Thermodynamic properties of crystalline polymeric C_{60} phases in the temperature region from $T \to 0$ to 340 K

A. V. Markin,[a] N. N. Smirnova,[a] B. V. Lebedev,[a] V. A. Davydov,[b]*
L. S. Kashevarova,[b] and A. V. Rakhmanina[b]

[a]*Research Institute of Chemistry,*
N. I. Lobachevsky Nizhnii Novgorod State University,
Building 5, 23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 6450. E-mail: lebedevb@ichem.unn.runnet.ru
[b]*L. F. Vereshchagin Institute of High Pressure Physics, Russian Academy of Sciences,*
142190 Troitsk, Moscow Region, Russian Federation.
Fax: +7 (095) 334 0012. E-mail: vdovydov@hppi.troitsk.ru

The temperature dependences of the heat capacity $C_p^\circ = f(T)$ were studied in an adiabatic vacuum calorimeter for the orthorhombic, tetragonal, and rhombohedral polymeric C_{60} phases in the 7—340 K temperature interval with an error of ~0.2%. Comparative analysis of C_p° of these phases formed by stacking of one-dimensional and two types of two-dimensional polyfullerenes C_{60}, was performed, and their fractal dimensionalities D were determined for temperatures below 50 K. The thermodynamic functions of the crystalline polymeric C_{60} phases were calculated in the temperature region from $T \to 0$ to 340 K: $C_p^\circ(T)$, $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$, and $G^\circ(T) - H^\circ(0)$. Assuming that $S^\circ(0) = 0$, the standard entropies of formation $\Delta_f S^\circ$ of these phases from graphite at $T = 298.15$ K and standard pressure were calculated. In addition, the entropies of transformation of the initial face-centered cubic phase of fullerite C_{60} in the crystalline polymeric C_{60} phases and entropies of their interconversions under the same conditions were estimated. The thermodynamic characteristics of the polymeric C_{60} phases were reviewed.

Key words: polyfullerenes C_{60}, calorimeter, heat capacity, thermodynamic functions, entropies of interconversions of crystalline polymeric C_{60} phases.

Transformations of fullerites C_{60} at high pressures and temperatures[1—8] are accompanied by the formation of new phases of the carbon system. Among them are crystalline phases based on dimers $(C_{60})_2$ and one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) polymers of C_{60} with regions of existence shown in the p—T diagram (Fig. 1). Although these phases are formed at a high pressure, they persist as metastable states under standard conditions when hardened under pressure and remain stable for any long time at atmospheric pressure and room temperature. The orthorhombic (O), tetragonal (T), and rhombohedral (R) phases are packings of linear (1D) and two types of two-dimensional (2D) polymers of C_{60} formed due to the 2 + 2-cycloaddition of C_{60} molecules.[9,10] 2D polymers can be formed with the tetragonal and hexagonal topologies of layers. However, pure samples of the O, T, and R phases are difficult to prepare. It is evident now that many samples reported in earlier studies as individual O, T, and R phases, are in fact mixtures of polymeric C_{60} phases. This disadvantage is inherent in many previous determinations of the thermodynamic properties of polymeric phases.[11—16] Thermodynamic studies have previously been performed mainly using differential scanning calorimeters, which provide only a qualitative pattern of the temperature dependence of the heat capacity. Results of calorimetric studies using high-precision adiabatic vacuum calorimeters are reported much more rarely.[14,16,17] The data on the thermodynamic properties of the metastable phases of fullerene C_{60}, obtained under different p—T conditions, are presented in previously published works.[18,19]

The purpose of this work is the calorimetric study of the temperature dependence of the isobaric heat capacity C_p° for the O, T, and R crystalline polymeric C_{60} phases in the 7—340 K temperature interval at standard pressure, calculation of the thermodynamic functions for the region from $T \to 0$ K to 340 K, and analysis of the obtained dependences of C_p° *vs.* T. In particular, it was of interest to determine the fractal dimensionalities D for them in the function of heat capacity of the multifractal variant of the Debye theory of heat capacity.[20,21] Special attention was given to the preparation of samples with

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 821—826, April, 2003.

