Theoretical Study of Thermodynamic Properties of a Family of Fullerites from C$_{36}$ to C$_{96}$ in the Equilibrium with Their Vapors

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On the basis of the correlative method of the unsymmetrized self-consistent field that yields the account of the strong anharmonicity of the lattice vibrations, it has been calculated the temperature dependence of saturated vapor pressure of higher and smaller fullerites, from C$_{36}$ up to C$_{96}$, and their thermodynamic properties along their sublimation curves. We have used the intermolecular potential of Girifalco with parameters recently calculated for these fullerenes. The calculations were accomplished up to the temperature of loss of stability (spinodal point) T_s. We compare our results with available experimental data and with quantities calculated earlier for the magnitudes of the most widespread of the fullerites, the C$_{60}$. The behavior of some characteristics is considered in their dependence on the number of atoms in the molecule. The saturated vapor pressures up to the spinodal points of the two-phase systems crystal−gas is approximated by the formula $\log P_{sat} = A - (B/T) - CT$, where the last term is related to the anharmonicity of the lattice vibrations. The coefficient A practically has no dependence on the number of atoms in the molecule (varying only by 2.2%); B increases monotonically, while C decreases from C$_{36}$ to C$_{96}$ by approximately twice. The isothermal bulk modulus B_T and the shear modulus C_{44} vanish at the spinodal points.

1. Introduction and Brief Survey

The possibility of the existence of a third, molecular form of the carbon, along with the graphite and the diamond, was theoretically investigated in the beginning of the seventies.[1,2] These molecules C$_{20+2n}$ (n is a positive integer number) have been experimentally discovered in the mid eighties.[3] Since the elaboration of effective technologies for the production, separation, and purification of fullerenes in quantities enough for growing crystals of macroscopic dimensions, the fullerites,[4] it has been observed a permanent interest to their experimental and theoretical investigation. Hitherto, the most widespread C$_{60}$ and the next to it C$_{70}$ are the most completely studied. It is known, for instance, that at low temperatures the molecules in their lattices are orientationally ordered, whereas at high temperatures they rotate rather freely in an fcc lattice (with a little mixture of the hcp phase in C$_{70}$). Similar behavior is to be expected also from other fullerites.

The theoretical study of the thermodynamics of the high-temperature modifications of the fullerites was initiated by Girifalco.[5] By considering that the form of the C$_{60}$ molecule is almost spherical and averaging the Lennard-Jones atom−atom potentials of a pair of molecules over all their orientations, he has deduced for the orientationally disordered phases (solid, gaseous, and hypothetical liquid) the intermolecular potential

$$\Phi_G(r) = -\alpha\left(\frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4}\right) + \beta\left(\frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}}\right) \quad (1)$$

Here, $s = r/2a$, r is the distance between the centers of the

molecules; a is the radius of their hard core,

$$\alpha = n^2 A/12(2a)^6, \beta = n^2 B/90(2a)^{12} \quad (2)$$

A and B are the coefficients to the attractive and repulsive terms of the atom−atom Lennard-Jones potential, while $n = 60$ is the number of atoms in the molecule. The parameters A and B were fitted in with experimental data for the lattice constant and heat of sublimation.

The C$_{70}$ molecule has a form similar to an oblong ellipsoid. The forms of molecules of the other fullerenes are even more complicated. Noticing that this molecule can be separated in five groups of 10 or 20 atoms, each one lying in a spherical shell of a certain radius, and generalizing the procedure of Girifalco, Verheijen et al.[6] have obtained the intermolecular potential for this fullerene. It has the form of a sum of 25 terms of the type 1, describing the interactions between different pairs of such shells of neighboring molecules.

Kniaz' et al.[7] and, independently, Abramo and Caccamo[8] used the Girifalco potential 1 for the orientationally disordered phases of C$_{70}$. This corresponds to approximating the form of the molecule to a sphere whose radius is determined by fitting in the calculated with this potential lattice constant with its experimental value. The idea of a spherical approximation for some of the higher fullerenes with radius related to the number of atoms in the molecule was used in refs 9 and 10 but regardless to the intermolecular potentials.

