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THE THIRD, MOLECULAR, FORM OF CARBON: FULLERENES, CARBON NANOTUBES AND ONIONS SOME PHYSICAL PROPERTIES OF FULLERITES

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Abstract

A brief review is presented of the pre-history and discovery of fullerenes (and then carbon nanotubes) that make the third molecular form of carbon, and of various, predominantly physical, properties of fullerites, i.e. of crystals composed of fullerene molecules. Particular attention is being given to the intermolecular forces, especially at orientationally disordered phases. The Girifalco potential is presented for eight fullerenes from C_{28} to C_{96} and its generalization is made for the interactions between the different fullerene molecules, C_m and C_n.

The thermodynamic properties of the high-temperature modifications of a family of the fullerites, from C_{36} up to the C_{96}, calculated in equilibrium with their saturated vapors on the basis of the correlative method of the unsymmetrized self-consistent field that enables one to take into account the strong anharmonicity of the lattice vibrations, are discussed. The calculations were accomplished up to the temperature of loss of stability (spinodal point) T_s. We compare our results with available experimental data. The behavior of some characteristics is considered in their dependence on the number of atoms in the molecule. Using the Lindemann's melting criterion we estimate a possible melting curve for the C_{60} fullerite.

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Keywords: fullerenes and fullerites, the Girifalco potential, the correlative method of the unsymmetrized self-consistent field, the sublimation curves, thermodynamic properties.

Resumen

Presentamos una breve revisión sobre la prehistoria y descubrimiento de los fullerenos y más tarde nanotubos que constituyen la tercera forma molecular del carbón y también sobre varias propiedades, predominantemente físicas, de los fulleritos, es decir, cristales compuestos por moléculas de fullereno. Particular atención es dada a las fuerzas intermoleculares, especialmente en fases de orientación desordenadas. El potencial de Girifalco es presentado para ocho fullerenos entre C_{28} y C_{96} y su generalización es hecha para las interacciones entre las diferentes moléculas fullerenos, C_m y C_n.

Las propiedades termodinámicas de las modificaciones a alta temperatura de una familia de los fulleritos, desde C_{36} hasta C_{96}, calculadas en equilibrio con su vapor saturado sobre la base del método correlativo del campo autoconsistente asimétrico que permite tomar en cuenta la fuerte anarmonicidad de las vibraciones de red, son discutidas. Los cálculos fueron logrados hasta la temperatura de pérdida de estabilidad T_s (punto espinodal). Comparamos nuestros resultados con datos experimentales disponibles. El comportamiento de algunas propiedades es considerado en su dependencia en el número de átomos en la molécula. Usando el criterio de fusión de Lindemann estimamos la posible curva de fusión del fullerito C_{60}.

Palabras claves: Fullerenos y fulleritos, el potencial de Girifalco, método correlativo del campo autoconsistente asimétrico, las curvas de la sublimación, propiedades termodinámicas.

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1. Pre-history and Discovery

In 2005, 20 years have passed, since Harold W. Kroto, Robert F. Curl Jr. and Richard E. Smalley discovered the new, molecular, form of carbon.[1] This was one of most important scientific findings of the 1980s, and in 1996 these investigators were awarded by the Nobel prize.

Carbon is one of most abundant elements in the universe. For a very long time it had been believed that there existed two of its polymorph (and at the same time allotropic) forms, very soft graphite and extra-hard diamond. The first one possesses the layered structure, with atoms in a layer being linked by covalent bonds, whereas layers interacting with each other by much weaker Van der Waals forces. The second one has the A_4 cubic lattice where all atoms are linked by very srtong covalent bonds. Graphite structure is absolutely stable, and diamond is metastable because has the less cohesive energy although the difference is very small (0,02 eV per atom).

In the mid-1960s it was discovered in the absorption spectrum of the interstellar dust the ultraviolet line of 2175 Å [2]. Jones in 1966 [3] considered the possibility of forming new types molecules with carbon atoms. Osawa in 1970 [4] (in Japan) and Yoshida and Osawa in 1971 [5] (again in Japan) investigated theoretically the distortion of a plane graphite layer owing to the replacement of some hexagons by pentagons and the formation of closed shells containing the 60 atoms. They conjectured that such a molecule would be stable. A little later, in 1973, soviet scientists Bonchvar and Galpern published a Hückel calculation on C_{60} [6], see also[7], and Davidson applied general theoretical group techniques to highly symmetric molecules, one of which was C_{60} [8]. The nonplanarity of atomic positions in the fullerene molecules leads to strong strains resulting in their lower stability. Fig. 1 shows the relations between the cohesive energies of the three forms of carbon. The fullerene molecules are less stable than graphite and even than diamond. True, the Van der Waals intermolecular bonds in fullerites reduce this difference. One can find more recent and detailed results in [9,10].

In 1985, Kroto *et al.*[1] identified such molecules obtained in their laboratory during spontaneous gas-phase nucleation of atoms evaporated from graphite by the laser irradiation. The terms *fullerenes* or *buckminsterfullerenes* have their origin in the name of the designer-inventor of the geodesic domes Buckminster Fuller. Sometimes they are termed also the *buckyballs*. By early 1990s, effective technologies (had been elaborated) for the production, separation and deep purification of fullerenes in quantities enough for growing crystals of macroscopic sizes, named *fullerites*,* e.g.[11–13].

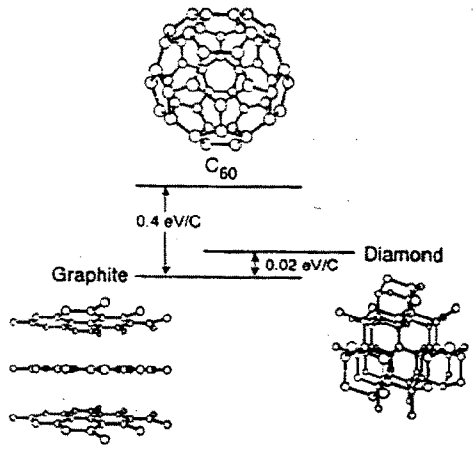


Fig. 1. Relations between the cohesive energies (per atom) of the three forms of carbon: graphite, diamond and C_{60} fullerene.

In Fig. 2, a schematic sketch is shown of an experimental setup for producing and analyzing the fullerenes.

