Thermodynamic properties of some polymeric forms of fullerite C_{60} at temperatures ranging from 0 to 320 K

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The temperature dependences of the heat capacity C°_p of fullerites C_{60} were studied at temperatures ranging from 5 to 320 K in an adiabatic vacuum calorimeter with an accuracy of 0.4—0.2%. The fullerite C_{60} samples were prepared by treating the starting fullerite C_{60} under 8 GPa at 920 and 1270 K and "quenched" by a sharp decrease in pressure to ~10^5 Pa and in temperature to ~300 K. Fullerite C_{60}(8 GPa, 920 K), a crystalline polymer with layered structure formed by polymerized fullerene C_{60} molecules, was obtained at 920 K and 8 GPa. Fullerite C_{60}(8 GPa, 1270 K), a three-dimensional polymer with a graphite-like structure formed by fragments of decomposed C_{60} molecules and containing many $C(sp^3)$—$C(sp^3)$ bonds, was obtained at 1270 K and 8 GPa. Both polymers are metastable polymeric phases. The anomalous character of the temperature dependence of the heat capacity was revealed in the 49—66 K range for the polymer formed at 1270 K. The thermodynamic functions of the substances under study were calculated for the 0—320 K region along with entropies of their formation from graphite. The entropies of transformation of the starting fullerite C_{60} into metastable phases and that of intertransformation of phases were estimated.

Key words: fullerites C_{60}(8 GPa, 920 K) and C_{60}(8 GPa, 1270 K); calorimetry, heat capacity; thermodynamic functions; entropies of intertransformation of phases.

When fullerite C_{60} is treated under high pressure and then both the pressure and temperature are sharply decreased, this "quenching" results in the formation of phases thermodynamically metastable under standard conditions.[1—5] Transformations of fullerite C_{60} afford the following important products: molecular crystals with intermolecular distances shorter than those in the starting fullerite; polymeric products, in particular, those with $C(sp^3)$—$C(sp^3)$ bonds between the C_{60} molecules; turbostrate fullerite consisting of residual C_{60} molecules linked by a network of hexahedrons of C atoms that were formed by the decomposition of some fullerene molecules; amorphous diamond of nanosize dimensions; and superhard fullerite consisting of carbon films in the sp^3- and sp^2-valent states (in a ratio of 4 : 1) that were formed by the complete decomposition of the C_{60} molecules.[6] Combined spectral, X-ray structural, and calorimetric tools have been used to study the properties and conditions of intertransformations of the phases.[7—13] However, differential scanning calorimeters, which are most often used in the calorimetric study of fullerites, give only a qualitative picture of temperature dependences of the heat capacity.[14] High-precision adiabatic vacuum calorimeters have been applied only in two works[11,12] on the temperature dependences of the heat capacities of fullerites in the 6—350 K region.

In this work, we used calorimetric methods to study graphite-like fullerite C_{60} obtained by treating C_{60} under 8 GPa and 1270 K.

Experimental

Starting fullerite C_{60} was prepared in the Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhnii Novgorod). Fullerite C_{60} was treated in the Scientific Technical Center "Superhard Materials" (Troitsk, Moscow Region) in a toroidal chamber under 8 GPa; one sample, C_{60}(8 GPa, 920 K), was obtained at 920 K, and another sample, C_{60}(8 GPa, 1270 K), was obtained at 1270 K. The procedure has been described previously.[15] After treatment, both fullerite samples were quenched to yield samples that were thermodynamically metastable phases under standard conditions. X-ray diffraction analysis was carried out on a Kord-6 diffractometer with a planar proportional chamber on fast delay lines. The accuracy of measurement of the angle was 0.02°; (Cu-Kα) radiation and a graphite monochromator were used. Diffraction patterns were obtained from regions of 250—300 μm. According to the published data,[8,16] an increase in the temperature transforms crystalline fullerite C_{60} (face centered cubic lattice) under the pressure of 8 GPa into orthorhombic, tet-

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 277—281, February, 2000.

ragonal, and finally into rhombohedral phases. At temperatures < 1000—1100 K, the C_{60} cavities were retained, whereas the C_{60} molecules polymerized to form one- and two-dimensional structures. In the rhombohedral phase, the polymerization resulted in the shortening of the bonds between molecules from ~2.9 Å in the starting C_{60} to 1.64—1.68 Å. The diffraction patterns of the crystalline and amorphous phases of the fullerites obtained at different temperatures are shown in Fig. 1. Indexing in the hexagonal structure of the rhombohedral cell of the C_{60}(8 GPa, 920 K) sample resulted in the following unit cell constants: a = 9.272(6) Å, c = 24.24(4) Å. The density of this sample found by the X-ray diffraction method was equal to 1.98 g cm^{-3}, and that obtained by weighing in a liquid was 1.96±0.02 g cm^{-3}. The rhombohedral structure was composed of layers of polymerized C_{60} molecules oriented perpendicular to the diagonal plane of the cubic unit cell.

