

Internet Electronic Journal Nanociencia et Moletrónica

Octubre 2004, Vol. 2; N°2, págs. 249-273

FULLERENES AS THE THIRD FORM OF CARBON. INTERMOLECULAR FORCES AND THERMODYNAMIC PROPERTIES OF A FAMILY OF FULLERITES

V.I.Zubov

*Russian Peoples' Friendship University, 117198, Moscow, Russia and
Instituto de Física, UFG, C.P. 131, 74001-970, Goiânia, GO, Brasil*

E-mail: zubov@fis.ufg.br; v_zubov@mail.ru

recibido: agosto 2004

revisado: agosto 2004

publicado: octubre 2004

Citation of the article:

V.I.Zubov. "FULLERENES AS THE THIRD FORM OF CARBON. INTERMOLECULAR FORCES AND THERMODYNAMIC PROPERTIES OF A FAMILY OF FULLERITES.", Internet Electrón. J. Nanocs. Moletrón. 2004, 2(2), 249-273:

<http://www.revista-nanociencia.ece.buap.mx>

Copyright © 2004 BUAP

FULLERENES AS THE THIRD FORM OF CARBON. INTERMOLECULAR FORCES AND THERMODYNAMIC PROPERTIES OF A FAMILY OF FULLERITES

V.I.Zubov

*Russian Peoples' Friendship University, 117198, Moscow, Russia and
Instituto de Física, UFG, C.P. 131, 74001-970, Goiânia, GO, Brasil*
E-mail: zubov@fis.ufg.br; v_zubov@mail.ru

recibido: agosto 2004

revisado: agosto 2004

publicado: octubre 2004

Internet Electron. J. Nanocs. Moletrón. 2004, 2(2), pags. 249-273

ABSTRACT

A brief review is being done on the pre-history and discovery of fullerenes that make the third, molecular, form of carbon and also on various 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 the equilibrium with their saturated vapors on the basis of the correlative method of the unsymmetrized self-consistent field that enable one to take in to account of 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. The saturated vapor pressures up to the spinodal points of the two-phase systems crystal – gas is approximated by the formula $\log P_{sat} = A - (B/T) - CT$, the last term being related to the anharmonic effects. 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 the C_{36} to the C_{96} by approximately twice. The isothermal bulk modulus B_T and the shear modulus C_{44} vanish at the spinodal points. Using the Lindemann's melting criterion we estimate a possible melting curve of the C_{60} fullerite.

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

<http://www.revista-nanociencia.ece.buap.mx>

RESUMEN

Hacemos una breve revisión sobre la prehistoria y descubrimiento de los fullerenos que constituyen la tercera forma (molecular) del carbón y también sobre varias propiedades de los fulleritos, es decir, cristales compuestos por moléculas de fullereno. Particular atención es dada a las fuerzas intermoleculares, especialmente en fases orientadamente 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 de alta temperatura de una familia de las fulleritas, desde C_{36} hasta C_{96} , calculada en el 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. La presión de vapor saturado hasta los puntos espinodales del sistema de dos fases cristal-gas es aproximado por la fórmula $\log P_{sat} = A - (B/T) - CT$, estando el último término relacionado a los efectos de anarmonicidad. El coeficiente A prácticamente no depende del número de átomos en la molécula (variando únicamente por 2.2%); B aumenta monótonamente, mientras C disminuye (decrece) aproximadamente dos veces entre C_{36} y C_{96} . Los módulos de elasticidad isotérmico B_T y de cizallamiento C_{44} se anulan en los puntos espinodales. Usando el criterio de fusión de Lindemann estimamos la posible curva de fusión de la 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.

1.-Pre-history and Discovery

Carbon is one of most abundant elements at the universe. It has been believed for a long time that there exist two its polymorph forms: very soft graphite that has a layered structure and extra-hard diamond possessing the A_4 cubic lattice. The first is absolutely stable, whereas the second is metastable because has the less cohesive energy although the difference is very small (0.02 eV per atom). Here we are concerned with fullerenes, which constitute the third, molecular, form of carbon.

In the mid-1960s it has been discovered in the absorption spectrum of the interstellar dust the ultraviolet line of 2175 \AA^1 . Jones in 1966² have considered the possibility of forming new type molecules with carbon atoms. Osawa in 1970³ (in Japanese) and Yoshida and Osawa in 1971⁴ (again in Japanese) have investigated theoretically the distortion of a plane graphite layer and the formation of closed shells containing the 60 atoms owing to the replacement of some hexagons by pentagons. They have conjectured that such a molecule would be stable. It consists of 20 hexagons and 12 pentagons. A little later, in 1973, Bonchvar and Gal'pern published a Hückel calculation on C_{60} ⁵ and in 1980 Davidson applied general theoretical group techniques to highly symmetric molecules, one of which was C_{60} ⁶. One can find more recent and detailed results in ^{7, 8}.

In 1985, Kroto *et al.*⁹ for the first time identified such molecules obtained in their laboratory during spontaneous gas-phase nucleation of atoms evaporated from graphite by laser irradiation. They received the name the *buckminsterfullerenes*, or *fullerenes* after the designer-inventor of the geodesic domes Buckminster Fuller. Sometimes they are termed also the *buckyballs*. By the early 1990s, it has been elaborated effective technologies for the production, separation and purification of fullerenes in quantities enough for growing crystals of macroscopic sizes, named *fullerites*,* e.g.^{10,12}. In Fig.1 it is demonstrated a schematic sketch of an experimental setup for producing and analyzing the fullerenes.

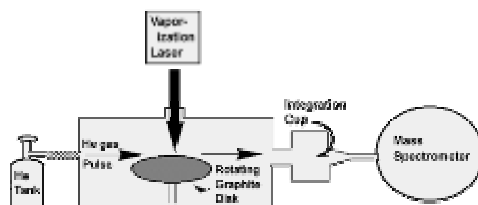


Fig. 1. A scheme of the setup used by Krätschmer *et al.* for producing and analyzing fullerenes.

<http://www.revista-nanociencia.ece.buap.mx>

* Such crystals doped by metal atoms are named *fullerides*.