The intermolecular potentials of Girifalco and Verheijen were employed on the basis of the correlative method of the unsymmetrized self-consistent field (CUSF, see, e.g., refs 11, 12) for the investigation of the whole sets of equilibrium thermodynamic properties of the high-temperature phases of the fullerites C$_{60}$[11−13] and C$_{70}$.[14,15] Broad regions of their diagram of states were considered, including the sublimation curves.[12,14]

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TABLE 1: Refined Characteristics of the Girifalco Potential (1) for Various Fullerenes

	$C_{60}{}^a$	C_{28}	C_{36}	C_{50}	C_{70}	C_{76}	C_{84}	C_{96}
$2a$ $(10^{-8}$ cm)	7.100	4.850	5.500	6.481	7.669	7.991	8.401	8.981
α $(10^{-14}$ erg)	7.494	16.059	12.49	8.980	6.424	5.916	5.353	4.684
β $(10^{-17}$ erg)	13.595	286.64	104.90	28.19	8.338	5.281	3.539	2.074
σ $(10^{-8}$ cm)	9.599	7.358	8.000	8.976	10.161	10.480	10.880	11.468
r_0 $(10^{-8}$ cm)	10.056	7.808	8.460	9.443	10.622	10.946	11.358	11.936
$-\epsilon/k_B$ (K)	3218	1775	2182	2813	3594	3807	4080	4468

^{a} Girifalco.[5]
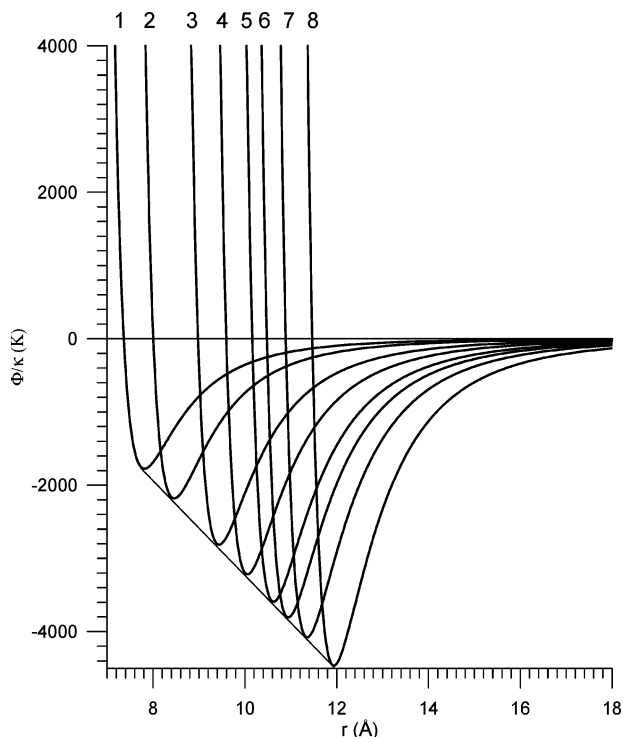
Figure 1. The Girifalco potential for eight fullerenes: C_{28} (1), C_{36} (2), C_{50} (3), C_{60} (4),[5] C_{70} (5), C_{76} (6), C_{84} (7), C_{96} (8).

Intramolecular vibrations[16−18] were taken into account. They give the main contribution to the specific heats. The agreement with experiment is good.

In recent years, a growing interest has been observed in the higher fullerites C_{76} and C_{84},[19−25] and in C_{96},[26] and also in the smaller ones, especially C_{36}.[27,28] A method was proposed[29] for the calculation of the coefficients of the potential of Girifalco 1 on the basis of the spherical approximation of the form of the molecules, starting from their magnitudes for the C_{60},[5] that is, without additional fitting parameters. The coefficients for a series of smaller and higher fullerenes, from C_{28} to C_{96}, have been calculated. The curves of the potentials for these fullerenes are shown in Figure 1, and the refined values of their basic characteristics are presented in Table 1. It is interesting that the coefficients α and β decrease with increasing number of atoms in the molecule, although the minimum point of the potential and the depth of its well increase. One can see from Figure 1 that the minimum points of the Girifalco potential for various fullerenes lie on a nearly straight line. This potential has been used for the calculation of the saturated vapor pressures and the thermodynamic properties of the two higher fullerites C_{76} and C_{84}.[30] A good agreement with available experimental data has been obtained.

Recently, computer simulation results have been published for the properties of C_{76} and C_{84} fullerites using the Girifalco potential.[31,32] Fernandes et al.[31] have utilized in particular our values of the parameters for this potential,[29,30] whereas Micali

et al.[32] adopted the effective radii of the molecule by fitting experimental data for the lattice parameters. Both approaches give close results.