The diffraction pattern of the sample obtained at 1270 K (see Fig. 1, curve *3*) was similar to that for graphite (see Fig. 1, curve *4*), differing in a larger width of peaks and a shorter, as compared to the turbostrate graphite, interplanar distance d_{002} (see Fig. 1, curve *4*). In addition, the maxima from planes (100) and (101) were not resolved on the X-ray pattern. Taking into account that the samples with a disordered structure had a high hardness ($H \gg 30$ GPa[3]) with interplanar distance shorter than that for graphite, we assumed that the structure of the sample synthesized at 1270 K contained a larger fraction of sp^3 bonds than the graphite sample. The density of the sample measured by weighing in the liquid was 2.18±0.02 g cm^{-3}.

A TAU-1 adiabatic vacuum calorimeter designed and created in VNIIFTRI (Moscow) was used for measuring the temperature dependence of the heat capacity of the synthesized fullerites.[17] The calorimetric tube was a thin-walled vessel of stainless steel with a volume of $1.5 \cdot 10^{-6}$ m^3 and a weight of $2.06 \cdot 10^{-3}$ kg. The temperature was measured by an iron-rhodium resistance thermometer ($R_0 \approx 100$ Ohm). The heat capacity of an empty calorimetric tube changed from 0.0038 J mol^{-1} K^{-1} (5 K) to 1.275 J mol^{-1} K^{-1} (340 K).

The heat capacity of fullerite C_{60}(8 GPa, 920 K) was measured between 5 and 320 K, and that of fullerite C_{60}(8 GPa, 1270 K) was measured between 5 and 307 K. The bodies of the samples under study loaded in a calorimetric tube were $0.4535 \cdot 10^{-3}$ and $0.4577 \cdot 10^{-3}$ kg, respectively. In 7 and 11 series of measurements reflecting the sequence of experiments, 125 and 115 experimental values of C°_p were obtained. The root-mean-square deviation of the C°_p points from the corresponding averaging curves $C^\circ_p = f(T)$ in the 5—90 K range was equal to ±0.06%, and in the 90—320 K range, it was ±0.07%. For both samples of the fullerites under study, the heat capacity with respect to the cumulative heat capacity of the calorimetric tube with the substance gradually increased from 2.6% at 5 K to 13% at 300 K.

Results and Discussion

The heat capacity of fullerites C_{60}(8 GPa, 920 K) and C_{60}(8 GPa, 1270 K) increases smoothly as the temperature increases (Fig. 2), but within the 49—66 K temperature range, an anomalous dependence of C°_p on T is observed for the sample obtained at 1270 K. The positive deviation of the heat capacity from the standard dependence on T was recorded for this interval (Fig. 3, dotted line in curve *2*). The maximum excessive value of the heat capacity ΔC°_p = 9.38 J mol^{-1} K^{-1} corresponds to the temperature T°_{tr} = 61 K. The excessive enthalpy calculated for the indicated anomaly ΔH°_{tr} = 107.7 J mol^{-1}, and entropy $\Delta S^\circ_{tr} = \Delta H^\circ_{tr}/T^\circ_{tr}$ = 1.8 J mol^{-1} K^{-1}. Based on the thermodynamic parameters and reproducibility of the anomaly on heating and cooling of the sample, we may assume that it corresponds to a relaxation transition of the "order→disorder" type related to the excitation of motion of atomic groups on heating of the fullerite and freezing of their motion on cooling.