2. A Family of Fullerenes

During the process of production, the mixtures of various fullerene molecules C_m are formed. Here $m = 20 + 6n$, n being a positive integer number. So, one can consider a *family of fullerenes*. Such a mixture can be separated using mass-spectrometers and organic solvents. The C_{60} molecule occupies an important place in the family of fullerenes. It exhibits the highest symmetry, has the highest cohesive energy per atom and, consequently, is the most abundant. It looks like a football that is close the sphere of radius $a \approx 3.55 \times 10^{-8} \text{ cm}$. Fig. 2 shows the relations between the energies of the three forms of carbon. The fullerene molecules are less thermodynamically stable than the diamond. True, the Van der Waals intermolecular bonds in fullerenes reduce this difference.

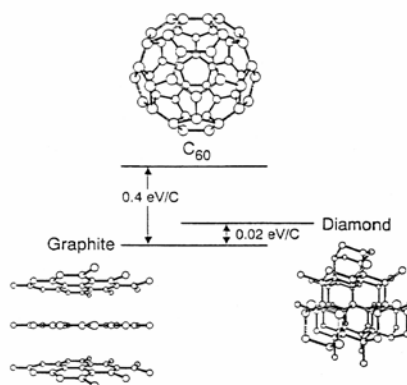


Fig. 2. Relations between the energies (per atom) of the three forms of carbon: graphite, diamond and C_{60} fullerene.

The 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 $a^{(1)} = a^{(2)} \cong 3.61 \cdot 10^{-8} \text{ cm}$ and $a^{(3)} \cong 4.26 \cdot 10^{-8} \text{ cm}$. These molecules are shown in Fig. 3.

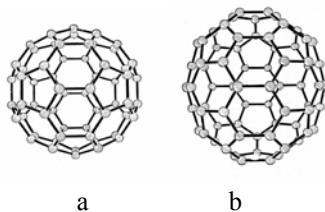


Fig. 3. The C_{60} (a) and C_{70} (b) fullerene molecules.

They and the corresponding fullerites have been most completely studied. The forms of molecules of the other fullerenes are more complicated. The C_m molecules with $m > 70$ are called the higher 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 giant 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 most completely studied. Let us take a brief look at some of their properties.

Aside the fullerenes, there exist also carbon onion structures, e.g.¹³ and nanotubes¹⁴.

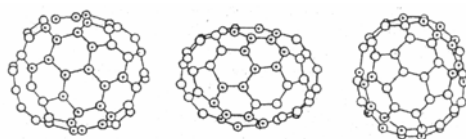


Fig.4. The molecule of a higher fullerene – C_{76} .

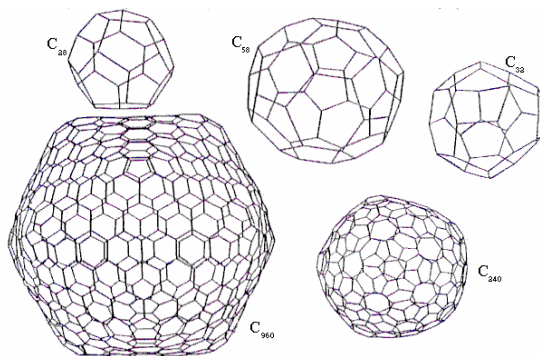


Fig. 5. Some smaller and giant fullerenes.

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.

However, in the C_{60} both ordered and disordered structures have cubic symmetry and the phase transition between them (orientational melting) is clearly observed at 261.4 K ¹⁵¹⁶, while the ordered phase of C_{70} has monoclinic lattice, and between it and the disordered phase there exist several intermediate states¹⁷¹⁸. Any way, at $T > 340\text{ K}$ in C_{70} the FCC lattice is realized, possibly with a little mixture of the HCP phase¹⁷ that is energetically very close to the former. Similar behavior is to be expected also for other (higher and smaller) fullerenes.

It has also been observed the transformation of C_{60} fullerite to new extrahard phases at high pressure and temperature¹⁹⁻²² and the polymerization of fullerenes at high pressures²³.

3.2. Magnetic Properties and Superconductivity

The fullerenes with admixtures of some organic molecules provide ferromagnetism with sufficiently low Curie temperatures T_C . In particular, for C_{60} with an admixture of tetrakisdimethylamino-ethylene, $T_C = 16.1\text{ K}$. The temperature dependence of the magnetization below T_C does not follow the behavior expected for a conventional ferromagnetic (a soft organic ferromagnetism)²⁴.

Electrical properties of fullerenes may vary over a broad range from a good insulator to a superconductor, depending on an admixture and environmental conditions. For instance, the pure C_{60} is a good insulator, whereas the compounds $A_3 C_{60}$, A is an interstitial alkali atom (alkali metal fullerenes) possess a considerable conductivity, i.e. constitutes an organic conductors (organic metals). At temperatures about $20 - 30\text{ K}$ (depending on lattice constant and alkali-ion identity), they transform into superconducting state owing the Cooper pairing of electrons²⁵. Note that at the mid-1990s, it has been published some reviews on fullerenes, e.g.²⁶⁻²⁹.

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

4. Statistical Thermodynamics of Fullerenes

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 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

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

and the potential between two C_{60} molecules³⁰⁻³¹ is

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

where r_{1i}, r_{2j} are the coordinates of carbon atoms, b_{1m}, b_{2n} are those of bond centers, and $q_{m,n}$ are the effective bond charges. 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 fullerenes was initiated by Girifalco³². 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 the intermolecular potential

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

Here $s = r/2a$, r is the distance between the centers of the molecules; $a = 3.55 \cdot 10^{-8}$ cm the radius of their hard core,

$$\begin{aligned}\alpha &= n^2 A / 12 (2a)^6, \\ \beta &= n^2 B / 90 (2a)^{12},\end{aligned}\tag{4}$$

A and B are the coefficients at the attractive and repulsive terms of the atom-atom Lennard-Jones potential (1), while $n = 60$ are the number of atoms in the molecule. The parameters A and B were fitted in²⁵ with experimental data for the lattice constant and heat of sublimation:

$$\begin{aligned}A &= 3.200 \times 10^{-59} \text{ erg.cm}^6, \\ B &= 5.577 \times 10^{-104} \text{ erg.cm}^{12}.\end{aligned}\tag{5}$$