The present work is devoted to a theoretical investigation and comparison analysis of thermodynamic properties of a family of fullerites from C_{36} to C_{96} along their sublimation curves.

2. Brief Sketch of the Method

The zeroth approximation of the CUSF includes the strong anharmonicity of the lattice vibrations up to the fourth order, and the perturbation theory takes into account the fifth and sixth anharmonic terms. Thus, taking into consideration the rotational and intramolecular degrees of freedom, the free Helmholtz energy and the equation of state of the crystal at a temperature $\Theta = kT$ under a pressure P are of the form

$$F = N\left\{\frac{K_0}{2} - \frac{5\Theta}{24}\left(\frac{\beta}{X}\right)^2 - \frac{\Theta}{4}\left(X + \frac{5\beta}{6X}\right)^2 - \right.$$

$$\left. \Theta \ln\left[\left(\frac{3m^2\Theta^3}{\hbar^4 K_4}\right)^{3/4} D_{-1.5}\left(X + \frac{5\beta}{6X}\right)\right]\right\} - \frac{N\Theta}{2}\ln\left(\frac{8I_1{}^2 I_2 \Theta^3}{\hbar^6}\right) -$$

$$N\Theta\sum_j g_j \ln\left(2\sinh\frac{\hbar\omega_j}{\Theta}\right) + F^2 + F^H \quad (3)$$

$$P = -\frac{a}{3v}\left[\frac{1}{2}\frac{dK_0}{da} + \frac{\beta\Theta}{2K_2}\frac{dK_2}{da} + \frac{(3-\beta)\Theta}{4K_4}\frac{dK_4}{da}\right] + P^2 + P^H \quad (4)$$

$$E^0 = \frac{N}{2}\left[K_0 + \frac{(15+\beta)\Theta}{2} + \hbar\sum_j g_j\omega_j\coth\frac{\hbar\omega_j}{2\Theta}\right] + E^2 + E^H \quad (5)$$

Here, N is the quantity of molecules (the Avogadro's number), m the mass of the molecule, I_1 and I_2 are the moments of inertia (for C_{60} $I_1 = I_2$), ω_j and g_j are the frequencies and degeneracies of the intramolecular vibrations, a is the distance between the nearest neighbors, $v(a) = V/N$ the volume of the unitary cell, and $\beta(K_2(3/\Theta K_4)^{1/2})$ is an implicit function determined by the transcendental equation

$$\beta = 3X\frac{D_{-2.5}(X + 5\beta/6X)}{D_{-1.5}(X + 5\beta/6X)} \quad (6)$$

where D_v are the parabolic cylinder functions,

$$K_{2l} = \frac{1}{2l+1}\sum_{k\geq1} Z_k \nabla^{2l}\Phi(R_k), \quad l = 0,1,2 \quad (7)$$

R_k are the radii of the coordination spheres, Z_k the coordination
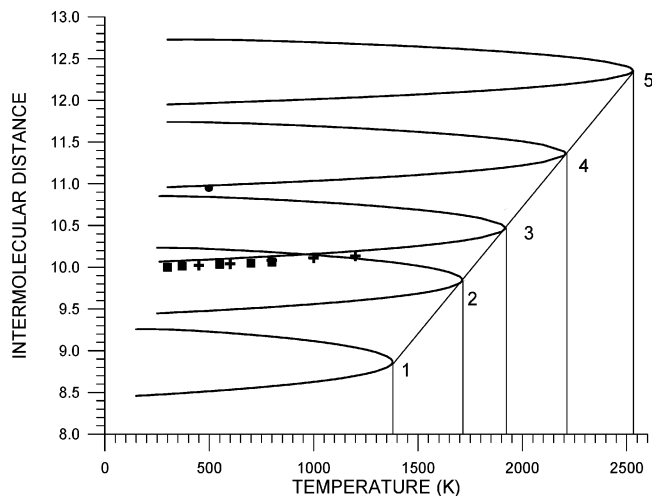
Figure 2. The intermolecular distances for fullerites along their sublimation curves: C_{36} (1), C_{50} (2), C_{60} (3), C_{76} (4), C_{96} (5). The vertical lines show the temperatures T_S. Experimental data for C_{60} are taken from works by Mathews et al.[33] (■), Fischer and Heiney[34] (+), and for C_{76} from work by Kawada et al.[19]

Figure 3. Saturated vapors pressures. Experimental data taken from refs 35−38.

