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Thermodynamic properties of the C_{60} fullerite at high temperatures: Calculations taking into account the intramolecular degrees of freedom and strong anharmonicity of the lattice vibrations

V. I. Zubov and N. P. Tretiakov
*Departamento de Física, Universidade Federal de Goiás, Caixa Postal 131, 74001-970, Goiânia, Goiás, Brazil**
and Department of Theoretical Physics, Peoples' Friendship University, Moscow, 117198, Russia

J. F. Sanchez
Department of Theoretical Physics, Peoples' Friendship University, Moscow, 117198, Russia

A. A. Caparica
Departamento de Física, Universidade Federal de Goiás, Caixa Postal 131, 74001-970, Goiânia, Goiás, Brazil
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Basing our calculations on the correlative method of the unsymmetrized self-consistent field for strongly anharmonic crystals, we study thermodynamic properties of the high-temperature (fcc) modification of the C_{60} fullerite. In this work a complete set of its thermal and elastic properties have been calculated at normal pressure from the experimental equilibrium point with the low-temperature phase to the instability temperature. In its high-temperature phase, the molecules rotate rather freely and the noncentral part of the intermolecular forces almost disappears. Because of this, it can be treated as a van der Waals crystal with a lot of intramolecular degrees of freedom. To take them into account we have used available information about the normal modes of intramolecular frequencies and their degeneracies. For the intermolecular forces the Girifalco potential and its Yakub approximation have been utilized. The intramolecular vibrations have no effect on the equation of state and related properties but are crucial in specific heats. Our results are in good agreement with experimental data. The possible melting temperature of the C_{60} fullerite and the behavior of its thermodynamic properties near the spinodal point are discussed. At this point the isothermal bulk modulus B_T and (unlike in familiar van der Waals crystals) the elastic constant C_{44} go to zero, and the thermal expansion coefficient a and the isobaric specific heat C_p tend to infinity. Other stability coefficients remain finite and positive. [S0163-1829(96)00618-2]

I. INTRODUCTION

Since their discovery[1] and especially after their preparation in solid state,[2] fullerenes have been the focus of attention of many scientific groups (see, e.g., the reviews[3–6]). Up to 1994, more than 3000 papers on fullerenes had been published. The vast majority of experimental and theoretical work on pure and doped solid fullerenes (fullerites and fullerides) deals with their magnetic properties and superconductivity, e.g., Refs. 3–7. At the same time, little is known about thermodynamic properties of fullerites.

The present work is devoted to the calculation of a complete set of equilibrium thermal and elastic properties, including the sound velocities, of the high-temperature modification of the fullerite C_{60} at normal pressure. The outline of our paper is the following. In Sec. II we discuss the known characteristic traits of the fullerite C_{60}, in particular, its low pressure crystallographic modifications and the phase transition between them, effective potentials of intermolecular forces, intramolecular degrees of freedom, and the strong anharmonicity of the lattice vibrations. In Sec. III we give the working formulas of the method that we use in our investigations—the correlative method of the unsymmetrized self-consistent field. In Sec. IV we present the results of our calculations, compare them with available experimental data, and discuss their temperature dependences including the behavior of stability coefficients near the spinodal point.

II. DISTINCTIVE FEATURES OF THE SUBJECT OF INVESTIGATION

It is well known that among fullerenes, the C_{60} molecules have the highest cohesive energy per atom and are the most abundant. This is one of the reasons why the C_{60} fullerene receives primary emphasis. Having near-spherical shape, these molecules at low pressures form crystal lattices of the cubic system. The low-temperature phase of the C_{60} fullerite is orientationally ordered and consists of four simple cubic sublattices which differ one from another by the orientations of molecules.[8,9] It is often referred to as the simple cubic (sc) lattice though it closely resembles the face-centered cubic (fcc) lattice apart from the orientations of molecules. In the high-temperature modification the molecules rotate almost freely,[8] forming the so-called plastic crystal.[5] It has the fcc lattice.[10]

Under normal pressure, the phase transition between the two phases occurs at 261.4 K,[9] with the discontinuity in the volume being less than 1%.[11] It is inherently an orientational order-disorder transition. Usually it is considered to be a polymorphic phase transition. However, in line with the

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aforesaid, it would be more properly classified as an orientational melting.

In the low-temperature modification just the noncentral part of the intermolecular potential provides the orientational ordering of molecules,[12,13] whereas in the high-temperature phase it disappears after averaging over all orientations of rapidly rotating molecules. Using the standard (12-6) Lennard-Jones function for the atom-atom interaction between two molecules and averaging, Girifalco has obtained the following intermolecular potential for the gaseous and fcc phases of the C_{60} fullerene:[14]

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

where $s = r/2a$, $a = 3.55$ Å, $\alpha = 7.494\times10^{-14}$ erg, and $\beta = 1.3595\times10^{-16}$ erg. It has a minimum point $r_0 = 10.0558$ Å and the depth of the potential well $\varepsilon/k = 3218.4$ K. Yakub has approximated the Girifalco potential (1) by a simpler Lennard-Jones-type function.[15] It can be written as

$$\Phi_Y(r) = \frac{\varepsilon}{34}\left[9\left(\frac{r_0}{r}\right)^{43} - 43\left(\frac{r_0}{r}\right)^{9}\right] \tag{2}$$

with the same ε and $r_0 = 10.04$ Å.