Noticing that the C_{70} molecule can be separated in five groups of 10 or 20 atoms, each one lying in a spherical shell of a certain radius R_i ($1 \leq i \leq 5$), and generalizing the procedure of Girifalco, Verheijen *et al.*³³ have obtained the intermolecular potential for its orientationally disordered phases

$$\begin{aligned}\Phi_V(r) &= -\frac{A}{48r} \sum_{j,i=1}^5 \frac{n_i n_j}{R_i R_j} \left[\frac{1}{(r+R_i+R_j)^3} + \frac{1}{(r-R_i-R_j)^3} - \right. \\ &\quad \left. - \frac{1}{(r+R_i-R_j)^3} - \frac{1}{(r-R_i+R_j)^3} \right] \\ &+ \frac{B}{360r} \sum_{j,i=1}^5 \frac{n_i n_j}{R_i R_j} \left[\frac{1}{(r+R_i+R_j)^9} + \frac{1}{(r-R_i-R_j)^9} - \right. \\ &\quad \left. - \frac{1}{(r+R_i-R_j)^9} - \frac{1}{(r-R_i+R_j)^9} \right]\end{aligned}\tag{6}$$

To calculate its parameters it is necessary a more detailed information on the shape of the molecule.

Kniaz', Girifalco and Fischer³⁴, and independent-ly, Abramo and Caccamo³⁵ utilized the Girifalco potential (3) for C_{70} . This corresponds to approximate 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 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.

Recently it has been proposed the method³⁶ 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

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

Note that early, the idea of a spherical approximation for some higher fullerenes with radius related to the number of atoms in the molecule was used by Saito *et al.*³⁷ and by Molchanov *et al.*³⁸ but regardless to the interaction potentials.

Using the known value of a_m for one fullerene, for instance for C_{60} , it is easy to obtain the effective radius for any other fullerene. Substituting it into (4) gives the coefficients α and β in (3) for the C_n fullerene. Generalizing the procedure mentioned above gives the potential of interactions between different fullerene molecules C_m and C_n ³⁹

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

Here $s = r/D_{mn}$, $D_{mn} = (a_m + a_n)$, a_m and a_n are their effective radii, $\delta = (a_m - a_n)/(a_m + a_n)$, 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 molecules³⁶.

We have calculated the effective radii (7) for a family of smaller and higher fullerenes, from C_{28} to C_{96} . Substituting it together with (5) into (4) and (9) obtained the coefficients α and β of the intermolecular potentials (3) for them and (8) for interactions of the C_{60} molecule with the molecules of some higher fullerenes from C_{70} to C_{96} and with the smaller one, C_{36} . Their characteristics are given in Table 1. 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. The Girifalco potentials for the eight fullerenes are shown in Fig. 6. One can see that their minimum points lie on a nearly straight line. Potential curves for interactions of C_{60} with some higher and smaller fullerenes are demonstrated in Figs. 7 and 8. It is apparent that the effective diameter of the hard core of the potential (8) D_{mn} is defined as the arithmetic mean between those of $C_m - C_m$ and $C_n - C_n$.

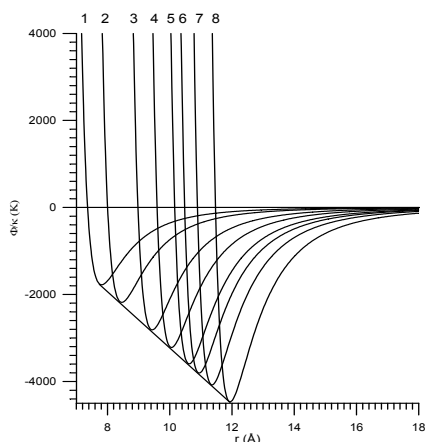


Fig. 6. The Girifalco potential for eight fullerenes: C_{28} (1), C_{36} (2), C_{50} (3), C_{60} (4)³², C_{70} (5), C_{76} (6), C_{84} (7), C_{96} (8).

Table I. 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	$a(10^{-14} \text{erg})$	$\beta(10^{-17} \text{erg})$	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	286.64	7.358	7.080	1775
36,36 ^b	5.500	-	12.49	104.90	8.000	8.460	2182
50,50 ^b	6.481	-	8.980	28.19	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

^aGirifalco³²

^bThe work³⁶

^cThe Work³⁹

and it is used for the calculations of the coefficients α and β (9). 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 1 that the r_0 and σ coincide with the corresponding arithmetic means within hundredths of percent while ε with the geometric mean $\varepsilon_{mn} = \sqrt{\varepsilon_{mm}\varepsilon_{nn}}$ within tenths of percent.

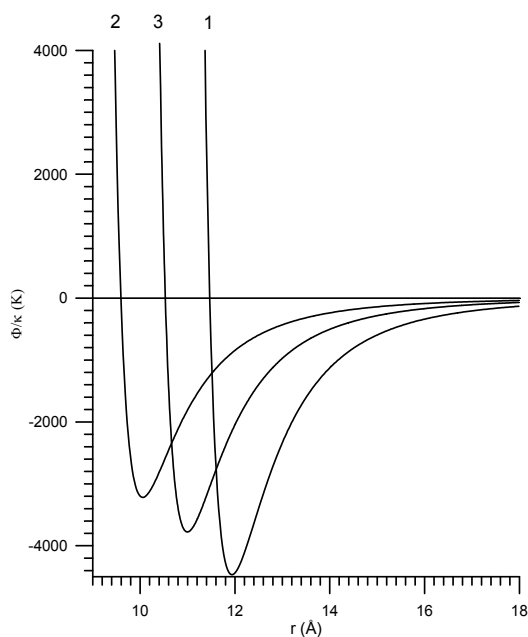


Fig. 7. Intermolecular potentials for $C_{60} - C_{60}$ (1), $C_{96} - C_{96}$ (2) and $C_{60} - C_{96}$ (3).

the r_0 and σ coincide with the corresponding arithmetic means within hundredths of percent while ε with the geometric mean $\varepsilon_{mn} = \sqrt{\varepsilon_{mm}\varepsilon_{nn}}$ within tenths of percent.