numbers, and F^2, F^H, P^2, P^H, E^2, and E^H are the corrections of the perturbation theory that contain in particular the anharmonicity of higher orders. It is seen from eq 4, for instance, that the rotational and intramolecular degrees of freedom have no influence on the thermal equation of state and on the properties related to it, the thermal expansion and the isothermal elastic moduli. But they give a significant contribution to the equation of energy (eq 5) and the main contribution to the specific heats of the fullerites (up to 80−90%). Because of this, the molar specific heats of the fullerites at high temperatures are much greater than those of the majority of other substances, and the difference between isobaric and isochoric specific heats as well as between isothermal and adiabatic elastic moduli are very small.

In the equilibrium of the crystal with its vapor, one has to add to eq 4 the condition of phase equilibrium (equality of the chemical potentials) and the equation of state of the gaseous phase. For the latter, one can use the virial expansion. Taking into account the second virial terms this reduces to

$$P = P_{id}(1 - BP_{id}/\Theta)$$

$$P_{id} = \Theta \left(\frac{K_4}{12\pi^2\Theta}\right)^{3/4} \exp\left[\frac{K_0}{2\Theta} - \frac{5}{24}\left(\frac{\beta}{X}\right)^2 - \frac{1}{4}\left(X + \frac{5\beta}{6X}\right)^2 + \frac{f^2 + f^H}{\Theta}\right] \bigg/ D_{-1.5}\left(X + \frac{5\beta}{6X}\right) \quad (8)$$

where $f^i = F^i/N$, $i = 2$, H. The set of equations 4 and 8, with the account of 6, determine the temperature dependence of the saturated vapor pressure P_{sat} (T) and of the distance between the nearest neighbors in the crystal $a(T)$ along the curve of phase equilibrium.

3. Results and Discussion

3.1. Sublimation Curves. We have solved these equations for several fullerites from C_{36} to C_{96}. The results for the mean intermolecular distances in C_{36}, C_{50}, C_{60}, C_{76}, and C_{96} together with the available experimental data for C_{60}[33,34] and C_{76}[19] are depicted in Figure 2. Remember[12] that the upper branches a_2-(T) of these curves correspond to the absolute unstable thermodynamic states, since on them the isothermal modulus of the crystal B_T is negative. At the temperature T_S, where both
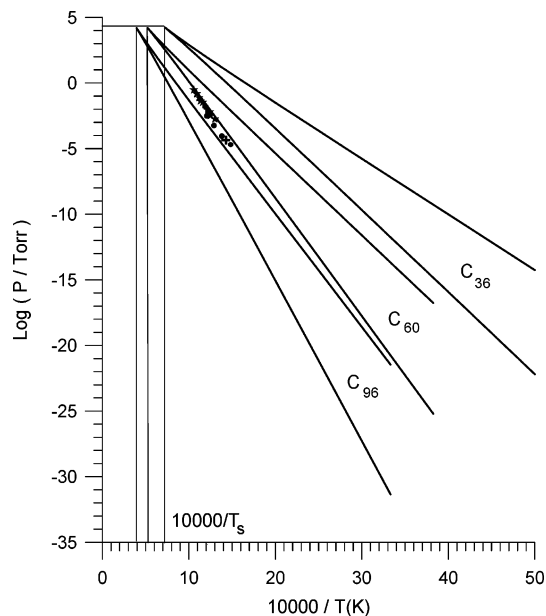
branches coalesce, T_S vanishes. From here it is seen the good agreement for the lower branches $a_1(T)$ with the available experimental data. Our results agree as well with numerical simulations performed recently for low temperatures.[31] It is interesting that the points $a(T_S)$ lie practically on a straight line.

To avoid encumbrance, the dependence of the logarithm of the saturated vapor pressures on the inverse of temperature is shown in Figure 3 only for C_{36}, C_{60}, and C_{96}. It is close to linear. For the lower branch this is in good agreement with available results of measurements for C_{60}[35−38] (and also for C_{70}, C_{76}, and C_{84}). More accurately, it is described along all the range of temperatures by the equation