These central forces are more short range than forces between the rare-gas atoms that form simple van der Waals crystals. Hence, when the phenomena related to intrinsic molecular degrees of freedom are not considered, the fcc phase of the C_{60} fullerite can be treated as a typical van der Waals crystal.[16,17] It is interesting that its density is very close to the density of solid Ar, and its scaling parameter in pressure ε/σ^3 is close to those of heavy rare-gas solids [σ is the distance at which $\Phi(\sigma) = 0$]. Note also that for C_{60} the de Boer parameter is

$$\Lambda = 2\pi\hbar/\sigma\sqrt{m\varepsilon} \approx 3.1\times10^{-3}. \tag{3}$$

For its fcc modification $kT/\varepsilon > 0.08$ and hence quantum effects are negligible throughout the region of its stability. For comparison, Xe has $\Lambda = 0.064$.[18] So, making the above-mentioned proviso, one can say that the fcc phase of C_{60} fullerite is a pure classical van der Waals crystal.

On the other hand, a C_{60} molecule containing 60 carbon atoms has 180 degrees of freedom: three coordinates of center of mass, three rotational degrees of freedom, and 174 intramolecular ones. The first group of degrees of freedom is related to the lattice vibrations. At the considered temperatures, the rotations of the C_{60} molecules lead to an addition of $3N\theta/2 = 3NkT/2$ to the internal energy and of $3Nk/2$ to the specific heats (N is the number of molecules, usually the Avogadro number, and $\theta = kT$ the absolute temperature in energy units). Generally speaking, the situation can be different for intramolecular degrees of freedom owing to a possible interaction between the lattice and intramolecular vibrations. The spectrum of such vibrations has been measured by Raman and infrared techniques[19–21] and calculated using first-principles theory[22] (see also references in those papers). In particular, it has been found that the crystalline environment has little effect on them. The reason is the great difference between frequencies: the normal modes of intramolecular frequencies ω_J of C_{60} vary from 5.1235×10^{13} to 3.0138×10^{14} s^{-1},[19] while our evaluations give for the effective mean-square frequency of the lattice vibrations from 6.25×10^{12} to 3.6×10^{12} s^{-1} depending on temperature. Molecular dynamic computations[23] have estimated the ‘‘melting’’ temperature of the C_{60} molecule itself at above 4000 K, which far exceeds the temperatures at which the solid fullerene under normal pressure is stable.[17] Consequently, the anharmonicity of the intramolecular vibrations in the C_{60} fullerite is negligible (perhaps except for the vicinity of the instability point of the fcc lattice, T_s) and there is no necessity to take it into account in the equation of state and the related properties. On the whole, the fcc fullerite C_{60} can be classified as a van der Waals crystal with a lot of intramolecular degrees of freedom.

As for the anharmonicity of the lattice vibrations of the C_{60} fullerite, it is strong at $T > 700$ K.[17] As this temperature is reached, the main anharmonic terms are no longer small corrections and must be included without resort to a perturbation technique. In our calculations we follow the correlative method of the unsymmetrized self-consistent field[24–30] (CUSF) that allows one to do this.

III. METHOD OF INVESTIGATION

In principle, the basic equations of the CUSF contain anharmonicity of any order. In the zeroth approximation, allowing for anharmonic terms up to fourth order and adding the contributions of the rotational and intramolecular degrees of freedom, we obtain the following expression for the Helmholtz free energy:

$$F^0 = N\left\{\frac{K_0}{2} - \frac{5\theta}{24}\left(\frac{\beta}{X}\right)^2 - \frac{\theta}{4}\left(X + \frac{5\beta}{6X}\right)^2 - \theta\ln\left[\left(\frac{3m^2\theta^3}{\hbar^4K_4}\right)^{3/4} D_{-1.5}\left(X + \frac{5\beta}{6X}\right)\right]\right\} - \frac{3N\theta}{2}\ln\left(\frac{2I\theta}{\hbar^2}\right) - N\theta\sum_j g_j\ln\left(2\sinh\frac{\hbar\omega_j}{\theta}\right). \tag{4}$$

Here m and I are the molecular mass and moment of inertia, ω_j the natural frequencies of the intramolecular vibrations, g_j their degeneracies,

$$X = K_2(3/\theta K_4)^{1/2}, \tag{5}$$

$K_0/2$ is the static lattice energy per molecule, K_2 and K_4 are the isotropic parts of the second- and fourth-order coefficients, and $\beta(X)$ is the solution of the transcendental equation

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

where D_1 are the parabolic cylinder functions.