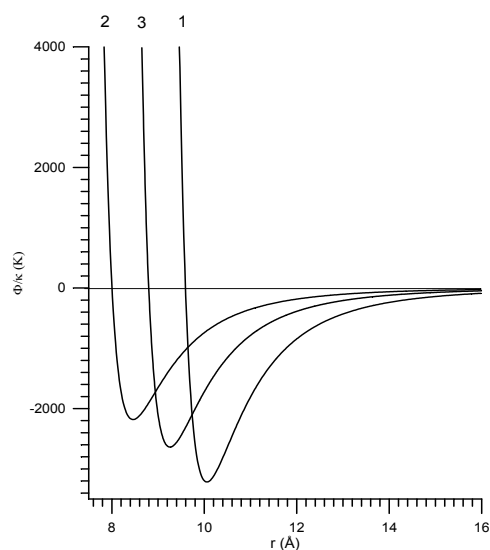


Fig. 8. Intermolecular potentials for $C_{60} - C_{60}$ (1), $C_{36} - C_{36}$ (2) and $C_{60} - C_{36}$ (3).

4.2. Brief Sketch of the Statistical-Mechanical Method

In our investigations we use the correlative method of the unsymmetrized self-consistent field (CUSF), see e.g.^{40 - 45}, that enables one to consider the strong anharmonicity of the lattice vibrations occurring temperatures higher than about one-half of the melting temperature. Its zeroth approximation includes the strong anharmonicity up to the fourth order, and taking into account the rotational and intramolecular degrees of freedom, the free Helmholtz energy and the equations of state of a cubic crystal at temperature $\Theta = kT$ under pressure P are of the form

$$F = N \left\{ \frac{K_0}{2} - \frac{5\Theta}{24} \left(\frac{\beta}{X} \right)^2 - \frac{\Theta}{4} \left(X + \frac{5\beta}{6X} \right)^2 - \Theta \ln \left[\left(\frac{3m^2\Theta^3}{\hbar^4 K_4} \right)^{3/4} D_{-1.5} \left(X + \frac{5\beta}{6X} \right) \right] \right\} \quad (10)$$

$$- \frac{N\Theta}{2} \ln \left(\frac{8I_1 I_2 I_3 \Theta^3}{\hbar^6} \right) - N\Theta \sum_j g_j \ln \left(2 \sinh \frac{\hbar \omega_j}{\Theta} \right) + F^2 + F^H$$

$$P = - \frac{a}{3v} \left[\frac{1}{2} \frac{dK_0}{da} + \frac{\beta\Theta}{2K_2} \frac{dK_2}{da} + \frac{(3-\beta)\Theta}{4K_4} \frac{dK_4}{da} \right] + P^2 + P^H; \quad (11)$$

$$E = \frac{N}{2} \left[K_0 + \frac{(15+\beta)\Theta}{2} + \frac{\hbar}{2} \sum_j g_j \omega_j \coth \frac{\hbar \omega_j}{2\Theta} \right] + E^2 + E^H \quad (12)$$

Here N is the quantity of molecules (the Avogadro's number), m the mass of the molecule, I_1 , I_2 and I_3 are the moments of inertia (for molecules of the spherical form, $I_1 = I_2 = I_3$), 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 unit cell, and $\beta \left(K_2 (3/\Theta K_4)^{1/2} \right)$ is an implicit function determined by the transcendental equation

$$\beta = 3X \frac{D_{-2.5}(X+5\beta/6X)}{D_{-1.5}(X+5\beta/6X)}, \quad (13)$$

where D_ν are the parabolic cylinder functions,

$$K_{2l} = \frac{1}{2l+1} \sum_{k \geq 1} Z_k \nabla^{2l} \Phi(R_k), \quad l = 0, 1, 2, \quad (14)$$

F^2 , F^H , P^2 , 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 (11) that the rotational and intra-molecular 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 (12) and the main contribution to the specific heats of the fullerites

$$\begin{aligned} C_V = & \frac{Nk}{4} \left(15 + \beta - \frac{X\beta'}{2} \right) + \\ & Nk \sum_j g_j \left(\frac{\hbar\omega_j}{\Theta} \right)^2 e^{\hbar\omega_j/\Theta} / (e^{\hbar\omega_j/\Theta} - 1)^2 + C_V^2 \\ & + C_V^H; \left(\beta' = \frac{d\beta}{dX} \right) \end{aligned} \quad (15)$$

that increases 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 thermodynamic properties of orientatio-nally disordered crystalline phases of various fullerites depending on the temperature and pressure, including their equilibrium with 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 this reduces to

$$\begin{aligned} P = & P_{id} (1 - BP_{id}/\Theta); \\ P_{id} = & \Theta \left(\frac{K_4}{12\pi^2\Theta} \right)^{3/4} \\ & \exp \left[\frac{K_0}{2\Theta} - \frac{5}{24} \left(\frac{\beta}{X} \right)^2 - \frac{1}{4} \left(X + \frac{5\beta}{6X} \right)^2 + \frac{f^2 + f^H}{\Theta} \right] / D_{-1.5} \left(X + \frac{5\beta}{6X} \right) \end{aligned} \quad (16)$$

where

$$B(\Theta) = -2\pi \int_0^{\infty} \left[\exp\left(-\frac{\Phi(r)}{\Theta}\right) - 1 \right] r^2 dr \quad (17)$$

is the second virial coefficient, $f^i = F^i/N$, $i = 2, H$. The set of equations (11) and (16) 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. Some Results

We have calculated the properties of C_{60} ⁴⁴⁻⁴⁶, C_{70} ⁴⁷⁻⁴⁸, C_{76} and C_{84} ⁴⁹. Here are presented some results⁵⁰ for a family of fullerites from C_{36} to C_{96} .

4.3.1. Sublimation Curves

The intermolecular distances in C_{36} , C_{50} , C_{60} , C_{76} and C_{96} together with the experimental data available for C_{60} ^{51, 52} and C_{76} ⁵³ are depicted in Fig. 9. 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.

