (0.380 g, 2.97 mmol) in 5 mL of THF] was added to a solution of the C_{60} fullerene (0.161 g, 0.22 mmol) in toluene (100 mL) with vigorous stirring for 2 h at 200 K. The reaction proceeded immediately after mixing the reactants. After precipitation of the $Li_{12}C_{60}(THF)_{1.4}$, the solution was decanted, and the product was washed three times with toluene, dried, and isolated. The yield of $Li_{12}C_{60}(THF)_{1.4}$ was 95 % with respect to the lithium weight. It is a black solid insoluble in aliphatic and aromatic hydrocarbons, highly sensitive to oxygen and moisture, and stable in an inert atmosphere.

The structure and properties of the compound synthesized were investigated using IR and Raman spectroscopy, ^{13}C and ^{7}Li NMR spectrometry, and TGA (Thermal Gravimetric Analysis). The theoretically proposed structure of $Li_{12}C_{60}$[3] agrees with the series of experimental data. The low-frequency shift of the $T_u(4)$ peak in the IR spectrum and of the A_g peak in the Raman spectrum on going from C_{60} to $Li_{12}C_{60}(THF)_{1.4}$ [(84 and 40) cm^{-1}, respectively] as well as the change of the ^{13}C NMR signal from 142.8 ppm (C_{60}) to 185 ppm ($Li_{12}C_{60}(THF)_{1.4}$) are indicative of the electron charge transfer from Li to C_{60}.[10] The single narrow resonance in the ^{7}Li NMR spectrum of $Li_{12}C_{60}(THF)_{1.4}$ (2.04 ppm in THF; 0.72 ppm in DMSO relative to LiCl) can be a result of an equivalent location of lithium atoms around the fullerene cage. Investigation of the thermal behavior of $Li_{12}C_{60}(THF)_{1.4}$ shows that this complex is stable up to $T = 470$ K. The decomposition of the compound begins at $T = 470$ K, and the weight loss in the $T = (470$ to $595)$ K temperature range is ~12 %. In this case, the sample weight decrease on heating is caused by the elimination of coordinated THF. The average $Li_{12}C_{60}$:THF molar ratio is estimated on the basis of TGA as 1:1.4.

The tested sample is relatively unstable in air, and therefore all operations related to its preparation for calorimetric measurements were conducted in a special box in a flow of high-purity argon.

Adiabatic Calorimetry. A precision automatic adiabatic calorimeter (BCT-3) was used to measure heat capacities over the temperature range $6 \leq (T/K) \leq 350$. The calorimeter was established in the "Termis" joint-stock company at the All-Russian Metrology Research Institute, Moscow region, Russia. The principle and structure of the adiabatic calorimeter are described in detail elsewhere.[11,12] Briefly, all measurements were monitored by a computer-measuring system consisting of a computer, analog-to-digital and digital-to-analog converters, and a switch. The calorimetric ampule is a thin-walled cylindrical vessel from titanium of $1.5 \cdot 10^{-6}$ m^3. Its mass is 2.0400 g. The miniature iron−rhodium resistance thermometer (a nominal resistance of 100 Ω) was applied 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 and of the analog-to-digital converter 0.1 μV. 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-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 α-Al_2O_3)[13,14] prepared at the Institute of Metrology of the State Standard Committee of the Russian Federation were measured over the temperature range $6 \leq (T/K) \leq 350$. The sample masses were (0.7682 and 1.5000) 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 $6 \leq (T/K) \leq 15$, ± 0.5 % between $T = (15$ and $40)$ K, and ± 0.2 % over the temperature range $40 \leq (T/K) \leq 350$ and the measuring of the phase transition temperatures within about ± 0.01 K and the enthalpies of transitions with the error of ± 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 ~ 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 coolant. 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 measurements was 0.2176 g, which was equivalent to 0.0002405 mol in terms of its molar mass, $M = 904.797$ $g \cdot mol^{-1}$. The molar mass of the object under study was calculated from the IUPAC table of atomic weights.[15] The experimental values of $C^{o}_{p,m}$ (158 points) were obtained in two series reflecting the sequence of experiments. The first series of measurements was completed over the temperature range $6 \leq (T/K) \leq 88$. The second series of $C^{o}_{p,m}$ measurements was carried out between $T = (80$ 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 to 350) K.