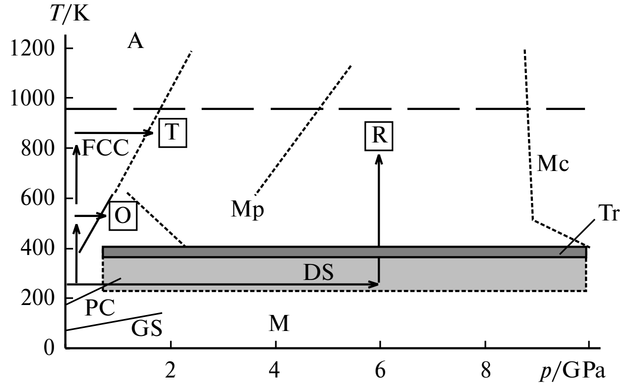


Fig. 1. p—T-Diagram of atomic (A), molecular (M), and various polymolecular (DS, Mp, Mc) carbon states formed on treating fullerite C_{60} under quasihydrostatic compression conditions; DS are the dimerized C_{60} states; Mc are the polymolecular three-dimensional (3D) structures; Mp are the polymerized C_{60} states based on one- and two-dimensional C_{60} polymers; Tr is the transition state (phase boundary) between the M and Mp regions of the diagram; O is the orthorhombic phase based on two types of 1D-C_{60}; T and R are the tetragonal and rhombohedral phases based on two types of 2D-C_{60}; FCC, PC, and GS are the face-centered cubic phase, primitive cubic phase, and glassy state of fullerite C_{60}, respectively; dotted and solid lines denote interfaces of regions of phase existence.

the maximum content of the polymeric phase under study.

Experimental

Synthesis of polymeric C_{60} phases. The preliminary studies showed[7] that the choice of the pressure and temperature of synthesis and also the route of achievement of the specified p and T parameters are important for preparation of the polymeric C_{60} phases. The routes of achievement of the p and T parameters of synthesis of the O, T, and R phases of C_{60} used in this work are shown by arrows in the diagram (see Fig. 1). Samples were synthesized on Maksim (piston—cylinder type) and Toroid high-pressure instruments. Doubly sublimed finely crystalline powder of fullerite C_{60} (C_{60} content ≥99.98 wt.%, produced at the Term USA Co.) was used as the starting material. Samples of the O, T, and R phases were prepared at pressures of 1.3, 2, and 6 GPa and temperatures of 560, 873, and 873 K, respectively. Times of isothermic storage were 20000, 2000, and 2000 s. Polymerized systems formed after the treatment of C_{60} were stable under standard conditions when hardened under pressure. Then the samples were removed from the high-pressure instrument and characterized by X-ray diffraction and vibrational spectroscopies, as in earlier works.[7,8] The X-ray diffraction patterns along with structural parameters of the crystalline polymeric C_{60} phases have been published.[7]

Samples with the highest content of the main phase, which was as high as ~95 mol.% for samples of the O and R phases and ~85 mol.% for the T phase sample, were selected for calorimetric studies. The characteristics of the crystalline phases under study were presented in earlier published works.[7,8] According to these data, the samples of the O and R phases contained insignificant admixtures of low-molecular C_{60} polymers, and the T phase sample contained the R phase.

Investigation of heat capacity. To study the temperature dependence of the heat capacity of the crystalline polymeric C_{60} phases, we used a BKT-3 automated adiabatic vacuum calorimeter. Its design and procedure of measurement of the heat capacity $C_p°$ have been described previously.[22,23] It was established from the results of calibrations and verifications of the calorimeter that the error of measurement of the heat capacity of substances at helium temperatures ranged within 2%, and as the temperature increased to 40 K, the error decreased to 0.5% and became equal to 0.2% in the 40—340 K temperature interval.

The heat capacity of the O phase of C_{60} (I) was studied in the 7—340 K interval, that of the C_{60} T phase (II) was studied in the region from 6 to 340 K, and that of the C_{60} R phase (III) was studied at 7—350 K. The weights of the substances under study placed in a calorimetric ampule were $0.4567 \cdot 10^{-3}$, $0.1988 \cdot 10^{-3}$, and $0.4514 \cdot 10^{-3}$ kg, respectively. In seven series reflecting the sequence of measurements of $C_p°$ 263 experimental $C_p°$ values were obtained for phase I, 202 values were obtained in three series for phase II, whereas in four series for phase III 187 $C_p°$ values were obtained. The heat capacity of the sample of C_{60} O phase was 10—30% of the total heat capacity of the calorimetric ampule filled with the substance, and that of the T phase was 5—15%. The ratio of heat capacities of the R phase sample and the calorimetric ampule with the substance changed with the temperature increase from 8% at 7 K to 23% at 350 K. Experimental $C_p°$ points were averaged on a personal computer using power and semilogarithmic polynomials. Their root-mean-square deviation from the corresponding averaging curves $C_p° = f(T)$ for the samples under study was within 0.5% in the 7—80 K interval and 0.07% in the 80—340 K interval.