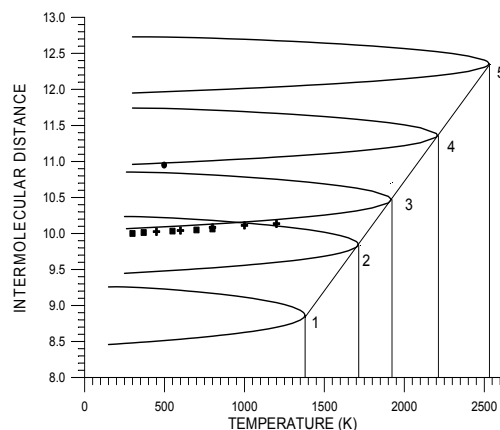


Fig. 9. The intermolecular distances for fullerites along their sublimation curves: C_{36} (1), C_{50} (2), C_{60} (3), C_{76} (4), C_{96} (5). The vertical lines show the temperatures T_S . Experimental data for C_{60} are taken from works by Mathews *et al.*⁵¹ (■), Fischer and Heiney (+)⁵², and for C_{76} from work by Kawada *et al.*⁵³.

<http://www.revista-nanociencia.ece.buap.mx>

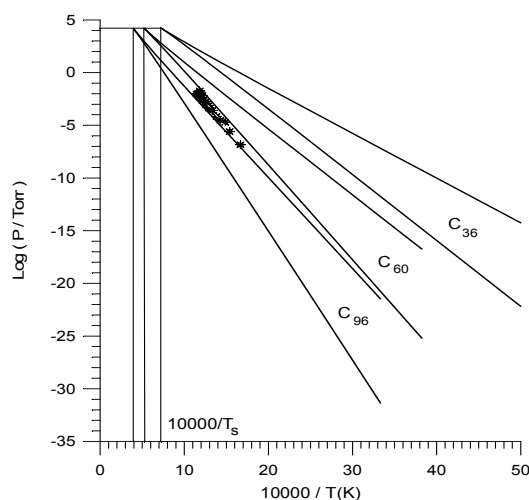


Fig. 10. Saturated vapors pressures. Experimental data are taken from 54–57.

To avoid encumbrance, the dependence of the logarithm of the saturated vapor pressures on the inverse of temperature is demonstrated in Fig. 10 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} ^{47–50} (and also for C_{70} , C_{76} and C_{84}). Their temperature dependence is described by the equation

$$\log P_{sat} = A - \frac{B}{T} - CT, \quad (18)$$

the last term being due to the anharmonicity of 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 twice. Such a behavior agrees with experimental estimations of A and B available for C_{60} , C_{70} , C_{76} and C_{84} ^{57–62}.

In Fig. 11 we show the temperature dependence of the enthalpies of sublimation of fullerenes. We compare them with the experimental data for C_{60} and C_{70} ⁶³, C_{76} ^{58–59} and C_{84} ^{61–62}. One can see the agreement within the limits of experimental error, with the exception of the result for C_{76} ⁵⁷ 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.*⁶⁴ 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} .

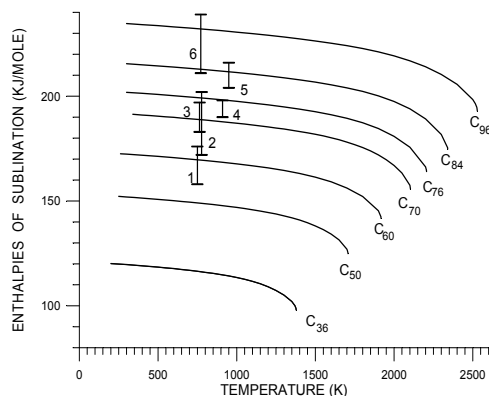


Fig. 11. Enthalpies of sublimation. Experimental data for C_{60} (1) and C_{70} (2) are taken from work by Markov *et al.*⁶³ (the values recommended), for C_{76} from works by Brunetti *et al.*⁵⁸ (3), Boltalina *et al.*⁵⁹ (4), and for C_{84} from works by Piacente *et al.*⁶¹ and Boltalina *et al.*⁶⁰.

4.3.2. Thermodynamic properties

Along the lower branches we have calculated the properties of the fullerites that are due to the lattice vibrations. All the elastic moduli 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 the atoms in molecules.

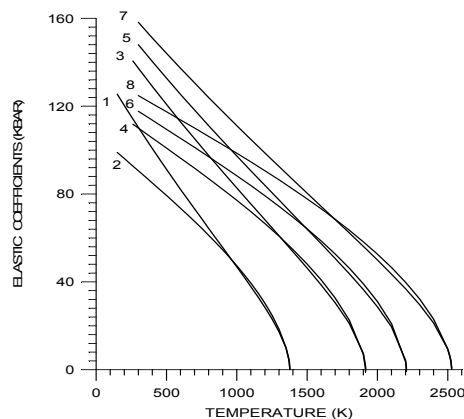


Fig. 12. Isothermal bulk moduli B_T (odd numbers) and shear coefficients C_{44} (even numbers) of the fullerites: C_{36} (1, 2), C_{60} (3, 4), C_{76} (5, 6), C_{96} (7, 8).

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 $(T_S - T)^{1/2}$,

Fig. 12. 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, C_{11}^T , $C_{11}^T - C_{12}^T$ and T/C_V , remain finite and positive up to and including this temperature. Note that recently, great interest has been expressed in the loss of the thermodynamic stability of crystals, see e.g. ^{65,66}.

The spectra of intra-molecular 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} fullerenes⁶⁷⁻⁶⁹. That's why, we have calculated the thermal properties only for these two fullerites. Their isobaric specific heats are shown in Fig. 13. 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 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 integral characteristics of their intramolecular vibrations. The agreement with experimental results available for C_{60} fullerite^{63, 66-71} is quite satisfactory.