$$\log P_{sat} = A - \frac{B}{T} - CT \quad (9)$$

in which the last term is due to the anharmonicity of lattice vibrations. Although the coefficient C is relatively small, yet at high temperatures it gives a noticeable contribution to P_{sat}. We have processed by this formula the results of our calculations up to the temperatures of the possible triple points crystal−liquid−vapor. The existent estimates for the C_{60} lie in the limits from 1450[12] to 1800 K.[39] We have taken the mean value 1620 K,[40] and for the other fullerites we have used the rule of the correspondent states. The behavior of all the three coefficients is shown in Figure 4. The constant term in eq 9 depends almost not at all on the number of atoms in the molecule, varying only by 2.2%. Thus, in the spinodal points the saturated vapor pressures of various fullerites differ very little from each other. The coefficient B grows monotonically, while C decreases from the C_{36} to the C_{96}, by about twice. Such a behavior corroborates the experimental estimations of A and B available for C_{60}, C_{70}, C_{76}, and C_{84}, see Table 2. There is a detour from this trend of the value of B for the C_{70} calculated using the Verheijen intermolecular potential.

All the data of measurements executed for C_{60}, C_{70}, C_{76}, and C_{84}, because of experimental difficulties in limited temperature intervals, have been processed in the linear approximation, that is, without the third term in eq 8. Markov et al.[25] based on the analysis of the results of various authors for C_{60} and C_{70} have given values recommended of the coefficients A and B for these
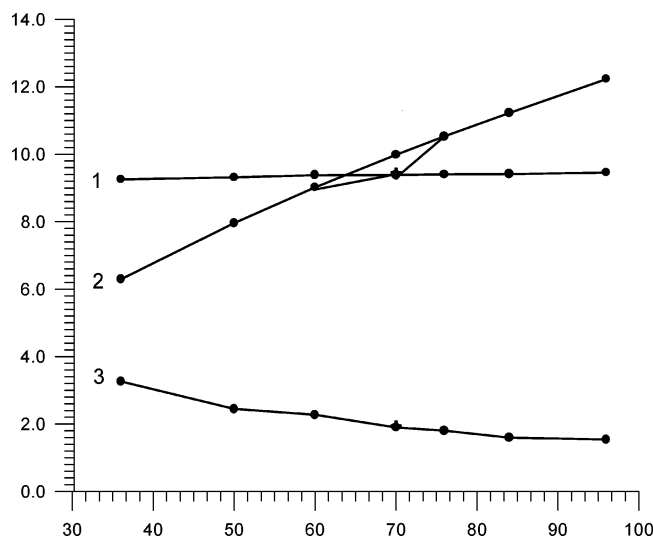
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Figure 4. Coefficients of eq 9: A (1), $10^{-3}B$ (2), $10^4 C$ (3).

TABLE 2: Coefficients of Eq 8

	C_{60}	C_{70}	C_{76}	C_{84}
A^a	9.3805	9.3975	9.4078	9.4115
A^b	10.85 ± 0.76	11.23 ± 1.49		
A^c			11.23 ± 0.20	10.92 ± 0.30
A^d			10.65 ± 0.47	10.92 ± 0.28
A^e			10.66 ± 0.92	11.28 ± 0.93
B^a	9019.6	9983.0	10 533.8	11 227.8
B^b	8738 ± 472	9768 ± 774		
B^c			$10\ 150 \pm 150$	$10\ 950 \pm 300$
B^d			9904 ± 356	$10\ 570 \pm 234$
B^e			$11\ 365 \pm 709$	$11\ 743 \pm 717$

a Our results. *b* Recommended experimental values obtained by Markov et al.[25] for C_{60} in the range of 660−990 K and for C_{70} of 650−904 K. *c* Experimental values obtained by Brunetti et al.[20] for C_{76} in the range of 834−1069 K and by Piacenti et al.[23] for C_{84} in the range of 920−1190 K. *d* Experimental values obtained by Boltanina et al.[21] for C_{76} in the range of 637−911 K and by Boltanina et al.[21] for C_{84} in the range of 658−980 K. *e* Experimental values obtained by Boltanina et al.[24] for C_{76} and C_{84} in the range of 681− 901 K.
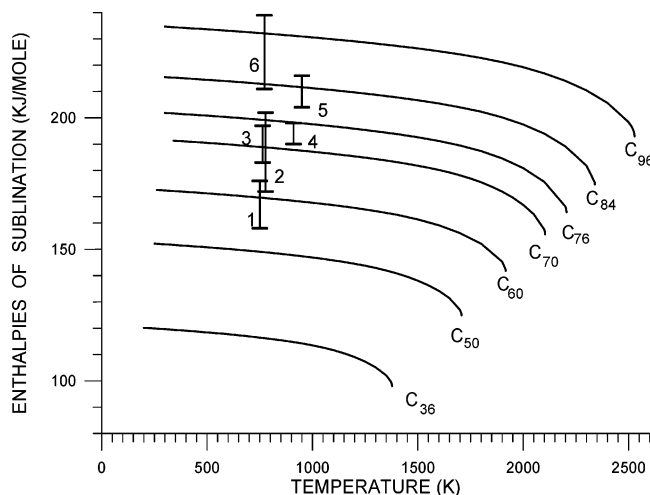