Differential Scanning Calorimety. An automatic thermoanalytical complex, viz., a differential scanning calorimeter operating on the principle of a triple thermal bridge (ADCTTB), was used to measure the heat capacities over the temperature range $330 \leq (T/K) \leq 520$.[16] The design of the device and the measurement procedure of the heat capacities were demonstrated in detail in the above-mentioned paper. The reliability of the calorimeter operation was checked by measuring the heat capacity of the standard sample of synthetic corundum and the thermodynamic characteristics of fusion of indium, tin, and lead. As the result of the calibrations, it was found that the calorimeter and the measurement technique make it possible to obtain the heat capacity values with the maximum error of ± 2 % and the transformation temperatures within ± 0.5 K. Since the heat capacity of the compound examined was also measured over the temperature range $330 \leq (T/K) \leq 350$ in the adiabatic calorimeter with the error of ± 0.2 % and the conditions of measurements in the dynamic device were chosen such that within the above temperature interval the $C^{o}_{p,m}$ values measured with the use of both calorimeters coincided, it was assumed that at $T \geq 350$ K the heat capacities were determined with the error of ± (0.5 to 2.0) %. The results for the heat capacity of the objects under study were obtained over the range 330 ≤

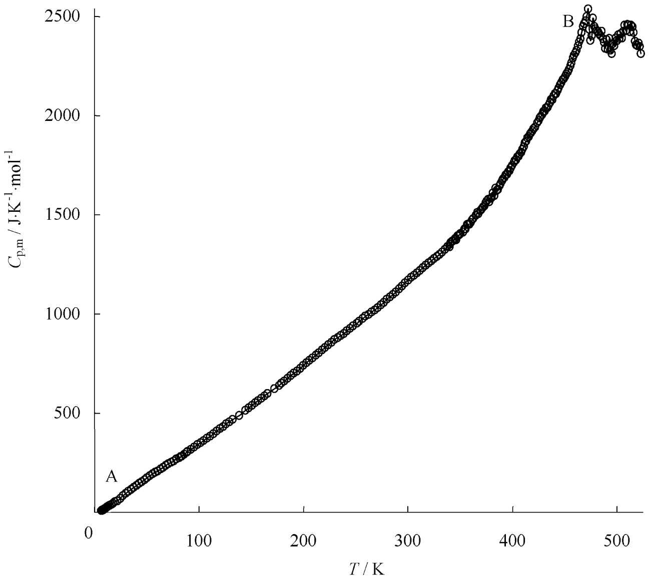

Figure 1. Curve of experimental molar heat capacities of $Li_{12}C_{60}(THF)_{1.4}$ vs temperature (T): AB, crystalline.

Table 1. Coefficients in the Fitting Polynomials for $C^{o}_{p,m} = A + B\cdot\ln(T/30) + C\cdot(\ln(T/30))^2 + D\cdot(\ln(T/30))^3 + E\cdot(\ln(T/30))^4 + F\cdot(\ln(T/30))^5 + G\cdot(\ln(T/30))^6 + H\cdot(\ln(T/30))^7 + I\cdot(\ln(T/30))^8 + K\cdot(\ln(T/30))^9$

		T/K	
		20 to 120	200 to 300
coefficients/ ($J\cdot K^{-1}\cdot mol^{-1}$)	$A\cdot 10^{-2}$	−3.73185	345.244
	$B\cdot 10^{-2}$	17.4475	−358.740
	$C\cdot 10^{-2}$	−31.9888	156.441
	$D\cdot 10^{-2}$	34.7172	−37.0464
	$E\cdot 10^{-2}$	−22.8510	5.17944
	$F\cdot 10^{-2}$	9.47471	−0.428202
	$G\cdot 10^{-2}$	−2.48998	0.0193960
	H	$0.402663\cdot 10^{2}$	$-3.71398\cdot 10^{-2}$
	I	$-0.0365729\cdot 10^{2}$	−
	K	$1.42830\cdot 10^{-1}$	−