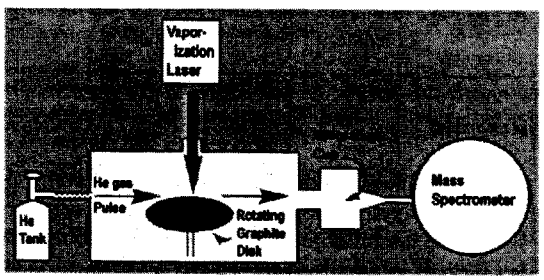


Fig. 2. A scheme of the setup used by Krätschmer *et al.* for producing and analyzing fullerenes.

This invokes to studies of fullerenes by thousands of researchers – experts in the areas of physics, chemistry, science of materials, biology, etc. Intensive efforts mounted by these scientists working in hundreds laboratories of various countries led to discoveries of many new interesting properties of fullerenes. Such properties cause to consider the fullerens not only as a new attractive matter for scientific inquiry but also as a basis for a wide range of practical implementations. Below we dwell briefly

* Such crystals doped by metal atoms or by other impurities are named *fullerides*.

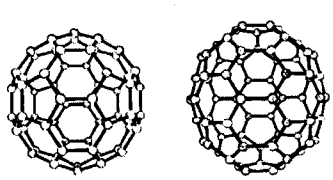
on some interesting physical properties of fullerenes, fullerites and fullerides, and on their possible applications.

2. A Family of Fullerenes

During the process of production, mixtures of various fullerene molecules C_m are formed. Here $m = 20 + 6n$, where n is a positive integer number. So, one can speak about a *family of fullerenes*. Such a mixture can be separated using mass-spectrometers and organic solvents. An essential characteristic of fullerenes is the bond alternation determining both their electronic properties and their ability to form intermolecular bonds.

The C_{60} molecule occupies a central place in the family of fullerenes. It exhibits the highest symmetry, has the highest cohesive energy per atom and, consequently, is the most abundant. Its atoms are placed at the vertices of 20 hexagons and 12 pentagons, so that each hexagon borders with 3 hexagons and 3 pentagons whereas each pentagons borders only with hexagons. The bonds linking two hexagons ([6,6]-bonds (1,39 ± 0,01) Å) are double and shorter than the single bonds between a hexagon and a pentagon ([6,5]-bonds, (1,44 ± 0,01) Å) [14–16]. Each atom occupies the equivalent position at the vertex of 2 and 1 pentagon. It looks like a football that is close to the sphere of radius $a \approx 3{,}55$ Å. The equivalence of the atomic positions facilitates forming these molecules from graphite in the course of its evaporation (by electric heating or laser irradiation) and condensation (in the stream of an inert gas). Because of this, in the production of fullerenes their mixtures contain 80 – 90 % of C_{60}.

Next to C_{60} in stability and hence in abundance is the C_{70} fullerene. Its form is similar to an oblong uniaxial ellipsoid with semi-axes $a^{(1)} = a^{(2)} \approx 3{,}61$ Å and $a^{(3)} \approx 4{,}26$ Å. One can envision the creation of the C_{70} molecule from C_{60} by insertion of the belt of 10 atoms into its equatorial area, accompanied by its stretching. There exist 5 groups of equivivalent position of atoms in this molecule. The content of the C_{70} in the mixtures obtained is about 10 %. The C_{60} and C_{70} molecules are shown in Fig. 3. They and the corresponding fullerites have been most completely studied.



a b

Fig. 3. The C_{60} (a) and C_{70} (b) molecules.

The molecular shapes of the other fullerenes are more complicated For instance, the atoms in the C_{76} molecule, Fig. 4, occupy 19 different positions.[17] The C_m molecules with $m > 70$ are called the larger fullerenes and with $m < 60$ the smaller ones. When the number of atoms comprises some hundreds we deal with giant fullerenes. Fig. 4 shows the C_{76} molecule in the three projections and Fig. 5 the molecules of some smaller and larger fullerenes.

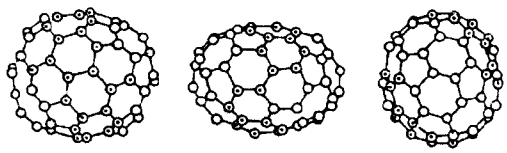


Fig. 4. The molecule of a larger fullerene – C_{76}.

Aside fullerenes, carbon nanotubes have been discovered, i.e. molecules of cylindrical form with lengths l far greater than their diameters d (the difference reaches two to three orders of magnitude), and onion structures. There exist the monolayer and multilayer nanotubes. By now, various methods for their production and investigation have been elaborated, and their possible applications are disscused, e.g.[17–24]. The carbon onions[25] are left exotics.

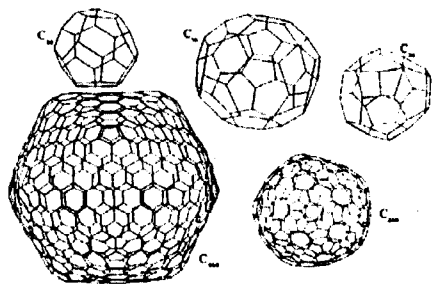


Fig. 5. Some smaller and larger fullerenes.

3. A Brief Survey of Experimental Data for Fullerites and Fullerides

As indicated above, hitherto the C_{60} and C_{70} fullerites have been the most completely studied. Let us take a brief look at some of their properties.

3.1. *Structure and Phase Transitions*

In both fullerites, at low temperatures, the molecules are orientationally ordered while at high

temperatures they rotate rather freely forming the so called plastic crystals with the fcc lattice. In the C_{60} both ordered and disordered structures have cubic symmetry, the low-temperature one consisting of four simple cubic sub-lattices, and the phase transition between them is clearly observed at 261,4 K [26,27]. The ordered phase of C_{70} has monoclinic lattice, and between it and the disordered phase there exist several intermediate states[28,29]. Anyway, at $T >$ 340 K in C_{70} the fcc lattice is realized, possibly with a little mixture of the hcp phase[28] (depending on substrate, process of preparation, etc.) that is energetically very close to the former. Similar behavior is to be expected also for other (larger and smaller) fullerites. Note that the above mentioned phase transition in C_{60}, being a first-order one, is accompanied by very small changes in various lattice characteristics such as the intermolecular distances. It can be considered as the orientational order-disorder transition rather than the polymorphic one. Sometimes such transitions are called the orientational melting. (Moreover, a transition between different orientationally ordered phases was observed at 85 K [30]). It is interesting that the density of the C_{60} fullerite 1,7 g/cm^3 is close to that of solid Ar; for comparison, those of diamond and graphite are 3,5 and 2,2 g/cm^3, respectively.