Figure 5. Enthalpies of sublimation. Experimental data for C_{60} (1) and C_{70} (2) taken from work by Markov et al.[25] (the values recommended), for C_{76} from works by Brunetti et al.[20] (3), Boltanina et al.[24] (4), and for C_{84} from works by Piacenti et al.[23] and Boltanin et al.[24]

fullerites. In Table 2, we compare our results with them and with experimental data for C_{76} [20−22] and for C_{84}.[22−24]

In Figure 5, we show the temperature dependence of the enthalpies of sublimation of fullerites. We compare them with
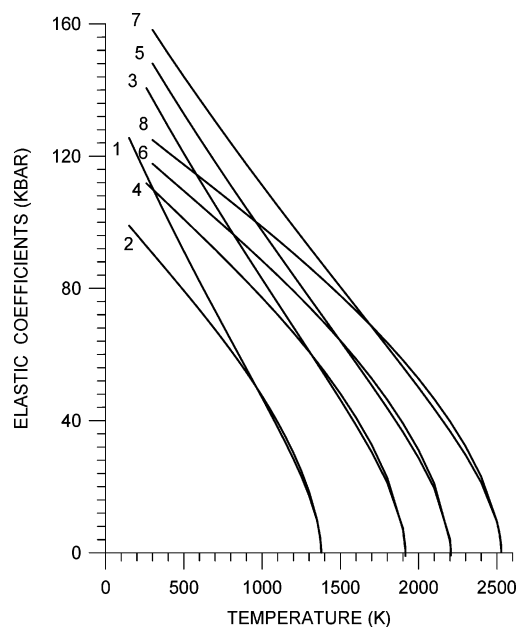

Figure 6. Isothermal bulk moduli B_T (odd numbers) and shear coefficients C_{44} (even numbers) for the fullerites: C_{36} (1, 2), C_{60} (3,4), C_{76} (5,6), C_{96} (7, 8).
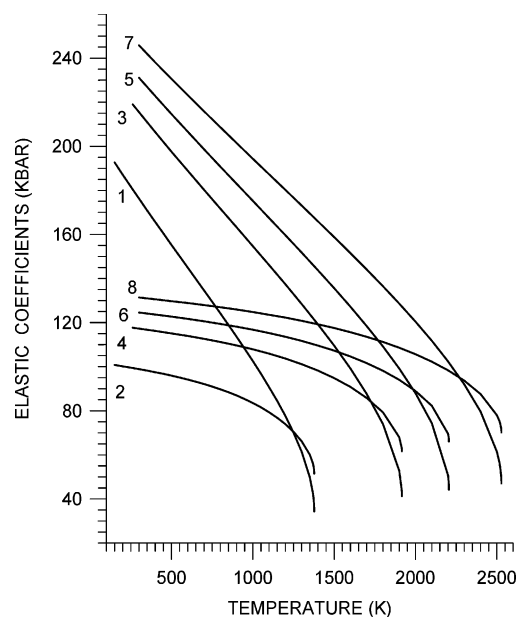

Figure 7. Isothermal coefficients of uniaxial tension C^T11 (odd numbers) and shear coefficients $C^T_{11} - C^T_{12}$. The numbers for various fullerites are the same as in Figure 6.

the experimental data for C_{60} and C_{70},[25] C_{76},[20,21] and C_{84}.[23,24] One can see the agreement within the limits of experimental error, with the exception of the result for C_{76} [20] whose difference from our calculations slightly extrapolates theses limits. Our results show an excellent agreement with computer simulations by Fernandes et al.[32] presented at 700 K (in kJ/mol): 170 ± 12 for C_{60}, 191 ± 13 for C_{70}, 198 ± 14 for C_{76}, and 212 ± 15 for C_{84}.

3.2. Thermodynamic Properties. Along the lower branches, we have calculated the thermodynamic properties of the fullerites that are due to the lattice vibrations.