Table 2. Fractal Dimensions and Characteristic Temperatures of $Li_{12}C_{60}(THF)_{1.4}$, C_{60}, and $C_{60}H_{36}$

	ΔT		Θ_{max}	δ
substance	K	D	K	%
$Li_{12}C_{60}(THF)_{1.4}$	25 to 45	1.5	176.0	1.3
C_{60}[17]	20 to 50	3.0	231.6	0.9
$C_{60}H_{36}$[22]	25 to 45	1.0	228.0	1.9

(T/K) ≤ 520 at the average rate of heating of the calorimeter and the substance of 0.025 $K\cdot s^{-1}$. The sample mass used for the calorimetric measurements was 0.2095 g. The heat capacity of the samples varied from 30 % to 70 % of the overall heat capacity of the calorimetric ampule with the substance over the range 330 ≤ (T/K) ≤ 520.

Results and Discussion

Low-Temperature Heat Capacity. All experimental results of the molar heat capacity of $Li_{12}C_{60}(THF)_{1.4}$ over the range from $T = (6 \text{ to } 520)$ K are plotted in Figure 1. The heat capacity $C^{o}_{p,m}$ of $Li_{12}C_{60}(THF)_{1.4}$ rises gradually with increasing temperature, and there are no distinctive features up to $T = 468$ K (Figure 1, point B). It was shown that the structure of the coordination compound was stable over the temperature range between $T = (6 \text{ and } 468)$ K; that is, no phase change, association, or thermal decomposition occurred. At $T > 468$ K (Figure 1, point B), we have the apparent heat capacities, and the main reason for this is the onset of thermal decomposition of the sample under study.

The experimental points of $C^{o}_{p,m}$ in the temperature interval between $T = (6 \text{ and } 468)$ K were fitted by means of the least-squares method, and polynomial equations of the $C^{o}_{p,m}$ vs temperature have been obtained. For example, the corresponding coefficients (A, B, C, etc.) are given in Table 1.

Their root-mean-square deviation from the smoothed $C^{o}_{p,m} = f(T)$ curve was ± 0.15 % in the range $T = (6 \text{ to } 40)$ K, ± 0.075 % from $T = (40 \text{ to } 80)$ K, ± 0.050 % between $T = (80 \text{ and } 350)$ K, and ± 0.5 % over the range from $T = (350 \text{ to } 468)$ K.

As Figure 1 illustrates, an orientation phase transformation and glasslike 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 fulleride.[17] The nature of these transitions is described sufficiently in full in ref 17. The above transformations do not become apparent in the compound under study due to 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.

The values of the fractal dimension D (Table 2)—the most significant parameter of the fractal version of Debye's theory of the heat capacity of solids[18−21]—were determined from the experimental results on the heat capacity of $Li_{12}C_{60}(THF)_{1.4}$ and literature data for C_{60} fullerite[17] and hydrofullerene $C_{60}H_{36}$.[22] In the fractal version of Debye's theory of the heat capacity of solids, the exponent of T in the expression for heat capacity is denoted fractal dimension D. The values of D allow one to estimate the topology of the structure. The values of D were estimated using the technique described, for example, in ref 20 with the use of eq 1

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

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

For sufficient accuracy, it can be taken that isobaric and isochoric heat capacities are equal at temperatures below 50 K. Then, using eq 1, we find that, in the temperature range 20 ≤ (T/K) ≤ 45, $D = 1.5$ for $Li_{12}C_{60}(THF)_{1.4}$, $D = 3$ for the C_{60}, and $D = 1$ for the $C_{60}H_{36}$. According to refs 18 to 20, $D = 1$ 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 $Li_{12}C_{60}(THF)_{1.4}$ has a mixed, chain-layer structure topology, whereas C_{60} has a spatial structure and $C_{60}H_{36}$ a chain structure topology.