Results and Discussion

All experimental $C_p°$ values and averaging curves for crystalline polymeric phases I—III are presented in Fig. 2 along with the temperature dependences of the heat capacity of the initial fullerite C_{60} given for comparison (see Ref. 24). Temperature dependences of the heat capacity of the crystalline polymeric C_{60} phases do not exhibit any features: the heat capacities smoothly increase as the temperature increases. The first order and G type transformations, which are observed in the curves obtained for the initial fullerite C_{60} in the 185—275 and 81.0—88.5 K temperature intervals (see Fig. 2, curves *2*; Fig. 3, curve *4*) do not occur. The first transformation is attributed to the change of the orientationally ordered primitive cubic (PC) C_{60} phase to the orientationally disordered face-centered cubic (fcc) phase in which the C_{60} molecules are in virtually free rotation.[24—26] The second transformation occurs due to "freezing" of the transition of the fullerene molecules from the orientation state with a higher energy to the orientation state with a lower energy on cooling and "thawing out" on heating.[24,27]

At $T < 70$ K, the $C_p°$ values of polymeric phases I—III under study differ strongly (see Fig. 3): $C_p°$ of phase I are

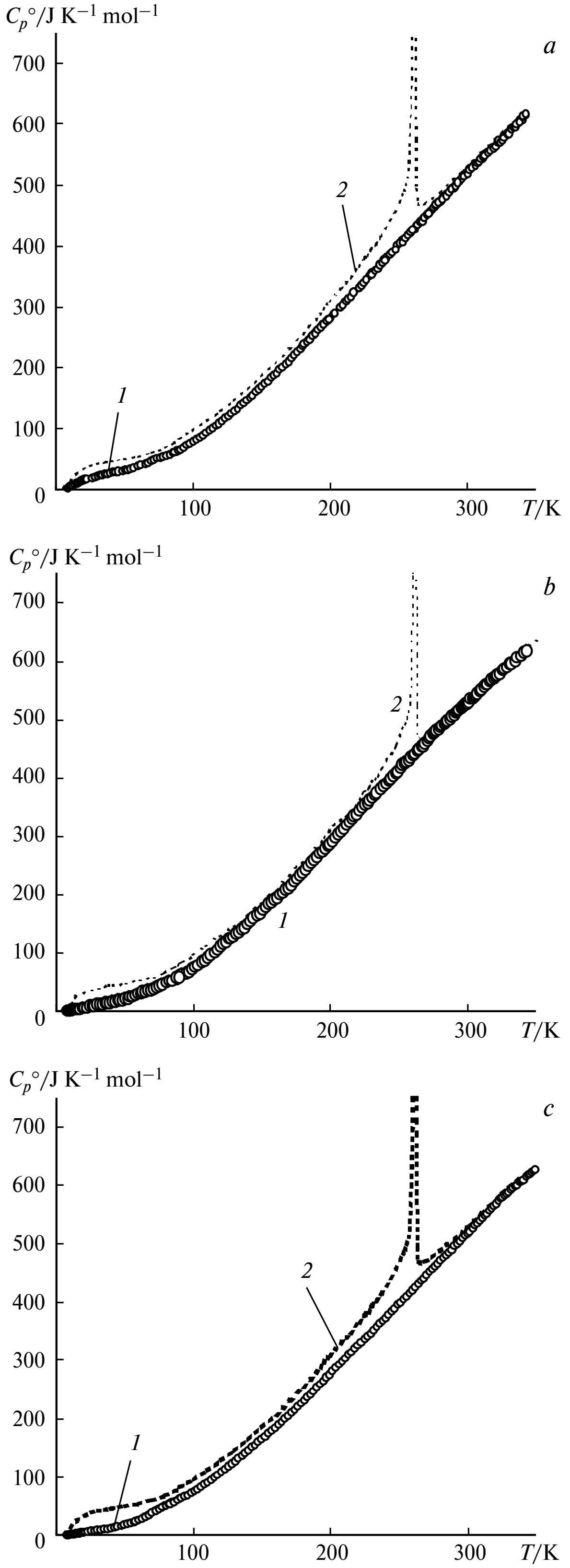


Fig. 2. Temperature plots of the heat capacity of the orthorhombic (*a*), tetragonal (*b*), and rhombohedral (*c*) crystalline polymeric C_{60} phases (*1*) and initial fullerite C_{60} ^{24} (*2*).