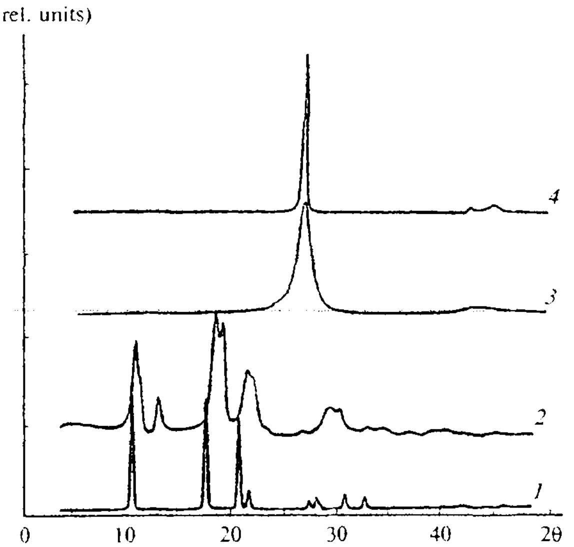


Fig. 1. Diffraction patterns of the starting fullerite C_{60} (*1*), fullerite C_{60}(8 GPa, 920 K) (*2*), fullerite C_{60}(8 GPa, 1270 K) (*3*), and graphite (*4*).

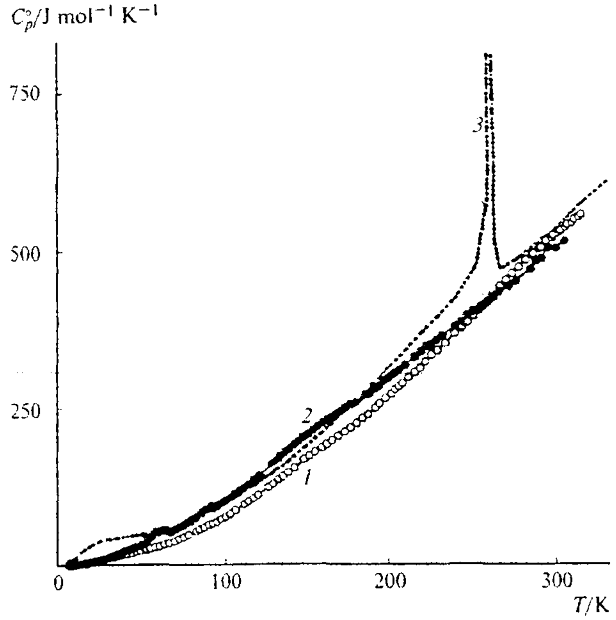


Fig. 2. Temperature dependences of the heat capacities of fullerite C_{60}(8 GPa, 920 K) (*1*), fullerite C_{60}(8 GPa, 1270 K) (*2*), and fullerite C_{60} (*3*).[21]

Both fullerites have no transformations of the first order and G type, which appear for the starting fullerite C_{60} within the 185—275 K interval and at 86 K, respectively (see Fig. 2, curve *1*). Disordering corresponds to the first transformation: transition to free rotation of C_{60} molecules in the points of the crystalline lattice and rearrangement of a simple cubic lattice into a face centered cubic lattice. The second transformation is related to the "freezing" of transition of the fullerene molecules from the orientation state with a high energy to the orientation state with a lower energy upon cooling and "thawing out" upon heating.[18] Similar transformations are absent in the fullerites under study due to the structural and physicochemical changes accompanying their preparation from fullerite C_{60} affected by the action of p and T. Since on treating C_{60} at 920 K and specified pressure, the two-dimensional polymerization of the fullerene molecules occurs, the oscillating molecular framework gains strength, and the heat capacity of the sample decreases. Evidently, this is the reason why the heat capacity C°_p of fullerite C_{60}(8 GPa, 920 K) is lower than that of the starting fullerite C_{60} (see Fig. 2, curves *1* and *3*, respectively).

For the sample of fullerite C_{60}(8 GPa, 1270 K), the C°_p values within the 70—180 K interval are higher, and at $T > 180$ K they are lower than those of the starting fullerite C_{60}. However, the differences in the heat capacities over this temperature range are low and do not exceed 2% at 300 K. In the low-temperature range (at $T < 70$ K, Fig. 3), the shapes of $C^\circ_p = f(T)$ functions for fullerites are similar, and the C°_p values at $T < 30$ K are similar even if they strongly differ from the heat capacities for the starting fullerite C_{60}. For example, the differences in heat capacities of C_{60} and fullerites C_{60}(8 GPa, 920 K) and C_{60}(8 GPa, 1270 K) at 25 K amount to 80%, at 40 K they are 60%, and at higher temperatures the differences decrease. For crystalline C_{60} and C_{60}(8 GPa, 920 K), the experimental data on C°_p are well described by the Debye function of the heat capacity