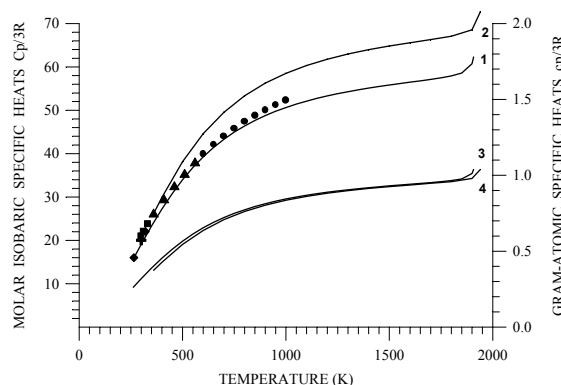


Fig. 13. Isobaric heat capacities for C_{60} and C_{70} . Experimental data are taken from works by Y. Jin *et al.*⁷⁰ (■), Matsuo *et al.*⁷¹ (+), Fischer *et al.*⁷² (◆), Lebedev *et al.*⁷³ (▲), and Markov *et al.*⁶³ (●).

5. On a Possible Melting Curve of C_{60} Fullerite

Shortly after the growth of macroscopic crystals C_{60} it has been started investigations on the possibility of its melting. Although the liquid phase of fullerites has yet been observed, discussions about its possible existence has persisted for years.

Hagen *et al.*⁷⁴ based on Monte Carlo simulations have reasoned that the liquid phase of C_{60} has no the region of absolute stability and hence cannot exist. However other authors basing on various methods, e.g.⁷⁵⁻⁷⁹, have drawn the possibility of its liquid phase, although in a narrow phase diagram range. The estimations 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. 9, rather than to the melting temperature. Note that Stetzer *et al.*⁸⁰ 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 estimation for the decomposition temperature of a single C_{60} molecule comprises yields about 4000 K⁸¹. Thus, the investigations of the possibility of the liquid phase for fullerites are hitherto being continued^{79, 82-84}.

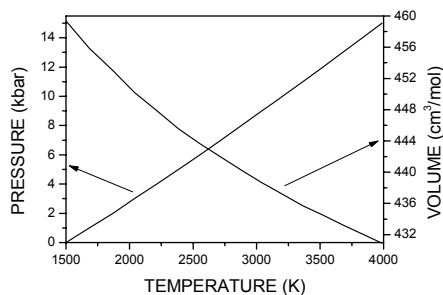
Owing to the lack of an unified rigorous microscopic theory for crystals and liquids, semi-empirical criteria for melting are of frequent use which are stated as a constancy of one or other characteristic of the solid phase on the melting curve (a peculiar kind of “integrals of movement along the melting curve”). They are: the Lindemann’s criterion, e.g.⁸⁵, the Ross’ criterion⁸⁶, the entropy⁸⁷ and energy⁸⁸ 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 utilized for calculations of the melting curve. For instance, the first implies that on the melting curve

$$\delta = \sqrt{\bar{q}^2} / a = const, \quad (19)$$

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

Calculating the mean-square displacements by the correlative method of unsymmetrized self-consistent field for strongly anharmonic crystals⁸⁹⁻⁹⁰ and utilizing the Lindemann’s criterion (19) we have estimated a possible melting curve $T_m(P)$, $V_S(T)$ of the C_{60} fullerite⁹¹. As mentioned above, the liquid phase of fullerites has yet been observed while the theoretical estimates of the triple point of C_{60} lie between 1400 and 1800 K. We have used our estimation $T_0 = 1500$ K⁴⁴ and calculated the Lindemann’s parameter (19) at this point $a(T_0) = 10.255 \times 10^{-8}$ cm: $\delta \cong 0.041$ ⁹⁰.

Note that this value is less than in simple Van der Waals crystals 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) at various fixed pressures up to



temperature $T_m(P)$ at which $\sqrt{\bar{q}^2}/a = 0.041$ and calculated the molar volume at this melting point $V_s = V(P, T_m)$. We have restricted ourselves to the temperature about 4000 K (and the pressure about 15 kbar) since at such temperature the C_{60} molecule is decomposed⁷⁹.

Fig. 14. The possible melting curve $P_m = P_m(T)$, $V_s = V_s(T)$ of the C_{60} fullerite.

The results are shown in Fig. 14. The temperature dependence of the melting pressure is described very well by the Simon equation

$$\frac{(P_m(T)/\text{bar}) - 1}{b} = \left(\frac{T}{T_0}\right)^c \quad (20)$$

Originally, this equation has been proposed for the melting curve of Ar (see, e.g.⁸⁷). For C_{60} fullerite we find $T_0 = 1500 \text{ K}$, $b = 6643.8$, $c = 1.209$. The temperature dependence of the molar volume along the melting curve is approximated by the formula

$$V_s(T) = V_s(T_0) - 29.20 \ln(T/T_0) \quad (21)$$

Note that this regularity 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 considerations⁹² and then has been confirmed experimentally⁹³. It holds also for alkali metals (sodium)⁹⁴.

Thus, we are finishing our review on the fullerenes and fullerites that has no pretensions on completeness. It may be pointed out that the knowledge of the thermal and elastic properties of fullerites is important in respect to their uses at various temperature and pressure conditions. One can utilize our intermolecular potential (8) with parameters listed in Table 1 in calculations of thermodynamic properties for the C_{60} fullerite mixed with higher and smaller ones. Interest has been expressed recently in investigations of mixtures of the fullerites⁹⁵⁻⁹⁶.

ACKNOWLEDGMENTS

The author is grateful to CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico (Brazil) for the financial support. This work has been presented in part at the XIV Simposio Peruano de Física (Trujillo, del 11 al 16 de agosto del 2003). The author is grateful to Comité Organizador for the local expenses payment.