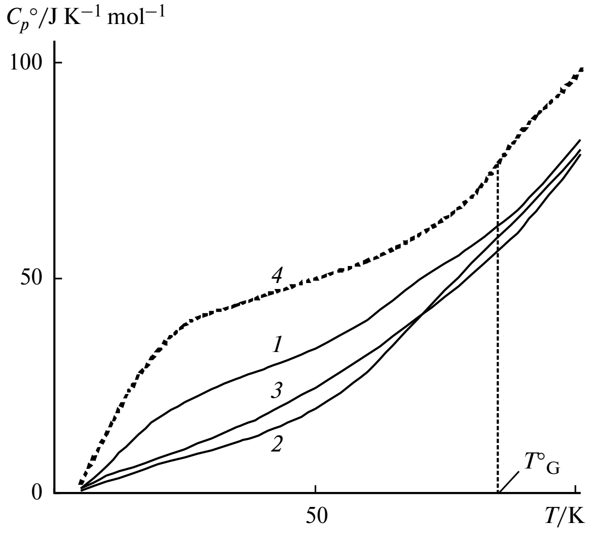


Fig. 3. Heat capacity in the region of low temperatures of the orthorhombic (*1*), tetragonal (*2*), and rhombohedral (*3*) crystalline polymeric C_{60} phases and initial fullerite C_{60} ^{24} (*4*).

by 30—50 and 17—60% higher than those for phases II and III, respectively, while $C_p°$ of phase II is by 20—35% lower than that for phase III. In the 70—100 K interval, the differences in heat capacities are 10—15%. At $T > 100$ K, $C_p°$ of the samples under study vary within the range of 2—4%, which is probably within experimental errors of measurement of heat capacities. In the whole temperature interval, the heat capacity of the initial fullerite C_{60} ^{24} is higher than that for the corresponding crystalline polymeric C_{60} phases. For example, at $T =$ 30 K, $C_p°$ of fullerite C_{60} exceeds the heat capacities of the O, T, and R phases by 43, 54, and 76%, respectively. This is evidently caused by a decrease in the contribution of rotational degrees of freedom to the heat capacity of the polymers, because the C_{60} molecules, being in free rotation in the monomeric (fcc) phase of the initial fullerite, are linked to each other through rigid covalent bonds in the case of polymeric phases.

The temperature dependence of the heat capacity has been studied previously[16] in the interval from $T \to 0$ to 340 K for the O phase prepared at $p = 5$ GPa and $T =$ 550 K (IV) and for a mixture of the T (60%) and R phases (40%) synthesized at $p = 3.5$ GPa and $T = 960$ K (V). The heat capacity of the R phase prepared at $p = 8$ GPa and $T = 920$ K (VI) was studied[17] in the region from $T \to 0$ to 320 K. The comparison of the heat capacity values of the crystalline polymeric C_{60} phases obtained in this work with the published data[16,17] shows that at $T < 50$ K $C_p°$ of the samples of the compared phases I and IV, II and V, III and VI differed, on the average, by 35%. When the temperature was increased to 100 K, the differences in $C_p°$ of samples I and IV did not exceed 2.5%, and those for samples II and V, III and VI did not exceed an average value of ±4%. A decrease in the numerical differences in heat capacities with the temperature increase to 350 K is observed only for the O phases, and the differences in C_p° are ~0.3%.

It is most likely that the different concentrations of the main phase in the samples under study is a reason for the discrepancy of the low-temperature heat capacities of the crystalline polymeric C_{60} phases obtained in this and other works.[16,17] For example, a lower C_p° value of phase IV compared to the heat capacity of phase II indicates that sample IV contains a remarkable fraction of 2D polymers of C_{60}.