As can be seen from comparison of the values of characteristic temperature Θ_{max} that have been calculated for the temperature interval 25 ≤ (T /K) ≤ 45, the $\Theta_{max}(C_{60}) > \Theta_{max}(C_{60}H_{36}) > \Theta 1(Li_{12}C_{60}(THF)_{1.4})$. It is very likely that C_{60} has a harder crystalline lattice than $C_{60}H_{36}$ and $Li_{12}C_{60}(THF)_{1.4}$ fulleride. That is confirmed by the character of ultralow temperature heat capacities vs T (Figure 2). Therefore, in this temperature interval the significant differences in a quantitative sense for objects under consideration takes place.

In Figure 3, the temperature dependence of the molar heat capacity $C^{o}_{p,m}$ for $Li_{12}C_{60}(THF)_{1.4}$ (curve 1), hydrofullerene $C_{60}H_{36}$[22] (curve 2), and fullerite C_{60}[17](curve 3) is shown. As can be seen, the molar heat capacities of $Li_{12}C_{60}(THF)_{1.4}$ are higher than the heat capacities of $C_{60}H_{36}$ and C_{60}. However, the plots of $C^{o}_{p,m}$ vs T are similar at $T \leq 250$ K. This is certainly not accidental since the main contribution to the heat capacity is made by the skeletal vibrations of spherical carbon surfaces of the above molecules in this temperature range. It is very likely

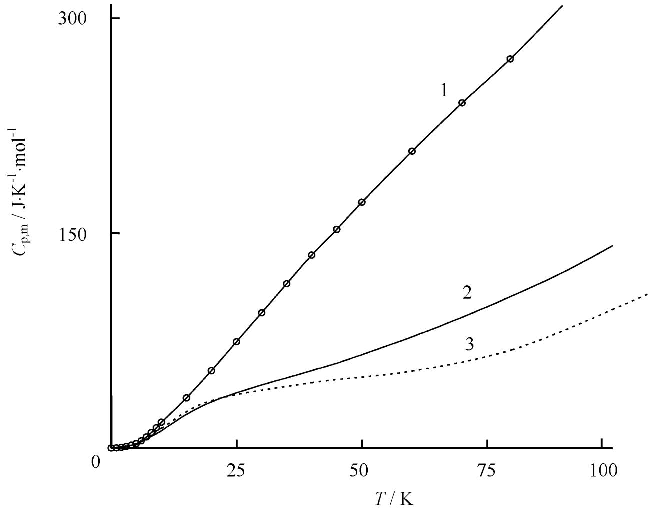

Figure 2. Curves of heat capacities of $Li_{12}C_{60}(THF)_{1.4}$ (1), $C_{60}H_{36}$[22] (2), and C_{60}[17] (3) in the low-temperature range.

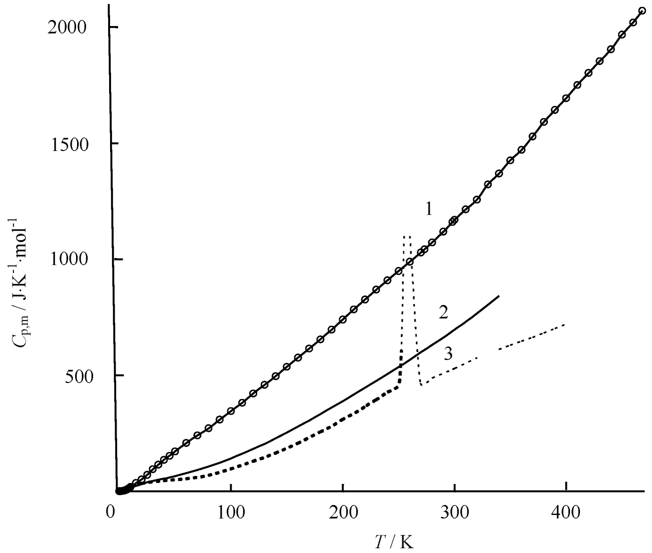

Figure 3. Curves of smoothed molar heat capacities of $Li_{12}C_{60}(THF)_{1.4}$ (1), $C_{60}H_{36}$[22] (2), and C_{60}[17] (3).