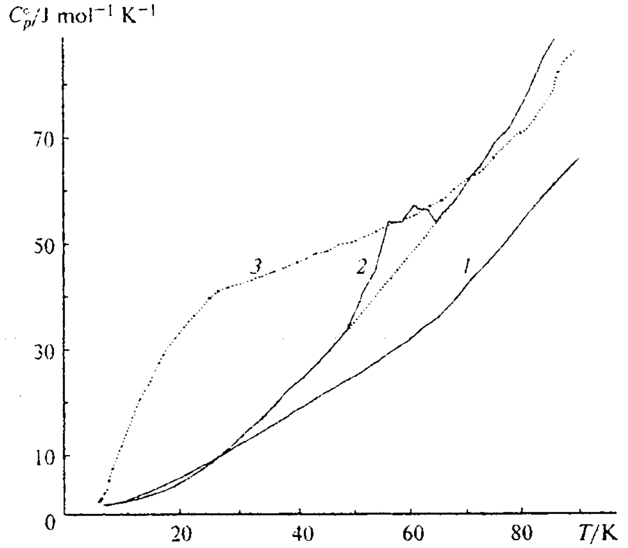


Fig. 3. Low-temperature heat capacities of fullerite C_{60}(8 GPa, 920 K) (*1*), fullerite C_{60}(8 GPa, 1270 K) (*2*), and fullerite C_{60} (*3*); dotted line on the $C^\circ_p = f(T)$ plot (curve *2*) is the standard run of the heat capacity of fullerite C_{60}(8 GPa, 1270 K) in the interval of the anomalous dependence of C°_p on T.

$$C^\circ_p = nD(\theta_D/T), \qquad (1)$$

where D is a function of the Debye heat capacity, and n and θ_D are empirical parameters (for C_{60}, $n = 10$ and $\theta_D = 58.82$ K; for fullerite, $n = 1$ and $\theta_D = 75$). Equation (1) with these parameters reproduces the corresponding experimental C°_p values within the 5—8 K interval with an accuracy of ±0.7 and ±0.2%, respectively. For fullerite C_{60}(8 GPa, 1270 K), we failed to select the Debye function of the heat capacity but found that the experimental C°_p values can satisfactorily be described by a third-power polynomial, which is characteristic, as a whole, of an amorphous substance.

$$C^\circ_p = 0.00097T^3 - 0.0107T^2 + 0.11883T + 0.00049. \qquad (2)$$

In the 5—9 K temperature range, the differences between the experimental C°_p values and those calculated by Eq. (2) do not exceed ±0.09% (C°_p/J mol^{-1} K^{-1}).

The values of fractal dimensionalities of D suggest the heterodynamic character of solids.[19—21] The D value can be obtained from the $\ln C_v$—$\ln T$ function[19,21] derived from the equation

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

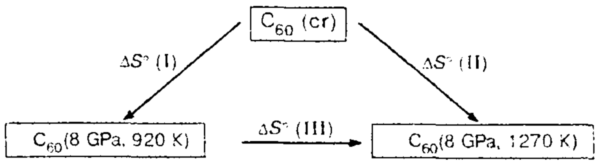
where k is the Boltzmann constant, N is the number of atoms in the molecule, $\gamma(D+1)$ is the γ function, $\xi(D+1)$ is the Riemannian ξ function, and θ_{max} is the maximum characteristic temperature. For the specific solid, $A = 3D(D+1)k\cdot N\gamma(D+1)\cdot\xi(D+1)$, where A is constant, Eq. (3) can be written in the form

$$\ln C_v = \ln A + D\ln(T/\theta_{max}). \qquad (4)$$

Without violating accuracy it can be assumed that at $T < 60$ K for measured fullerites $C^\circ_p \approx C_v$ and then, using the corresponding experimental data on the heat capacity within the 20—55 K range, we obtain for C_{60}(8 GPa, 920 K) $D = 1.48$ and for C_{60}(8 GPa, 1270 K) $D = 2.24$. Since solids with the layered structure are characterized by the value of $D = 2$ and the three-dimensional solids are characterized by $D = 3$, it can be deduced that the fullerite C_{60}(8 GPa, 920 K) shows a layered chain structure, whereas the fullerite C_{60}(8 GPa, 1270 K) exhibits structure that is intermediate between a layered and a three-dimensional topology.

Equations (1) and (2) were used for the extrapolation of C°_p of fullerites from 5 to 0 K, assuming that they reproduce the heat capacity in the specified temperature interval with the same accuracy as in the 5—8 K interval. The extrapolation of C°_p was necessary for the calculation of enthalpies, entropies, and Gibbs functions of fullerites in the 0—320 K region (Table 1). For 298.15 K and p = 101.325 kPa, the values of the functions of the fullerites under study and starting fullerite C_{60} are presented in Table 2. The calculation procedure of the functions has previously been published.[22] The zero entropy $S^{\circ}_0 \approx 35$ J mol^{-1} K^{-1} of fullerite C_{60}(8 GPa, 1270 K) was estimated from the known data,[23] and S°_0 for crystalline fullerite C_{60}(8 GPa, 920 K) was accepted to be zero.