At certain conditions the polymerization in fullerites takes place[9,10]. A wide variety of structures appear upon polymerization: dimers, one-, two-dimensional polymers (1D and 2D), etc. It is interesting that the dimers possess a minimum of energy, Fig. 6 [9].

The transformation of C_{60} fullerite to new extrahard phases has also been observed at high pressure and temperature.[31-34]

3.2. *Magnetic and Electric Properties*

The fullerites with admixtures of some organic molecules provide ferromagnetism with sufficiently low Curie temperatures, T_C; in particular, for C_{60} with an admixture of tetrakis-dimethylamino-ethylene, T_C = 16,1 K. The temperature dependence of the magnetization below T_C does not follow the behavior expected for a conventional ferromagnetic (soft organic ferro-magnetism)[35].

The electrical properties of fullerites and fullerides vary over a broad range. from a good insulator to a superconductor, depending on admixture and environmental conditions. The pure fullerites at low temperatures are insulators and semiconductors at high temperatures. For instance, the width of the forbidden band in C_{60} is 1,5 – 1,95 eV [36,37], and in C_{70} 1,91 eV [22]. The C_{60} fullerite at moderate temperatures is a good insulator, whereas the compounds A_3C_{60} in which A is an interstitial alkali atom (alkali metal fullerides) possess considerable conductivity[38], i.e. it constitutes an organic conductor (organic metal).

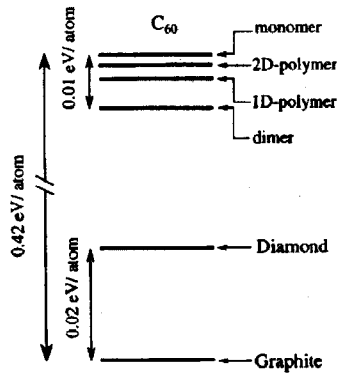


Fig. 6. Energy levels for various solid states of carbon.

At not very low temperatures depending on alkali-ion identity and lattice constant, they transform into a superconducting state owing to the Cooper paring of electrons[39]. Some experimental data[40] are listed in Table 1.

Table 1. Experimental lattice parameters and critical temperatures of various polycrystalline fullerides based on C_{60}.

Fulleride	Lattice constant (Å)	T_C(K)
C_{60}	14,161	-
K_3C_{60}	14,240	19
K_2CsC60	14,292	24
KRb_2C_{60}	14,323	27
Rb_3C_{60}	14,384	29
$Rb_2Cs\ C_{60}$	14,431	31
$RbCs_2C_{60}$	14,555	33

One can see that the change of one interstitial atom by a larger one increases the critical temperature together with the lattice parameter, the dependence between them being near linear. Anticipating that a similar correlation takes place also for changing from C_{60} to larger fullerenes with larger lattice parameters one can evaluate T_C for larger fullerides. The critical temperatures have been estimated for some superconductors based on C_{76} and C_{84} [41], Table 2.

Of other properties let us mention the following: the catalytic capability of fullerenes in the manufacture of synthetic diamond, see e.g.[22], their photoconductivity,[42] light absorption[43], photo-luminiscence[44], and absorption properties of carbon nanotubes[24].

Table 2. The lattice parameters and critical temperatures evaluated for fcc supercon-ducrors based on the C_{76} and C_{84} fullerides.

Fulleride	Lattice constant (Å)	T_C (K)
K_3C_{76}	15,12	62
Rb_3C_{76}	15,30	72
Rb_2CsC_{76}	15,37	76
K_3C_{84}	15,54	84
K_2RbC_{84}	15,59	86
Rb_3C_{84}	15,72	92
Rb_2CsC_{84}	15,79	96

The above-listed properties of fullerites and fullerides open up the prospects for using these materials in various magnetic, electric and optic devices.

Note that in the latter half of 1990s and in the early 2000s, it has been published some reviews on fullerenes, e.g.[10,22,45–48]

4. Statistical Thermodynamics of Fullerites

4.1. *Intermolecular Forces*

It is well known that at the core of theoretical investigations of thermodynamic properties of materials, along with calculation techniques are the interaction potentials. For molecular crystals, very profitable is the atom-atom potentials approach. In this case, intermolecular potentials are expressed in terms of interaction potentials between atoms included into the neighboring molecules and, if it is necessary, between charges located at the atomic nuclei and at the covalent bonds. The carbon atoms are retained in the fullerene molecule by covalent bonds and interact with atoms of other molecules through Van der Waals forces. They are described adequately by the Lennard-Jones potential

$$\Phi_{LJ}(r) = -A/r^6 + B/r^{12} = 4\varepsilon\left[\left(\sigma/r^{12}\right) - \left(\sigma/r^6\right)\right], \quad (1)$$

and the potential between two C_{60} molecules[49, 50] is of the form

$$\Phi_{12} = 4\varepsilon\sum_{i,j=1}^{60}\left[\left(\frac{\sigma}{\left|\vec{r}_{1i}-\vec{r}_{2j}\right|}\right)^{12} - \left(\frac{\sigma}{\left|\vec{r}_{1i}-\vec{r}_{2j}\right|}\right)^{6}\right] + \sum_{m,n=1}^{90}\frac{q_m q_n}{\left|\vec{b}_{1m}-\vec{b}_{2n}\right|} \quad (2)$$

where $r_{1i,\,2j}$ are the coordinates of carbon atoms, b_{1m}, b_{2n} are the bond centers, and $q_{m,n}$ are the effective bond charges. These are precisely non-central forces which provide the stability of the orientationally ordered modification of the C_{60} fullerite at low temperatures.

For orientationally disordered (gaseous, high-temperature crystalline and hypothetical liquid) phases, the Coulombic parts disappear by virtue of the electro-neutrality of molecules.