REFERENCES

1. T.P.Stecher and B.Donn, *Astrophys. J.*, 142, 1681, (1965).
2. D.E.H. Jones, *New. Scient.*, **32**, 354 (1996).
3. E.Osawa, *Kagaku* 25, 854 1970) (in Japanese).
4. Z.Yoshida and E.Osawa, *Aromaticity*, Kagakudojin, Kyoto, 1971 (in Japanese), pp. 174 –178.
5. D.A.Bochvar and E.G.Gal'pern, *Dokl. Akad. Nauk SSSR* 209, 610 (1973) (in Russian); *Proc. Acad. Sci. USSR*, 209, 239, (1973).
6. R.A.Davidson, *Ther. Chim. Acta* 58, 193 (1981).
7. Y.Iwasa, K.Tanoue, T.Mitani, and T.Yagi, *Phys. Rev. B* 58, 16374 (1998).
8. T.L.Makarova, *Superconductors* 35, 243 (2001).
9. H.W.Kroto, J.R.Heath, S.C.O'Brien, R.F.Curl, and R.E.Smalley, *Nature*, 318, 162 (1985).
10. W.Krätschmer, L.D.Lamb, K.Fostinoupolos and R. D.Huffman, *Nature* 347, 354 (1990).
11. W.Krätschmer, *Z. Phys.* D19, 405 (1991).
12. W.Krätschmer and R.D.Huffman, In *The Fullerenes* (Edited by H.W.Kroto, J.E.Fischer and D.E.Cox), p. 5. Pergamon Press, Oxford – New York – Seoul – Tokyo (1993).
13. S.Tomita, M.Fujii, S.Hayashi, *et al.*, *Chem. Phys. Lett.* 305, 225 (1999).

14. L. A. Girifalco, M. Hodak and R.S.Lee, *Phys. Rev. B* 62, 13104 (2000).
15. J. de Bruijn, A. Dworkin, *et al.*, *Europhys. Lett.* 24, 551 (1993).
16. H.A.Ludwig, W.H.Fietz, F.W.Hornung, *et al.*, *Z. Phys.* B96, 179 (1994).
17. G. B. M. Vaughan, P. A. Heiney, J.E.Fischer, *et al.*, *Science* 254, 1350 (1991).
18. M. A. Verheijen, H. Meekes, P. Bennema, *et al.*, *Chem. Phys.* 166, 287 (1992).
19. V. Blank, M. Popov, S. Buga, *et al.*, *Phys. Lett.* A188, 281 (1994).
20. O. Bashkin, V. I. Rashchupkin, N.P.Kobelev, *et al.*, *Pis'ma Zh. Eksp. Teor. Fiz.* 59, 258 (1994).
21. V. V. Brazhkin and A. G. Lyapin, *Usp. Fiz. Nauk* 166, 893 (1996).
22. V. D. Blank, S. G.Buga, N. R. Serebrynaya, *et al.*, *Phys. Lett.* A220, 149 (1996).
23. A. Soldatov and O. Anderson, *Appl. Phys. - Mater* 64, 227 (1997).
24. P. M. Allemand, K. C. Klemeni, A. Koch *et al.*, *Science* 253, 301 (1991).
25. M.Schlüter, M.Lannoo, M.Needels, *et al.*, See Ref. 10, p. 303.
26. The Fullerenes, Edited by H.W.Kroto, J.E.Fischer and D.E.Cox. Pergamon Press, Oxford – New York York – Seoul – Tokyo 1993.
27. J.E.Fischer and P.A.Heiney, *J. Phys. Chem.Solids* 54, 1725 (1993).
28. A.V.Eletskii and B.M.Smirnov, *Usp. Fiz. Nauk* 165 977 (1995).
29. V.Buntar, F.M.Sauerzopf and H.W.Weber, *Austr. J. Phys.* 50, 329 (1997).
30. Lu, J., Li, X. and Martin, R.M. (1992). *Phys. Rev. Lett.*, 68, 1551.
31. Sprik, M., Cheng, A. and Klein, M. L. (1992). *J. Phys. Chem.*, 96, 2027.
32. L.A.Girifalco, *J. Phys. Chem.* 96, 858 (1992).
33. M. A. Verheijen, H. Meekes, P. Bennema, *et al.*, *Chem. Phys.* 166, 287 (1992).
34. K. Kniaz', L. A. Girifalco and J.E.Fischer, *J. Phys. Chem.* 99, 16804 (1995).
35. M. C. Abramo and C. Caccamo, *J. Phys. Chem. Solids* 57, 1751 (1996).
36. V.I.Zubov, *Molec. Mater.* 13, 385 (2000).
37. Y. Saito, T. Yoshikawa, N. Fujimoto, and H. Shi-nihara, *Phys. Rev.*, B48, 9182 (1993).
38. S. P. Molchanov, A. M. Popov, A. B. Suhorukov, *Poverhnost*, № 8-9, 42 (1994), in Russian.
39. V.I.Zubov, *Fullerenes, Nanotubes and Carbon Nanostructures* 12, 499 (2004).
40. V. I. Zubov and Ya. P. Terletsky, *Ann. Phys.* (Germany) 24, 97 (1970).
41. V. I. Zubov, *Phys. stat. Solidi(b)* 87, 385; 88, 43 (1978).
42. V.I.Yukalov and V.I.Zubov, *Fortschr. Phys.* 31, 627 (1983).
43. V. I. Zubov, J. F.Sanchez, N.P.Tretiakov and A. E. Yusef, *Int. J. Mod. Phys.* B9, 803 (1995).