The changes in entropies during hypothetical transformations of fullerite C_{60} into the fullerites hereby described and intertransformations of fullerites at 298.15 K and standard pressure (see Table 1) are presented in the following scheme.



$\Delta S^{\circ}(\mathrm{I}) = -122$ J mol^{-1} K^{-1},
$\Delta S^{\circ}(\mathrm{II}) = -45$ J mol^{-1} K^{-1},
$\Delta S^{\circ}(\mathrm{III}) = 77$ J mol^{-1} K^{-1}.

Table 1. Thermodynamic functions of fullerites under study calculated per mole of C_{60} (M = 720.66 g mol^{-1})

T/K	$C^{\circ}_p(T)$	$S^{\circ}(T) - S^{\circ}(0)$	$H^{\circ}(T) - H^{\circ}(0)$	$-[G^{\circ}(T) - H^{\circ}(0)]$
	J mol^{-1} K^{-1}		kJ mol^{-1}	
		Crystalline C_{60}(8 GPa, 920 K)		
5	0.20	0.069	0.00026	0.0001
10	1.41	0.518	0.00386	0.0013
15	3.25	1.412	0.01529	0.0060
20	5.67	2.676	0.03744	0.0161
25	8.49	4.237	0.07268	0.0332
30	11.62	6.058	0.1229	0.0589
40	18.04	10.280	0.2713	0.1400
50	24.23	14.970	0.4827	0.2661
100	75.39	45.680	2.847	1.721
150	165.50	92.680	8.794	5.108
200	264.30	153.20	19.42	11.21
250	338.80	225.20	35.69	20.62
300	519.0	308.20	58.54	33.92
		Amorphous C_{60}(8 GPa, 1270 K)		
5	0.45	0.44	0.00119	0.00103
10	1.10	0.92	0.00482	0.00440
15	2.43	1.60	0.0134	0.0106
20	4.65	2.58	0.0306	0.0209
25	8.15	3.97	0.0621	0.0370
30	12.74	5.84	0.1140	0.0613
50	35.10	17.24	0.5785	0.2837
100	101.30	62.47	4.01	2.237
150	202.40	121.90	11.51	6.771
200	292.90	192.60	23.90	14.61
250	396.20	269.20	41.16	26.13
300	499.60	350.30	63.48	41.60

Table 2. Thermodynamic functions of fullerite C_{60} [21] and fullerites at 298.15 K and standard pressure

Fullerene (8 GPa, 920 K)	C°_p	$S^{\circ}(T)$	$H^{\circ}(T) - H^{\circ}(0)$	$-[G^{\circ}(T) - H^{\circ}(0)]$
	J mol^{-1} K^{-1}		kJ mol^{-1}	
C_{60}	524.8	426.5	72.44	54.72
C_{60}(8 GPa, 920 K)	514.8	304.7	57.51	33.30
C_{60}(8 GPa, 1270 K)	495.5	382	62.49	51.40

It can be seen that during the two-dimensional polymerization of fullerene molecules the entropy decreases. This loss is related, on the one hand, to the loss of entropy of free rotation of the fullerene molecules and, on the other hand, to the appearance of a polymeric framework with a more rigid configuration than the crystalline lattice of fullerite C_{60}. In process II, the entropy decrease is much lower than that in process I. In this process, fullerite C_{60} is graphitized, and its molecules are decomposed. This results in an increase in the entropy with the simultaneous cross-linking of carbon hexagons formed during the decomposition of C_{60} by carbon atoms in the sp^3-valent state. This cross-linking is accompanied by a decrease in the entropy that overlaps the entropy increase due to the decomposition of the C_{60} molecules and subsequent combination of the fragments formed. In process III, the entropy increases because the increase in entropy during amorphization of fullerite C_{60}(8 GPa, 920 K) is not compensated by a decrease in the entropy during cross-linking of fragments of the fullerene molecules in the synthesis of C_{60}(8 GPa, 1270 K) from fullerite C_{60}.

The authors thank G. A. Dubitsky for help in the work and N. P. Serebryanaya for X-ray analysis of fullerites.

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Received February 5, 1999;
in revised form May 18, 1999