The theoretical study of the thermodynamics of the high-temperature modifications of the C_{60} fullerite (and its vapor) was initiated by Girifalco[51]. Considering that the shape of the C_{60} molecule is almost spherical and averaging the Lennard-Jones atom-atom potentials (1) of a pair of molecules over all their orientations, he has deduced for the orientationally disordered phases the intermolecular potential

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

where $s = r/2a$, r is the distance between the centers of the molecules; a = 3,55·10 ^{8} cm is the radius of their hard core,

$$\alpha = n^2 A/12(2a)^6, \qquad \beta = n^2 B/90(2a)^{12} \quad (4)$$

A and B are the coefficients at the attractive and repulsive terms of the atom-atom Lennard-Jones potential (1), while n = 60 is the number of atoms in the molecule. The parameters A and B were fitted in[51] with experimental data for the lattice constant and heat of sublimation:

$$A = 3{,}200 \times 10^{-59}\ erg.cm^6, \qquad B = 5{,}577 \times 10^{-104}\ erg.cm^{12}. \quad (5)$$

Verheijen *et al.*[52], noticing that the C_{70} molecule (that has a shape similar to an oblong ellipsoid) can be separated into five groups of 10 or 20 atoms, each one lying in a spherical shell of a certain radius R_i ($1 \le i \le 5$), and generalizing the procedure of Girifalco, have obtained for its orientationally disordered phases the intermolecular potential in Eq. (6).

Kniaz', Girifalco and Fischer[53], and independently, Abramo and Caccamo[54] utilized the Girifalco potential (3) for C_{70}. This corresponds to an approximation of the shape 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 use of the same values of the parameters A and B for various fullerenes reflects

the generality of Van der Waals atom-atom interactions in carbon. But the necessity of fitting the effective radius of the sphere to the experimental lattice parameter renders this method unsuitable in the case of fullerenes for which there are hitherto no experimental data.

$$\Phi_{ij}(r) = -\frac{A}{48r}\sum_{i,j=1}^{5}\frac{n_i n_j}{R_i R_j}\left[\frac{1}{(r+R_i+R_j)^3}+\frac{1}{(r-R_i-R_j)^3}-\frac{1}{(r+R_i-R_j)^3}-\frac{1}{(r-R_i+R_j)^3}\right] \quad (6)$$
$$+\frac{B}{360r}\sum_{i,j=1}^{5}\frac{n_i n_j}{R_i R_j}\left[\frac{1}{(r+R_i+R_j)^9}+\frac{1}{(r-R_i-R_j)^9}-\frac{1}{(r+R_i-R_j)^9}-\frac{1}{(r-R_i+R_j)^9}\right]$$

Recently the method has been proposed the method [55] for the calculation of the coefficients of the Girifalco potential (3) for various fullerenes starting from their magnitudes for the C_{60} and using simple topological considerations, without additional fitting parameters. Since the atoms of the fullerene molecules are situated on their surfaces, i.e. on two-dimensional manifolds, one can concede that the ratio of its effective radii be

$$a_n/a_m = \sqrt{n/m} \quad (7)$$

Note that earlier, this idea of a spherical approximation for some larger fullerenes with a radius related to the number of atoms in the molecule was used by Saito *et al.*[56] and by Molchanov *et al.*[57] but regardless of the interaction potentials.

Using the known value of a_m for one of fullerenes, for instance for C_{60}, it is easy to obtain the effective radius for any other fullerene. Substituting it together with (5) into (4) gives the coefficients α and β in (3) for the C_n fullerene. They have been calculated for a family of smaller and larger fullerenes, from C_{28} to C_{96}. The Girifalco potential for the eight fullerenes are shown in Fig. 7. One can see that their minimum points lie on a nearly straight line.

A generalization of the above mentioned procedures of Girifalco[51] and of Verheijen *et al.*[52] gives the potential of interactions between two different fullerene molecules C_m and C_n in the orientational disordered phases [58]:

$$\Phi_{mn}(r) = -\frac{\alpha}{s}\left(\frac{1}{(s-1)^3}+\frac{1}{(s+1)^3}-\frac{1}{(s-\delta)^3}-\frac{1}{(s+\delta)^3}\right) \quad (8)$$
$$+\frac{\beta}{s}\left(\frac{1}{(s-1)^9}+\frac{1}{(s+1)^9}-\frac{1}{(s-\delta)^9}-\frac{1}{(s+\delta)^9}\right).$$

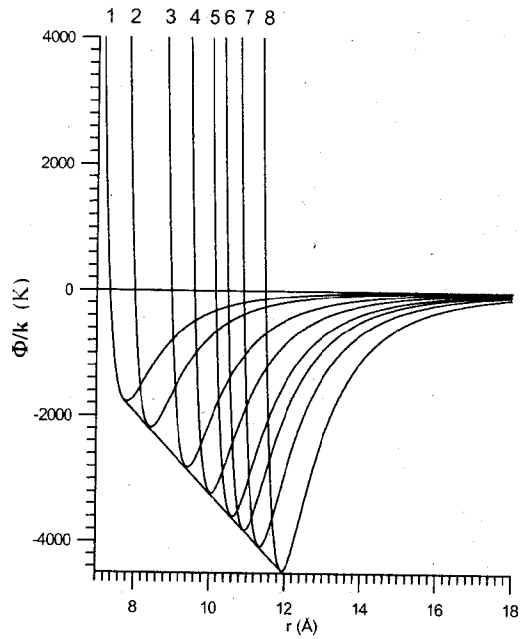


Fig. 7. The Girifalco potential for eight fullerenes: C_{28} (1), C_{36} (2), C_{50} (3), C_{60} (4)[51], C_{70} (5), C_{76} (6), C_{84} (7), C_{96} (8).

Here $s = r/D_{mn}$, $D_{mn} = (a_m + a_n)$, a_m and a_n are the radii of their effective spheres, $\delta = (a_m - a_n)/(a_m + a_n)$, and the coefficients α and β are defined by the formulae

$$\alpha = \frac{mnA}{48a_m a_n (a_m + a_n)^4}, \quad \beta = \frac{mnB}{360a_m a_n (a_m + a_n)^{10}} \quad (9)$$

One can readily see that when $m = n$, the potential (8) transforms to the Girifalco potential (3) for the two C_n fullerene molecules [55].

Substituting the calculated effective radii (7) together with (5) into (9), have been obtained the coefficients α and β of the potential (8) for interactions of the C_{60} molecule with the molecules of some larger fullerenes from C_{70} to C_{96} and with the smaller one, C_{36}. Their characteristics are given in Table 3. It is interesting that the coefficients α and β of the Girifalco potential (3) decrease with increasing number of atoms in the molecule, although the minimum point of the potential and the depth of its well of course increase with such a number.