The low-temperature region (T < 70 K) exhibits not only the numerical differences in C_p° of the crystalline polymeric C_{60} phases but also a different character of the temperature dependence of the heat capacity (see Fig. 3). The latter is caused by the heterodynamic nature of their structures.[28] According to the Tarasov theory of heat capacity of solids,[28,29] which is a particular case of the fractal theory of heat capacity,[20,21] the ratio between C_p° and T at low temperatures is described by power functions. For solids with the chain-like structure, the exponent at T is equal to 1, whereas it is 2 for layered structures and 3 for spatial structures. In the fractal variant of the Debye theory of heat capacity, the exponent at T in the heat capacity function is denoted as D and defined as the fractal dimensionality.[20] The D value can be estimated using the temperature plot of the heat capacity from the slope of the corresponding rectilinear regions of the plot of $\ln C_v$ *vs.* $\ln T$, accepting that at $T < (50—60)$ K $C_p^\circ = C_v$. This follows, in particular, from the equation

$$C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/\theta_{max})^D, \qquad (1)$$

where N is the number of particles in a molecule of the repeated unit, 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. The fractal dimensionality D can take values from 1 to 4, depending on the structure of solids.[21] Formula (1) can be written in the form

$$C_v = A(T/\theta_{max})^D, \qquad (2)$$

where $A = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)$. The D and θ_{max} values of the O, T, and R phases, obtained from the data on heat capacities of phases I—III, are presented in Table 1 along with the error (δ) of Eq. (1) to describe the experimental heat capacities of phases I—III in the 30—50 K interval. Thus, the determined fractal dimensionalities confirm the chain structure of the orthorhombic C_{60} phase and the planar structure of the tetragonal C_{60} phase. As for the rhombohedral C_{60} phase, it appears to have the planar-chain structure.

Table 1. Fractal dimensionalities (D) and characteristic temperatures (θ_{max}) of the crystalline polymeric C_{60} phases

Compound	ΔT/K	D	θ_{max}/K	δ (%)
O-Phase C_{60}	25—50	1.0	159.5	1.0
T-Phase C_{60}	30—50	1.9	215.0	1.2
R-Phase C_{60}	30—50	1.7	291.6	1.1

At T < 12 K, the heat capacities of all the considered phases converge, the fractal dimensionalities increase, and

Table 2. Thermodynamic functions of the orthorhombic C_{60} phase calculated per mole of C_{60} (M = 720.66 g mol^{-1})

T/K	$C_p^\circ(T)$	ΔS°*	ΔH°**	$-[G^\circ(T) - H^\circ(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	1.030	0.3447	0.0013	0.00043
10	6.230	2.455	0.0180	0.00654
15	12.25	6.180	0.0650	0.0277
20	17.29	10.42	0.1393	0.0692
25	21.00	14.69	0.2353	0.1320
30	24.01	18.80	0.3481	0.2158
35	26.48	22.69	0.4745	0.3197
40	28.81	26.39	0.6132	0.4425
45	31.25	29.93	0.7635	0.5833
50	33.60	33.37	0.9270	0.7416
60	40.35	40.07	1.296	1.109
70	49.47	46.99	1.745	1.544
80	57.40	54.13	2.282	2.049
90	67.03	61.39	2.899	2.627
100	80.83	69.15	3.636	3.279
110	96.30	77.57	4.521	4.012
120	113.2	86.66	5.567	4.832
130	131.5	96.44	6.790	5.747
140	150.9	106.9	8.200	6.763
150	171.4	118.0	9.811	7.887
160	192.8	129.7	11.63	9.125
170	214.9	142.1	13.67	10.48
180	237.6	155.0	15.93	11.97
190	260.7	168.5	18.42	13.59
200	284.0	182.4	21.15	15.34
210	307.6	196.9	24.10	17.24
220	331.3	211.7	27.30	19.28
230	355.1	227.0	30.73	21.47
240	379.1	242.6	34.40	23.82
250	403.1	258.5	38.31	26.32
260	427.2	274.8	42.46	28.99
270	451.3	291.4	46.86	31.82
280	475.2	308.2	51.49	34.82
290	498.7	325.3	56.36	37.99
298.15	517.5	339.4	60.50	40.70
300	521.7	342.6	61.46	41.33
310	544.0	360.1	66.79	44.84
320	565.8	377.7	72.34	48.53
330	587.7	395.5	78.11	52.39
340	610.9	413.3	84.10	56.44
345	623.7	422.4	87.19	58.53

* $\Delta S^\circ = S^\circ(T) - S^\circ(0)$.