that the addition of hydrogen atoms—atoms of a small atomic mass and an electronegativity close to that of carbon atoms—seems to slightly affect the changes of the above skeletal vibrations and their contribution to the heat capacity of hydrofullerene in comparison with the corresponding skeletal vibrations of fullerene C_{60}.

Standard Thermodynamic Functions of $Li_{12}C_{60}(THF)_{1.4}$ Fulleride. To calculate the standard thermodynamic functions (Table 3) of $Li_{12}C_{60}(THF)_{1.4}$ fulleride, its smoothed molar heat capacities $C^{o}_{p,m}$ were extrapolated from the temperature of the measurement beginning at approximately $T = 6$ K to $T \to 0$ K with the Debye law in the low-temperature limit[23]

$$C^{o}_{p,m} = nD(\theta_D/T) \qquad (2)$$

where $n = 8$ is the number of degrees of freedom; D is the Debye function; and $\theta_D = 59.88$ K refers to the Debye characteristic temperature. Using the above parameters,[23] eq 2 describes the $C^{o}_{p,m}$ values of the compound over the range $6 \leq (T/K) \leq 12$ with the error of ± 0.84 %. In calculating the functions, it was assumed that eq 2 reproduced the $C^{o}_{p,m}$ values of $Li_{12}C_{60}(THF)_{1.4}$ at $T \leq 6$ K with the same error.

Table 3. Smoothed Molar Heat Capacities and Thermodynamic Functions of Crystalline $Li_{12}C_{60}(THF)_{1.4}$Fulleride [$M = 904.797$ 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	3.07	0.00510	1.54	0.00256
10	18.1	0.0528	7.54	0.0227
15	35.1	0.187	18.2	0.0860
20	50.69	0.4016	30.45	0.2073
30	94.38	1.116	58.77	0.6475
40	134.6	2.263	91.50	1.397
50	171.6	3.791	125.5	2.481
60	207.2	5.696	160.1	3.909
70	240.9	7.930	194.5	5.682
80	271.5	10.50	228.7	7.798
90	308.8	13.39	262.7	10.25
100	345.1	16.67	297.2	13.05
110	381.1	20.29	331.6	16.20
120	420.8	24.30	366.6	19.69
130	458.7	28.70	401.8	23.53
140	495.4	33.47	437.1	27.73
150	536.2	38.63	472.7	32.28
160	576.0	44.19	508.6	37.18
170	614.5	50.14	544.7	42.45
180	654.6	56.49	580.9	48.08
190	696.6	63.24	617.4	54.07
200	740.0	70.42	654.2	60.42
210	783.7	78.04	691.4	67.15
220	826.8	86.10	728.9	74.25
230	868.7	94.57	766.5	81.73
240	909.2	103.5	804.4	89.58
250	948.8	112.8	842.3	97.82
260	988.3	122.4	880.3	106.4
270	1029	132.5	918.3	115.4
280	1072	143.0	956.5	124.8
290	1118	154.0	994.9	134.5
298.15	1160	163.3	1027	142.8
300	1169	165.4	1034	144.7
310	1215	177.3	1073	155.2
320	1257	189.7	1112	166.2
330	1300	202.5	1151	177.5
340	1349	215.7	1191	189.2
350	1402	229.5	1231	201.3
360	1466	243.8	1271	213.8
370	1529	258.8	1312	226.7
380	1592	274.4	1354	240.1
390	1670	290.7	1396	253.8
400	1750	307.8	1439	268.0
410	1836	325.7	1484	282.6
420	1928	344.5	1529	297.6
430	2016	364.2	1575	313.2
440	2105	384.9	1623	329.2
450	2193	406.3	1671	345.6
460	2309	428.8	1720	362.6
468	2457	447.8	1761	376.5