The potential curves for interactions of C_{60} with some higher and smaller fullerenes are demonstrated in Figs. 8 and 9. It is apparent that the effective diameter of the hard core of (8) D_{mn} is defined as the arithmetic mean between those of C_m–C_m and C_n–C_n and it is used for the calculations of the coefficients α and β (9), whereas formulae for the distance r_0 where

$\Phi_{mn}(r_0) = 0$ for the minimum point σ and for the depth of the potential well ε are not available. It can be seen from Table 2 that the r_0 and σ coincide with the corresponding arithmetic means within hundredths of a percent while ε with the geometric mean $\varepsilon_{mn} = \sqrt{\varepsilon_{mm}\varepsilon_{nn}}$ within tenths of percent.

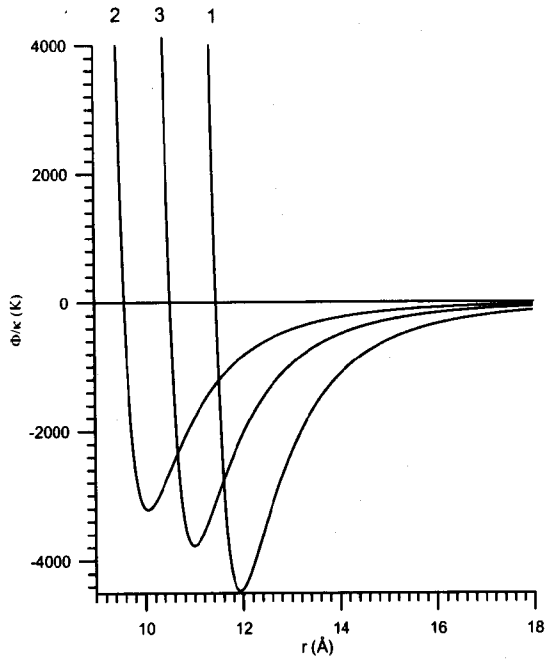


Fig. 8. Intermolecular potentials for $C_{60} - C_{60}$ (1), $C_{96} - C_{96}$ (2) and $C_{60} - C_{96}$ (3).

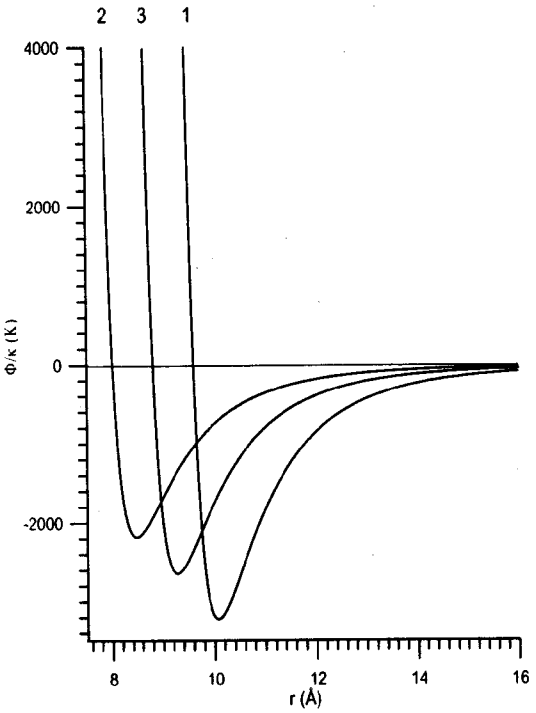


Fig. 9. Intermolecular potentials for $C_{60} - C_{60}$ (1), $C_{36} - C_{36}$ (2) and $C_{60} - C_{36}$ (3).

4.2. *Peculiarities of Systems*

The Girifalco potential (as well as the Verheijen one (6) and the generalized potential (8)) is more short-range than the Lennard-Jones potential (1) that is typical for simple Van der Waals crystals (Ar and other solidified inert gases). Hence, when the

Table 3. Characteristics of the potentials (3) and (8) for various fullerenes (D_{mn}, σ and r_0 in 10^{-8} cm).

m, n	D_{mn}	δ	a (10^{-14} erg)	ß (10^{-17} erg)	σ	r_0	$-\varepsilon/K_B$ (K)
60, 60[a]	7,100	-	7,494	13,595	9,599	10,056	3218
28, 28[b]	4,850	-	16,058	286,640	7,358	7,080	1775
36, 36[b]	5,500	-	12,490	104,900	8,000	8,460	2182
50, 50[b]	6,481	-	8,980	28,190	8,976	9,443	2813
70, 70[b]	7,669	-	6,424	8,338	10,161	10,622	3594
76, 76[b]	7,991	-	5,916	5,281	10,480	10,946	3807
84, 84[b]	8,401	-	5,353	3,539	10,880	11,358	4080
96, 96[b]	8,981	-	4,684	2,074	11,468	11,936	4468
60, 36[c]	6,300	0,127	9,365	34,813	8,800	9,260	2639
60, 70[c]	7,384	0,0385	6,918	9,914	9,880	10,340	3400
60, 76[c]	7,545	0,059	6,612	8,326	10,035	10,502	3497
60, 84[0]	7,750	0,084	6,245	6,695	10,239	10,705	3616
60, 96[c]	8,040	0,117	5,764	4,957	10,530	10,999	3777

[a]Girifalco [51] [b]The work [55] [c]The work [58]

main contribution to the specific heats of the fullerites

$$C_i = \frac{Nk}{4}\left(15+\beta-\frac{X\beta'}{2}\right)+ \\ Nk\sum_j g_j\left(\frac{\hbar\omega_j}{\Theta}\right)^2 e^{\hbar\omega_j/\Theta}\Big/\left(e^{\hbar\omega_j/\Theta}-1\right)^2 \\ +C_i^2+C_i^H; \qquad \left(\beta'=\frac{d\beta}{dX}\right) \tag{15}$$

that increase with temperature reaching about 80 – 90 % and making the difference between the isobaric and isochoric heats and between the isothermal and adiabatic elastic moduli very small.