** $\Delta H^\circ = H^\circ(T) - H^\circ(0)$.

Table 3. Thermodynamic functions of the tetragonal C_{60} phase calculated per mole of C_{60} (M = 720.66 g mol^{-1})

T/K	$C_p°(T)$	$\Delta S°$*	$\Delta H°$**	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	0.972	0.3396	0.0013	0.0004
10	3.849	1.910	0.0134	0.0057
15	5.942	3.851	0.0377	0.0200
20	8.097	5.858	0.0729	0.0443
25	10.18	7.870	0.1182	0.0786
30	12.60	9.937	0.1750	0.1231
35	15.16	12.07	0.2443	0.1781
40	17.90	14.27	0.3269	0.2439
45	20.91	16.55	0.4238	0.3209
50	24.48	18.93	0.5370	0.4095
60	32.05	24.04	0.8184	0.6240
70	40.88	29.62	1.182	0.8919
80	50.68	35.71	1.638	1.218
90	62.00	42.34	2.203	1.608
100	77.00	49.62	2.895	2.067
110	94.65	57.76	3.750	2.603
120	114.9	66.85	4.797	3.225
130	130.7	76.78	6.038	3.943
140	153.5	87.35	7.466	4.763
150	175.8	98.70	9.112	5.693
160	196.0	110.7	10.98	6.739
170	215.3	123.2	13.03	7.908
180	241.9	136.2	15.31	9.204
190	267.0	150.0	17.86	10.63
200	291.7	164.3	20.65	12.21
210	318.8	179.2	23.71	13.92
220	344.2	194.3	26.95	15.79
230	367.2	210.1	30.52	17.81
240	391.1	226.3	34.31	19.99
250	416.8	232.9	35.95	22.29
260	440.1	249.8	40.24	24.70
270	465.9	266.8	44.76	27.28
280	490.0	284.3	49.55	30.04
290	510.4	301.8	54.56	32.97
298.15	527.3	316.2	58.78	35.49
300	531.3	319.5	59.76	36.08
310	553.4	337.2	65.19	39.36
320	575.0	355.2	70.83	42.82
330	594.7	373.2	76.68	46.46
340	613.3	391.2	82.72	50.28

* $\Delta S° = S°(T) - S°(0)$.

** $\Delta H° = H°(T) - H°(0)$.

Table 4. Thermodynamic functions of the rhombohedral C_{60} phase calculated per mole of C_{60} (M = 720.66 g mol^{-1})

T/K	$C_p°(T)$	$\Delta S°$*	$\Delta H°$**	$-[G°(T) - H°(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
5	0.4758	0.1602	0.0006	0.00020
10	2.563	1.077	0.0078	0.00293
15	4.463	2.363	0.0240	0.0114
20	6.504	3.927	0.0514	0.0271
25	8.181	5.564	0.0883	0.0508
30	9.987	7.209	0.1335	0.0828
35	11.90	8.89	0.1881	0.1230
40	13.89	10.61	0.2525	0.1717
45	16.57	12.39	0.3283	0.2291
50	19.50	14.28	0.4182	0.2958
60	28.13	18.55	0.6536	0.4591
70	40.73	23.80	0.9958	0.6699
80	53.20	30.08	1.468	0.9386
90	65.10	37.03	2.059	1.274
100	78.51	44.56	2.775	1.681
110	94.03	52.75	3.636	2.167
120	111.0	61.65	4.661	2.738
130	129.0	71.24	5.860	3.402
140	148.0	81.49	7.244	4.165
150	168.0	92.38	8.823	5.034
160	189.1	103.9	10.61	6.015
170	211.0	116.0	12.61	7.114
180	233.7	128.7	14.83	8.337
190	257.0	142.0	17.28	9.690
200	280.7	155.7	19.97	11.18
210	304.6	170.0	22.90	12.81
220	328.6	184.7	26.06	14.58
230	352.6	199.9	29.47	16.50
240	376.6	215.4	33.12	18.58
250	400.6	231.3	37.00	20.81
260	424.8	247.4	41.13	23.21
270	449.0	263.9	45.50	25.76
280	473.3	280.7	50.11	28.48
290	497.8	297.7	54.96	31.38
298.15	517.6	311.8	59.10	33.86
300	522.1	315.0	60.06	34.44
310	546.3	332.5	65.41	37.68
320	569.8	350.2	70.99	41.09
330	592.2	368.1	76.80	44.68
340	612.8	386.1	82.82	48.45
350	630.7	404.1	89.05	52.41

* $\Delta S° = S°(T) - S°(0)$.