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 respective temperatures. The zero entropy of $Li_{12}C_{60}(THF)_{1.4}$ was assumed to be zero. The calculation procedure was described in detail in ref 24. The errors determined for the function values are ± 2 % at $T < 15$ K, ± 0.5 % from (15 to 40) K, ± 0.3 % from $T = (40$ to $350)$ K, and ± 1.5 % in the temperature range between $T = (350$ and $468)$ K.

The thermodynamic functions of fullerite C_{60}, hydrofullerene $C_{60}H_{36}$, and $Li_{12}C_{60}(THF)_{1.4}$ fulleride at $T = 298.15$ K and $p° = 0.1$ MPa calculated from the results of the present work and the data cited in refs 16 and 17 are given in Table 4. A substantial difference is obvious in these values. The difference arose, certainly, for the same reasons as in the case of the heat capacities of these compounds.

Table 4. Molar Heat Capacity and Thermodynamic Functions of $Li_{12}C_{60}(THF)_{1.4}$, C_{60}, and $C_{60}H_{36}$ [$T = 298.15$ K, $p^o = 0.1$ MPa]

	$C^o_{p,m}$	$H^o(T) - H^o(0)$	$S^o(T)$	$-[G^o(T) - H^o(0)]$
substance	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$J \cdot K^{-1} \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
$Li_{12}C_{60}(THF)_{1.4}$	1160	163.3	1027	142.8
C_{60}[17]	524.8	72.44	426.5	54.72
$C_{60}H_{36}$[22]	690.0	84.94	506.8	66.17

Using the value of the absolute entropy of $Li_{12}C_{60}(THF)_{1.4}$ (Table 3) and the elemental substances, viz., carbon,[25] hydrogen,[26] oxygen,[26] and lithium,[25] the standard entropy of formation at $T = 298.15$ K was estimated to be $\Delta_f S^o_m(298.15, Li_{12}C_{60}(THF)_{1.4}, cr) = -(574.3 \pm 1.9)\ J \cdot K^{-1} \cdot mol^{-1}$.

The values obtained fit the equation

$$12Li\ (cr) + 65.6C\ (gr) + 5.6H_2\ (g) + 0.7O_2\ (g) \rightarrow Li_{12}C_{60}(C_4H_8O)_{1.4}\ (cr) \quad (3)$$

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

Conclusions

This paper reports low-temperature heat capacities measured by adiabatic calorimetry and differential scanning calorimetry of the crystalline coordination compound $Li_{12}C_{60}(THF)_{1.4}$. Additionally, the standard thermodynamic functions of $Li_{12}C_{60}(THF)_{1.4}$ (cr) over the range from $T \rightarrow 0$ K to $T = 468$ 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 based on 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 $Li_{12}C_{60}(THF)_{1.4}$ were compared with the corresponding data for C_{60} and $C_{60}H_{36}$.

Literature Cited

(1) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. Solid C_{60}: a new form of carbon. *Nature* **1990**, *347*, 354–358.

(2) Cristofolini, L.; Ricco, M.; Renzi, R. NMR and high-resolution x-ray diffraction evidence for an alkali-metal fulleride with large interstitial clusters: $Li_{12}C_{60}$. *Phys. Rev. B* **1999**, *59*, 8343–8346.

(3) Kohanoff, J.; Andreoni, W.; Parrinello, M. A possible new highly stable fulleride cluster: $Li_{12}C_{60}$. *Chem. Phys. Lett.* **1992**, *198*, 472–476.

(4) Tomaselli, M.; Meier, B. H.; Ricco, M.; Shiroka, T.; Sartori, A. NMR evidence for sp^3 carbon in the low-temperature phase of Li_xC_{60}. *Phys. Rev. B.* **2001**, *63*, 113405−1113405−4.