44. V. I. Zubov, N. P. Tretiakov, J.F. Sanchez and A. A. Caparica, *Phys. Rev.* B53, 18, 12080 (1996).
45. V.I.Zubov, J.F.Sanchez-Ortiz, J.N.Teixeira Rabelo and I.V.Zubov, *Phys. Rev.* B55, 6747 (1997).
46. V. I. Zubov, J. F. Sanchez, N. P. Tretiakov, *et al.*, *Carbon* 35, 729 (1997).
47. V. I. Zubov, N. P. Tretiakov, I. V. Zubov, *et al.*, *J. Phys. Chem. Solids* 58, 12, 2039 (1997).
48. V. I. Zubov, N. P. Tretiakov, I. V. Zubov and J. B. Marques Barrio, *J. Phys. Chem. Solids* 60, 547 (1999).
49. V.I.Zubov, N.P.Tretiakov and J.N.Teixeira Rabelo, *Molec. Mater.* 13, 349 (2000).
50. V. I. Zubov, I.V.Zubov and J.N.Teixeira Rabelo, *J. Phys. Chem.* B107 (2003).
51. C. K. Mathews, S. Radjagopalan, K.V.G.Kutty, *et al.*, *Solid Stat. Commun.* 85, 377 (1993).
52. J. E. Fischer and P.A.Heiney, *J. Phys. Chem Solids* 54, 1725 (1993).
53. H. Kawada, Y. Fujii, H. Nakao, *et al.*, *Phys. Rev.* B51, 8723 (1995).
54. J. Abrefah, D. R. Olander, M. Balooch and W. J. Siekhaus, *Appl. Phys. Lett.* 60, 1313 (1992).
55. C.K.Mathews, M.Sai Baba, T.S.L. Narasimhan, *et al.*, *J. Chem. Phys.* 96, 3566 (1992).
56. V. Piacente, G. Gigli, P.Scardala, A.Giustini and D. Ferro, *J. Chem. Phys.* 99, 14052 (1995).
57. M.V. Korobov, E.V. Skokan, D.Iu. Borisova, L.M. Homich, *Zh. Fiz. Khim.* 70, 999 (1996) (in Russian).
58. B. Brunetti, G. Gigli, E. Giglio, V. Piacente and P. Scardala, *J. Phys. Chem.* B101, 10715 (1997).
59. O. V.Boltalina, V.Iu.Markov, A.Ya.Borchevskii, *et al.*, *Rapid Commun. Mass. Spectrom.* 12, 1028 (1998).
60. O. V.Boltalina, V.Iu.Markov, A.Ya.Borchevskii, *et al.*, *Mendeleev Commun.*, 1998, p. 143.
61. V.Piacente, C.Patchette, G.Gigli and P.Scardala, *J. Phys. Chem.* A101, 4303 (1997).
62. Boltalina, V.Iu.Markov, A.Ya.Borchevskii, *et al.*, *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials* 6, 614 (1998).
63. V.Iu. Markov, O.V.Boltalina, L.N.Sidorov, *Zh. Fiz. Khim.* 75, 5 (2001) (in Russian).
64. F. M. S. S.Fernandes, F. M. M. Freitas and R. P.S. Fartaria, *J. Phys. Chem.* B107, 276 (2003).
65. G.E.Norman and V.V.Stegailov, *Dokl. Phys.* 47, 667 (2002).

66. M.N.Krivoguz, G.E.Norman, V.V.Stegailov, *et al. J Phys. A – Math. Gen.* 36, 6041 (2003).
67. Zh. Dong, P. Zou, J. M. Holen, P. C.Eklund, *et al., Phys. Rev.* B48, 2863 (1993).
68. M. C. Martin, X. Du, J. Kwon and L. Mihali, *Phys. Rev.* B50, 171 (1994).
69. G. Onida, W. Andreoni, J. Kohanoff and M. Pari-nello, *Chem. Phys. Lett.* 219, 1 (1994).
70. Y. Jin, J. Cheng, M. Varma-Nair, *et al., J. Phys. Chem.* 96, 5151 (1992).
71. T.Matsuo, H.Suga, W.I.F.David, *et al., Solid Stat. Commun.* 83, 711 (1993).
72. J.E.Fischer, A.R.McGhie, J.K.Estrada, *et al., Phys. Rev.* B53, 11418 (1996).
73. B. V. Lebedev, K.B.Zhogova, T.A.Bykova, *et al. Izv. Ross. Akad. Nauk, Ser. Khim.* 1966, p. 2229 (in Russian).
74. M. H. J. Hagen, E.J.Meijer, G.C.A.M.Mooij, *et al., Nature* 365, 425 (1993).
75. N. W. Ashcroft, *Europhys. Lett.* 16, 355 (1991); *Nature* 365, 387 (1993).
76. A. Cheng, M.L.Klein and C.Caccamo, *Phys. Rev. Lett.* 71, 1200 (1993).
77. C.Caccamo, *Phys. Rev.* B51, 3387 (1995).
78. M. Nasegava and K. Ohno, *Phys. Rev.* E54, 3928 (1996).
79. M. A. Abramo and G. Coppolino, *Phys. Rev.* B58, 2372 (1998).
80. M. R. Statzer, P. A. Heiney, J. E. Fischer and A.R. McGhie, *Phys. Rev.* B55, 127 (1997).
81. S.G.Kim and D.Tománek, *Phys. Rev. Lett.* 72, 2418 (1994).
82. M. Nasegava and K. Ohno, *J. Chem. Phys.* 113, 4315 (2000).
83. A. L. C. Ferreira, J. M. Pacheco and J. P. Prates-Ramalho, *J. Chem. Phys.* 113, 738 (2000).
84. M. A. Abramo, C. Caccamo, D. Costa and G. Pelicane, *Europhys. Lett.* 54, 468 (2001).
85. G. Leibfried, *Gittertheorie der mechanischen und thermischen Eigenschaften der Kristalle*, Springer-Verlag, Berlin, 1955, in German.
86. M. Ross, *Phys. Rev.* 184, 233 (1969).
87. S. M. Stishov, *Usp. Fiz. Nauk* 114, 3 (1974), in Russian.
88. V. I. Zubov, *Zh. Fiz. Khimii* 55, 2171 (1981), in Russian.
89. V. I. Zubov, M.F.Pascual, J.N.Teixeira Rabelo and A.C. de Faria, *Phys. stat. sol.(b)* 182, 315 (1994).
90. V. I. Zubov and C. G.Rodrigues, *Phys. stat. sol.(b)* 222, 471 (2000).
91. V. I. Zubov, C. G. Rodrigues and I.V.Zubov, *Phys. stat. sol.(b)* 238, 110 (2003).
92. V. B. Magalinskii and V. I.Zubov, *Phys. stat. sol. (b)* 105, K139 (1981).
93. A. N. Utyuzh and V. V. Kechin, *Zh. Eksp. Teor. Fiz.* 85, 795 (1983), in Russian.
94. V. I. Zubov and V. B. Magalinskii, *Teplofiz. Vys. Temp.* 21, 394 (1983), in Russian.

95. K. Kniaz', J. E. Fischer, L.A. Girifalco, *et al.*, *Solid State Commun.* 96, 739 (1995).
96. D. Havlik, W. Schranz, M. Haluska, *et al.*, *Solid State Commun.* 104, 775 (1997).