We study the thermodynamic properties of high-temperature disordered crystalline phases of various fullerites depending on the pressure and temperature, including their equilibrium with their vapor. In the last case, one has to add to the equation of state (11) 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 it is conveniently expressed in the form

$$P_{sat} = P_{id}\left(1-BP_{id}/\Theta\right) \tag{16}$$

where

$$P_{id} = \Theta\left(\frac{K_4}{12\pi^2\Theta}\right)^{3/4}\times \\ \exp\left[\frac{K_0}{2\Theta}-\frac{5}{24}\left(\frac{\beta}{X}\right)^2-\frac{1}{4}\left(X+\frac{5\beta}{6X}\right)^2+\frac{f_2+f_H}{\Theta}\right]\; D_{-1.5}\left(X+\frac{5\beta}{6X}\right) \tag{17}$$

is the saturated vapor pressure in the ideal-gas approximation, $f^i = F^i/N$, $i = 2, H$, and

$$B(\Theta) = -2\pi\int_0^\infty\left[\exp\left(-\frac{\Phi(r)}{\Theta}\right)-1\right]r^2dr \tag{18}$$

is the second virial coefficient. The set of equations (11) and (16), (17) together with (13) 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 sublimation curve.

4.3. *Results*

We have investigated the properties of the C_{60}[63,68–70], C_{70}[71,72], C_{76}[73] and C_{84}[73]. Here we presente results [74] for the whole family of fullerites from C_{36} to C_{96}.

4.3.1. *Sublimation Curve*

The nearest neighbor distances (the average distances between the centers of molecules) for five fullerites C_{36}, C_{50}, C_{60}, C_{76} and C_{96} together with the experimental data available for C_{60}[75,76] and C_{76}[77] are depicted in Fig. 10. The upper branches $a_2(T)$ of these curves correspond to the absolute unstable thermodynamic states, since on them the isothermal bulk modulus of the crystal B_T is negative. At the temperature T_S, where both branches coalesce B_T vanishes. From here it is seen the good agreement for the lower branches $a_1(T)$ with experiment. 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 demonstrated in Fig. 11 only for C_{36}, C_{60} and C_{96}. For the lower branch this is in good agreement with available results of measurements for C_{60}[78-81] (and also for C_{70}, C_{76} and C_{84}). Their temperature dependence is described by the equation

$$\log P_{sat} = A-\frac{B}{T}-CT, \tag{19}$$

The last term being due to the anharmonicity of the lattice vibrations. The constant term A depends almost not at all on the number of atoms in the molecule, varying only by 2,2%. The coefficient B grows monotonically, while C decreases from the C_{36} to the C_{96}, by about a factor of two. Such a behavior

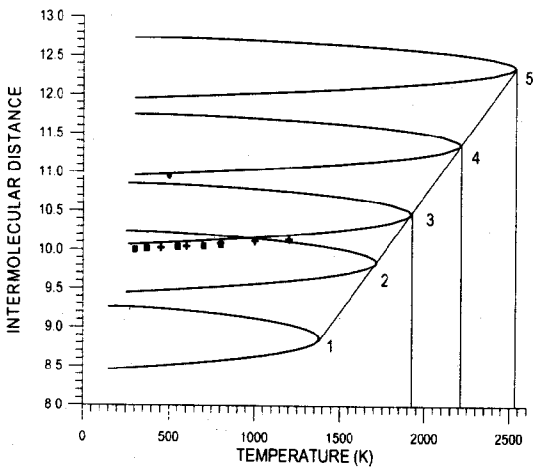


Fig. 10. The intermolecular distances in fullerites along their sublimation curves: C_{36} (1), C_{50} (2), C_{60} (3), C_{76} (4), C_{96} (5). The vertical lines show the temperatures T_S. Experimental data for C_{60} are taken from work by Mathews *et al.*[75] (■), Fischer and Heiney (+)[76], and for C_{76} from work by awada *et al.*[77]

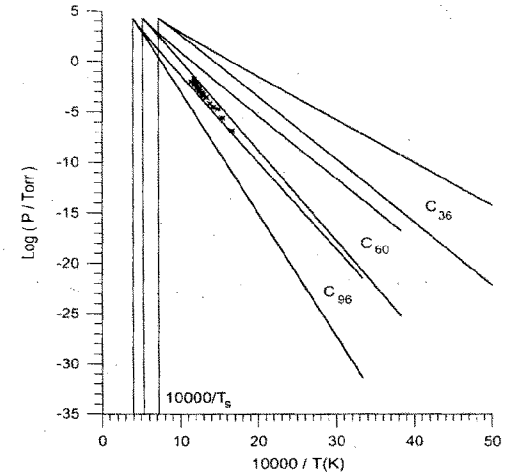


Fig. 11. Saturated vapor pressures. Experimental data are taken from [78–81].

agrees with experimental estimations of A and B available for C_{60}[82], C_{70}[82], C_{76}[83-85] and C_{84}[85-87].

Fig. 12 shows the temperature dependence of the sublimation enthalpies of fullerites. We compare them with available experimental data. One can see the agreement within the limits of experimental error, with the exception of the C_{76} whose difference from our calculations is slightly beyond these limits. Note also that our results show an excellent agreement with recent computer simulations by Fernandes *et al.*[88] 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}.

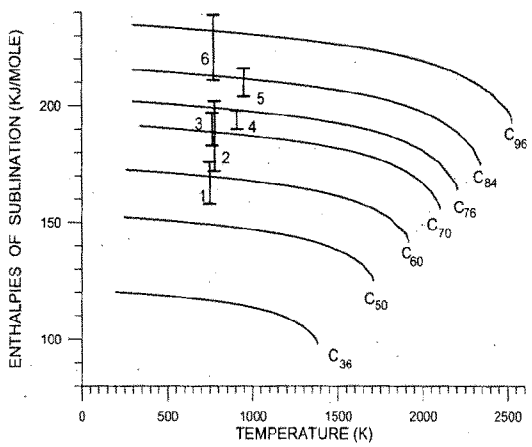


Fig. 12. Enthalpies of sublimation. Experimental data for C_{60} (1) and C_{70} (2) are taken from work by Markov *et al.*[82] (the recommended values), for C_{76} from work by Brunetti *et al.*[83] (3), Boltalina *et al.*[87] (4), and for C_{84} from work by Piacente *et al.*[86] and Boltalina *et al.*[87].

4.3.2. *Thermodynamic properties*

Along the lower branches we have calculated the complete sets of thermodynamic properties of these fullerites that are due to lattice vibrations, namely, the components of the isothermal elastic tensor and the thermal expansion coefficient.