(5) Schnadt, J.; Bruhwiler, P. A.; Martensson, N.; Lassesson, A.; Rohmund, F.; Campbell, E. E. B. Electron-spectroscopy study of LiC_{60}: Charge transfer and dimer formation. *Phys. Rev. B.* **2000**, *62*, 4253–4256.

(6) Sun, Q.; Jena, P.; Wang, Q.; Marquez, M. First-principles study of hydrogen storage on $Li_{12}C_{60}$. *J. Am. Chem. Soc.* **2006**, *128*, 9741–9745.

(7) Zimmermann, U.; Malinowski, N.; Burkhardt, A.; Martin, T. P. Metal-coated fullerenes. *Carbon* **1995**, *33*, 995–1006.

(8) Markin, A. V. The heat capacity and standard thermodynamic characteristics of $Li_{12}C_{60}$ fulleride and its complex with THF. *12th European Conference on Thermophysical Properties*, France, Pau, 2008; pp 343−344.

(9) Titova, S. N.; Domrachev, G. A.; Khorshev, S. Ya.; Obédkov, A. M.; Kalakutskaya, L. V.; Ketkov, S. Yu.; Cherkasov, V. K.; Kaverin, B. S.; Zhogova, K. B.; Lopatin, M. A.; Karnatsevich, V. L.; Gorina, E. A. Stoichiometric synthesis of fullerene compounds with lithium and sodium and analysis of their IR and EPR spectra. *Phys. Solid State* **2004**, *46*, 1323–1327.

(10) Reed, C. A.; Bolskar, R. D. Discrete fulleride anions and fullerenium cations. *Chem. Rev.* **2000**, *100*, 1075–1120.

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

(12) Malyshev, V. M.; Milner, G. A.; Sorkin, E. L.; Shibakin, V. F. An automatic and low-temperature calorimeter. *Pribory i tekhnika eksperimenta* **1985**, *6*, 195–197.

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

(14) 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.

(15) Coplen, T. B. Atomic weights of the elements 1999 (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73*, 667–683.

(16) Kabo, A. G.; Diky, V. V. Details of calibration of a scanning calorimeter of the triple heat bridge type. *Thermochim. Acta* **2000**, *347*, 79–84.

(17) 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. *Rus. Chem. Bull.* **1996**, *45*, 2113–2117.

(18) Yakubov, T. S. About heat capacity of solids having fractal character. *Dokl. Akad. Nauk SSSR* **1990**, *310*, 145–149.

(19) 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, 1996.

(20) 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.

(21) Lebedev, B. V.; Markin, A. V. Thermodynamics of C_{60} Polyfullerites. *Phys. Solid. State* **2002**, *44*, 434–436.

(22) Lebedev, B. V.; Bykova, T. A.; Lobach, A. S. Thermodynamic properties of hydrofullerene $C_{60}H_{36}$ from 5 to 340 K. *J. Thermal Anal. Calorim.* **2000**, *62*, 257–265.

(23) Rabinovich, I. B.; Nistratov, V. P.; Telnoy, V. I.; Sheiman, M. S. *Thermochemical and thermodynamic properties of organometallic compounds*; Begell House, Inc. Publishers: NY, 1999.

(24) McCullough, J. P.; Scott, D. W. *Calorimetry of Non-reacting Systems*; Butterworth: London, 1968.

(25) Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*; Hemisphere Publishing Corp.: NY, 1984; p 1.

(26) Chase, M. W., Jr. NIST-JANAF Thermochemical tables. *J. Phys. Chem. Ref. Data, Monograph* **1998**, *9*, 1–1951.

Received for review October 16, 2008. Accepted December 13, 2008. The work was performed with the financial support of the Russian Foundation of Basic Research (Project No. 08-03-00214a) and Federation Agency for Science and Innovations (contract 02.513.11.0002).

JE800765S