** $\Delta H° = H°(T) - H°(0)$.

the $C_p°$ values are well described by the Debye function of heat capacity

$$C_p° = n\boldsymbol{D}(\theta_D/T), \tag{3}$$

where $\boldsymbol{D}$ is the symbol of the Debye function of heat capacity; n and θ_D are the specially selected parameters; for phase I n = 3, θ_D = 61.68 K, for phases II and III n = 1, and θ_D = 42.68 and 55.20 K, respectively. Equation (3) with these parameters in the 7—12 K interval describes the heat capacities of the substances with an error of ~0.60%.

The temperature dependences of the heat capacity of the crystalline polymeric C_{60} phases were used for the calculation of their thermodynamic functions for the region from $T \to 0$ to 340 K (Tables 2—4). The enthalpy $H°(T) - H°(0)$ and entropy $S°(T) - S°(0)$ were calculated by numerical integration of the curves $C_p° = f(T)$ and $C_p° = f(\ln T)$ over T values. The Gibbs function

$G°(T) - H°(0)$ was calculated from the $H°(T) - H°(0)$ and $S°(T) - S°(0)$ values at the corresponding temperatures. The procedure of calculation of these functions has been described previously.[30]

The standard entropies of formation of the polymeric C_{60} phases were calculated from the absolute entropies of these phases and entropies of carbon in the form of graphite. The $S°$(I), $S°$(II), and $S°$(III) values at 298.15 K and standard pressure were taken equal to the corresponding $S°(T) - S°(0)$ values at $T = 298.15$ K (see Tables 2—4). The zero entropies $S°(0)$ of the polymeric C_{60} phases under study were neglected because it has been shown[31] that for any crystalline polymers $S°(0)$ are low and lie, most likely, within errors of measurement of $C_p°$ and calculation of $S°(T)$. The $S°$ value for graphite was taken from the reference book.[32] The calculated $\Delta_f S°$ values for phases I, II, and III were −5, −28.2, and −32.6 J K^{-1} mol^{-1}, respectively. These values refer to hypothetical processes that occur at $T = 298.15$ K and $p = 101.325$ kPa

$$60\ \mathrm{C\ (gr)} \longrightarrow \mathrm{O\text{-}C_{60}\ (cr)},$$

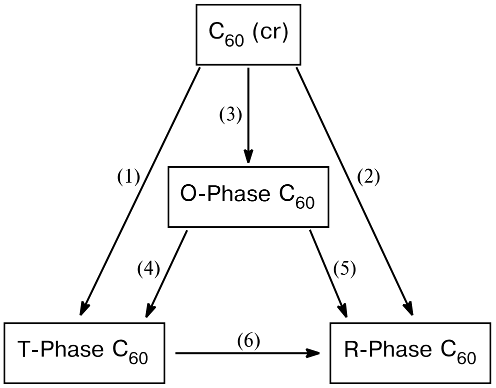
$$60\ \mathrm{C\ (gr)} \longrightarrow \mathrm{T\text{-}C_{60}\ (cr)},$$

$$60\ \mathrm{C\ (gr)} \longrightarrow \mathrm{R\text{-}C_{60}\ (cr)},$$

where gr is graphite, and cr is crystals.

The hypothetical cycle of transformations of the initial fullerite C_{60} into the studied crystalline polymeric C_{60} phases is presented in Scheme 1. The entropies of their interconversions at $T = 298.15$ K and standard pressures, calculated from the absolute entropies of the reactants at the indicated T and p, are presented below. The $S°(C_{60})$ values for calculations were taken from the previously published work,[24] $S°$(I), $S°$(II), and $S°$(III) were determined in this work (see Tables 2—4), and $S°(0)$ of the polymeric C_{60} phases were also accepted to be zero.

Scheme 1



Reaction	(1)	(2)	(3)	(4)	(5)	(6)
$-\Delta S$ /J K^{-1} mol^{-1}	110.3	114.7	87.1	23.2	27.6	4.4

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 02-03-06510, 01-03-32061, 00-03-40136, and 00-03-32600), the Ministry of Science, Industry, and Technologies of the Russian Federation (decision of 15.01.1996), and the INTAS (Grants 00-807 and IR-97-1015).

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Received May 31, 2002;
in revised form November 1, 2002