It is known that elastic tensors (isothermal and adiadatic) of cubic crystals have three different components, in the Foight designations[89] they are $C_{11}^{T,S}, C_{12}^{T,S}\ C_{44}^{T,S}$. The first is the coefficient of uniaxial tension and the last the shear coefficient; the adiabatic shear coefficient is equal to isothermal $C_{44}^{S} = C_{44}^{T}$, and the bulk moduli are expressed in terms of C_{11} and C_{12}: $B_{T,S} = \left(C_{11}^{T,S} + 2C_{12}^{T,S}\right)/3$

Sometimes it is more convenien to use, in place of C_{12}, the difference C_{11}-C_{12} This, as well as C_{44}, has the same value for the thermal and isobaric processes and determines the velocities for transverse wave propagation in elastic media. Furthermore, it is one of the stability coefficients for cubic crystals.

It is well known[90] that the conditions for stability of a thermodynamic system is the positivity of the stability determinant, i.e. the Jacobian of the transformation from the intensive variables, temperature T and generalized forces (for crystals the components of the stress tensor $\hat{\sigma}$) to the extensive ones (entropy S and the components of the deformation tensor $\hat{\varepsilon}$ multiplied by the volume V). In the case of cubic crystals,

$$B_T > 0;\ C_{11}^{T} > 0;\ C_{11} - C_{12} > 0;\quad C_{44} > 0;\ T/C_{V} > 0\,. \tag{20}$$

The violation of any of these inequalities implies the loss of thermodynamic stability (the spinodal point).

All the elastic moduli (Figs. 13, 14) decrease monotonically as the temperature increases. For heavy fullerites they are greater than for the light ones. The thermal expansion coefficient exhibits an opposite dependence on the temperature and on the number of atoms in molecules.

Two of the coefficients of thermodynamic stability, the bulk modulus B_T and the shear modulus C_{44}, vanish at $T = T_S$, both as $(T_S - T)^{1/2}$. 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. Other stability coefficients remain finite and positive up to and including this temperature.

Note that recently, great interest has been expressed in the loss of thermodynamic stability of crystals, see e.g. [91,92].

In Fig. 15 we show the thermal expansion coefficients of the fullerites. Its behavior is opposite to that of the elastic properties.

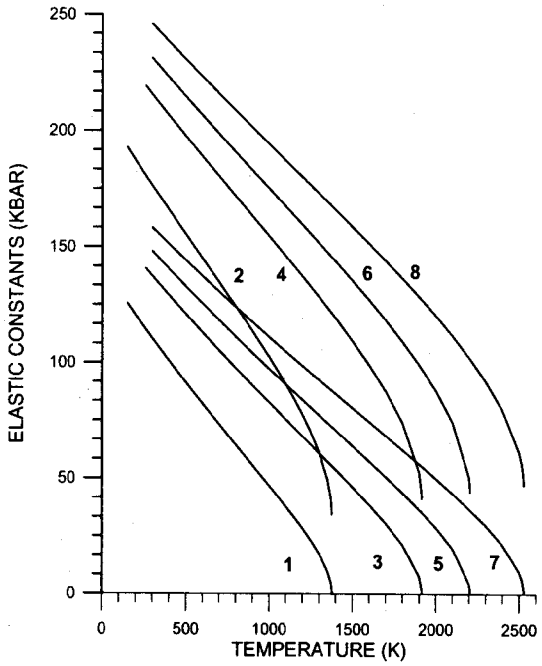


Fig. 13. The Isothermal bulk moduli B_T (odd numbers) and coefficients of uniaxial tension C_{11}^T (even ones) of the fullerites: C_{36} (1, 2), C_{60} (3, 4), C_{76} (5, 6), C_{96} (7, 8).

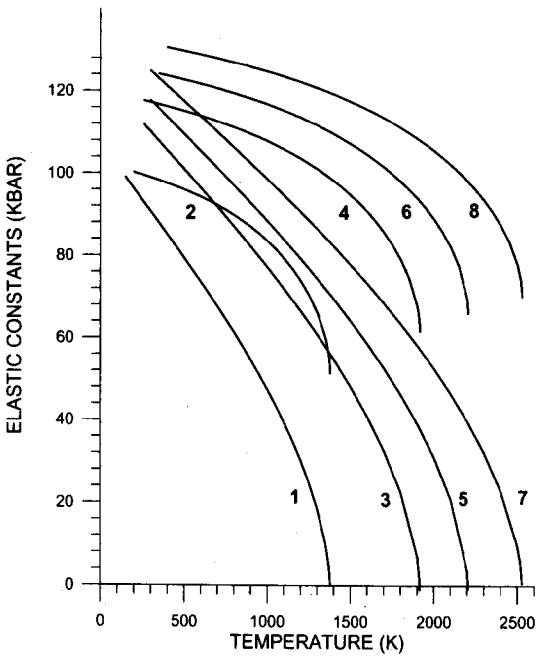


Fig. 14. The shear moduli C_{44} (odd numbers) and $C_{11} - C_{12}$ (even ones) of the fullerites: C_{36} (1, 2), C_{60} (3, 4), C_{76} (5, 6), C_{96} (7, 8).

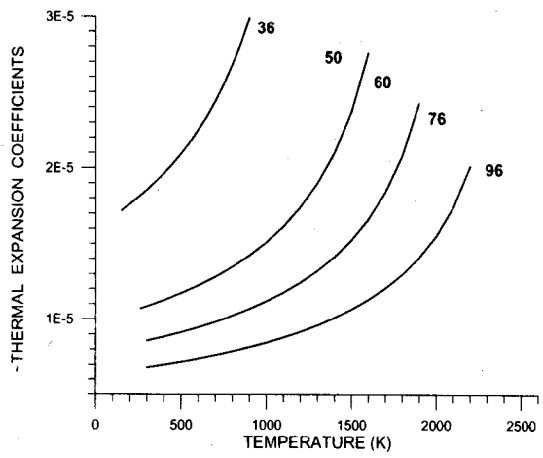


Fig. 15. Thermal expansion coefficients of the fullerites.

As noted above, 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[59–62]. That is why; we have calculated the thermal properties only for these two fullerites. Their isobaric specific heats are shown in Fig. 16. Their molar values are considerably greater than those of the majority of other substances. Moreover C_{70} it is larger than C_{60} because of the larger number of its intra-molecular 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 encore characteristics of their intramolecular vibrations. The agreement with experimental results available for C_{60} fullerite[82,93–96] is quite satisfactory.