Figures 6 and 7 show the elastic properties, which are also the coefficients of thermodynamic stability of the crystals. They all decrease monotonically as the temperature increases. Besides, in the heavy fullerites they are greater than in the light ones.
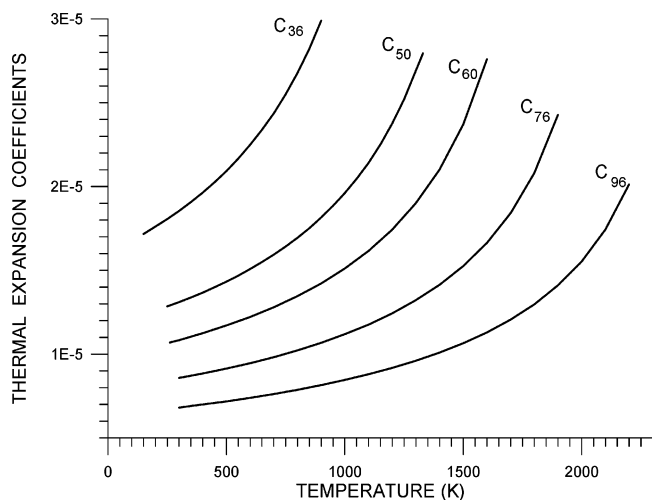
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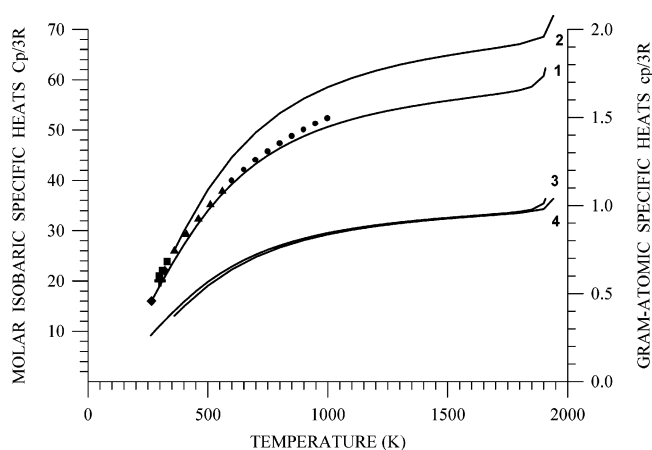**Figure 8.** Thermal expansion coefficients of the fullerites.

Figure 9. Isobaric heat capacities for C_{60} and C_{70}. Experimental data are taken from works by Y. Jin et al.[41] (■), Matsuo et al.[42] (+), Fischer et al.[43] (◆), Lebedev et al.[44] (▲), and Markov et al.[25] (●).

At $T = T_S$ the bulk modulus B_T vanishes together with the shear modulus C_{44}, both as the $^1/_2$ power of $T_S - T$. Other stability coefficients remain finite and positive up to and including this temperature. Therefore, T_S is the spinodal point (the point of the loss of the thermodynamic stability), in the present case for the two-phase system crystal−vapor.

In Figure 8, the thermal expansion coefficient of fullerites is shown. It increases with the temperature. For the heavy fullerites, it is smaller than for the light ones. Near the spinodal point, it grows sharply tending to infinite when $T \rightarrow T_S$. That is why we take here a smaller temperature.

The spectra of intramolecular vibrations ω_j and g_j that give the prevalent contribution to the specific heats of the fullerites are known for C_{60} and C_{70} fullerenes.[16−18] That is why we have calculated the thermal properties only for these two fullerites. Their isobaric specific heats are shown in Figure 9. Their molar values are considerably greater than those of the majority of other substances. Besides for C_{70} it is higher than for C_{60} because of the greater number of its intramolecular degrees of freedom. At the same time, the gram atom specific heats of both fullerites are very close to each other (except for the small vicinity of the points T_S, where the contribution of the lattice vibrations grows sharply). This is an indication of the proximity of the integral characteristics of their intramolecular vibrations. The

agreement with experimental results available for C_{60} fullerite[25,41−44] is quite satisfactory.

So, the good agreement with experimental data that we have obtained for thermodynamic properties of fullerites C_{60}[11−13] and C_{70},[14,15] and also for sublimation characteristics of C_{76} and C_{84},[30,31] allows us to expect an agreement of results of our present calculations for other fullerites with those of measurements that will appear in the future.

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