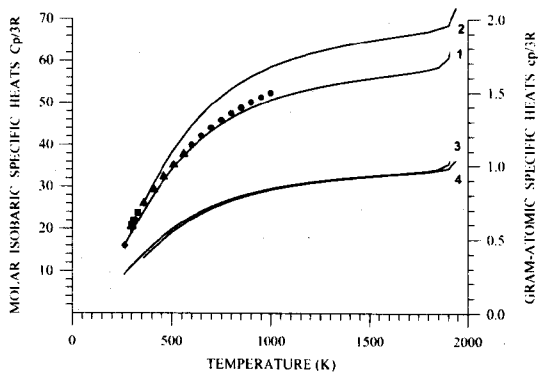


Fig. 16. Isobaric heat capacities for C_{60} and C_{70}. Experimental data are taken from works by Y. Jin *et al.*[93] (■), Matsuo *et al.*[94] (✚), Fischer *et al.*[95] (♦), Lebedev *et al.*[96] (●), and Markov *et al.*[82] (▲).

5. On a Possible Melting Point Curve for Fullerites

Shortly after the growth of macroscopic crystals of C_{60} it investigations were started on the possibility of their melting. Although the liquid phase of fullerites has not yet been observed, discussions about its possible existence has persisted for years.

Hagen *et al.*[97] based on Monte Carlo simulations have reasoned that the liquid phase of C_{60} lacks the region of absolute stability and hence cannot exist. However, other authors based on various methods, e.g.[98–102], have drawn the possibility of its liquid phase, although in a very narrow phase diagram range. The estimates of its melting temperature (triple point) vary from 1400 to 1800 *K*. In our opinion, upper values are closer to the spinodal point of the solid phase, see Fig. 10, rather than to the melting temperature. Note that Stetzer *et al.*[103] have reported that C_{60} crystals heated at 1260 *K* for more than 10 min decomposed into amorphous carbon. However, this result has not been reproduced in other institutions, whereas the molecular dynamics estimate for the decomposition temperature of a single C_{60} molecule comprises yields about 4000 *K* [104]. Thus, the investigations of the possibility of the liquid phase for fullerites are hitherto continuing[102,105–107].

Owing to the lack of an unified rigorous microscopic theory for crystals and liquids, semi-empirical criteria for melting are of frequent use which are stated as a constancy of one or other characteristic of the solid phase on the melting curve (a peculiar kind of "integrals of movement along the melting curve"). They are: the Lindemann's criterion, see e.g.[89], the Ross' criterion[108], the entropy[109] and energy[110] rules. The value of such a characteristic computed at a single melting point P, $T_m(P)$, $a(P, T_m)$ that is considered to be known, can be used for calculations of the melting curve. For instance, the Lindemann's criterion implies that on the melting curve

$$\delta = \sqrt{\overline{\vec{q}^2}} \Big/ a = const, \qquad (21)$$

where $\vec{q}^2 = 3\overline{q_\alpha^2}$ is the mean-square displacement of a molecule from its lattice points points and a the nearest-neighbor distance.

Calculating the mean-square displacements for strongly anharmonic crystals[111, 112] and applying the Lindemann's criterion (20) we have estimated a possible melting curve $T_m(P)$, $V_S(T)$ of the C_{60} fullerite[113]. As mentioned above, the liquid phase of fullerites has yet to be observed while the theoretical estimates of the triple point of C_{60} lie between 1400 and 1800 K. We have used our estimate T_0 = 1500 K [63] and calculated the Lindemann's parameter (21) at this point $a(T_0)$ = 10,255x10^{-8} cm: $\delta \cong 0.041$ [113]. Note that this value is less than in a simple Van der Waals crystal (solid Ar) by a factor 1,9 – 2,4. Such a distinction is caused by the presence of the finite-size hard core in the Girifalco potential. Then, we solved the equation of state (11) for various fixed pressures up to the temperature $T_m(P)$ at which $\delta = 0,041$ and calculated the molar volume at this melting point $V_S = V(P, T_m)$. We have restricted ourselves to a temperature of about 4000 K (and the pressure about 15 kbar) since at such a temperature the C_{60} molecule decomposes[104].

The results are shown in Fig. 17. The temperature dependence of the melting point pressure is described very well by the Simon equation

$$\frac{(P_m(T)/\text{bar}) - 1}{b} = \left(\frac{T}{T_0}\right)^c \qquad (22)$$

Originally, this equation was proposed for the melting curve of Ar (see, e.g.[109]). For the C_{60} fullerite we find T_0 = 1500 K, b = 6643,8, c = 1,209. The temperature dependence of the molar volume along the melting curve is approximated by the formula

$$V_s(T) = V_s(T_0) - 29,20 \ln(T/T_0) \qquad (23)$$

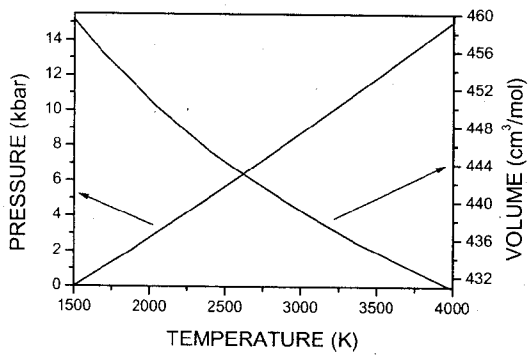


Fig. 17. The possible melting curve $P_m = P_m(T)$, $V_s = V_s(T)$ of the C_{60} fullerite.

Note that the regularity (23) is valid for many materials. At first the logarithmic dependence of the molar volume on the melting temperature has been established for solidified noble gases from thermodynamic considerations[114] and then has been confirmed experimentally[115]. It holds also for alkali metals (sodium)[116].

6. Conclusions

Thus, we are finishing our review on the fullerenes and fullerites that has no pretensions of completeness. Note also that the international industrial corporation Mitsubishi utilizes fullerenes in the manufacture of accumulators[22]. A possibility of materials based on polymerized fullerenes has been discussed[117,118]. It may be pointed out that the knowledge of the thermal and elastic properties of fullerites is important with respect to their use at various temperature and pressure conditions. One can use our intermolecular potential (8) with parameters listed in Table III in calculations of thermodynamic properties for the C_{60} fullerite mixed with larger and smaller ones. Interest has been expressed recently in investigations of mixtures of the fullerites[119,120]. There are experiments in the use of fullerenes in pharmacology[121]. Recently, Domrachev, *et al.* published their encouraging results for metal-fullerene composites technology[122].

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