For a crystal with central pairwise intermolecular forces

$$K_{2l}=\frac{1}{2l+1}\sum_{\vec{n}\neq 0}\Delta^{2l}\Phi(|\vec{r}|)|_{\vec{r}=\hat{A}\vec{n}}$$

$$=\frac{l}{2l+1}\sum_{k\geqslant 1}Z_k\left[\Phi^{(2l)}(R_k)+\frac{2l}{R_k}\Phi^{(2l-1)}(R_k)\right],$$

$$l=0,1,2,\ \ldots \qquad (7)$$

where $\hat{A}$ is the lattice matrix, $\vec{n}$ are the integer component vectors, Z_k and $R_k=\nu_k a$ the coordination numbers and radii, a is the nearest-neighbor distance, and ν_k are structural coefficients; for the fcc lattice $\nu_k=\sqrt{k}$.

Differentiation of (4)–(6) with respect to volume and temperature gives all scalar thermodynamic functions of a cubic crystal under hydrostatic pressure P, in the zeroth approximation. So we have the equation of state of the fcc phase of the fullerite:

$$P^0=-\frac{a}{3\nu}\left[\frac{1}{2}\frac{dK_0}{da}+\frac{\beta\theta}{2K_2}\frac{dK_2}{da}+\frac{(3-\beta)\theta}{4K_4}\frac{dK_4}{da}\right] \qquad (8)$$

$[\nu(a)=V/N$ is the volume of the unit cell], its internal energy

$$E^0=\frac{N}{2}\left[K_0+\frac{(15+\beta)\theta}{2}\right]+N\sum_j g_j\frac{\hbar\omega_j}{2}\coth\frac{\hbar\omega_j}{2\theta}, \qquad (9)$$

isochoric specific heat

$$C_{\nu}^0=\frac{Nk}{4}\left(15+\beta-\frac{X\beta'}{2}\right)$$

$$+Nk\sum_j g_j\left(\frac{\hbar\omega_j}{\theta}\right)^2 e^{\hbar\omega_j/\theta}/(e^{\hbar\omega_j/\theta}-1)^2, \qquad (10)$$

isothermal bulk modulus

$$B_T^o=\frac{2}{3}P^o+\frac{a^2}{18\nu}\left[\frac{d^2K_0}{da^2}+\beta\theta\frac{d^2}{da^2}\ln K_2\right.$$

$$\left.+\frac{(3+\beta)\theta}{2}\frac{d^2}{da^2}\ln K_4+\frac{\theta\beta'}{X}\left(\frac{\partial X}{\partial a}\right)^2\right], \qquad (11)$$

and thermal coefficient of pressure

$$\Gamma^o\equiv\left(\frac{\partial P^o}{\partial T}\right)_\nu=-\frac{ka}{6\nu}\left(\frac{\beta}{K_2}\frac{dK_2}{da}+\frac{3-\beta}{2K_4}\frac{dK_4}{da}-\frac{\beta'}{2}\frac{\partial X}{\partial a}\right), \qquad (12)$$

where $\beta'=d\beta/dX$.

The isothermal elastic constants are expressed in terms of the second derivatives of the Helmholtz free energy with respect to components of the strain tensor.[31] From (4)–(6) it follows for a cubic strongly anharmonic crystal under hydrostatic pressure that

$$C_{11}^0=\eta_0(\theta,a)+\sum_{k\geqslant l}Z_k^{(400)}\xi_0(\theta,a;k)-P^0, \qquad (13)$$

$$C_{12}^0=\eta_0(\theta,a)+\sum_{k\geqslant 1}Z_k^{(220)}\xi_0(\theta,a;k)+P^0, \qquad (14)$$

$$C_{44}^0=\sum_{k\geqslant 1}Z_k^{(220)}\xi_0-\frac{a^2}{15\theta\nu}\left[\varphi^2\overline{q^4}+\varphi(2\psi+\chi)\left(\frac{1}{7}\overline{q^6}\right.\right.$$

$$\left.+\frac{1}{3}\overline{q^4}\ \overline{q^2}\right)+\frac{\overline{q^2}}{12}\left(\frac{2}{7}\overline{q^6}+\frac{1}{3}\overline{q^4}\ \overline{q^2}\right)(2\psi+\chi)^2$$

$$\left.+\frac{\overline{q^8}}{756}(16\psi^2+12\psi\chi+9\chi^2)\right]-P^0. \qquad (15)$$

Here we use the following notation:

$$\eta_0=\frac{a^2\theta}{18\nu}\left[(X\beta'-\beta)\left(\frac{1}{K_2}\frac{dK_2}{da}\right)^2-\frac{X\beta'}{K_2K_4}\frac{dK_2}{da}\frac{dK_4}{da}\right.$$

$$\left.+(2\beta+X\beta'-6)\left(\frac{1}{2K_4}\frac{dK_4}{da}\right)^2\right], \qquad (16)$$

$$\xi_0=\frac{R_k^4}{2\nu}\left[\hat{D}^2\Phi(R_k)+\frac{\beta\theta}{K_2}\hat{D}^2\Phi_2(R_k)\right.$$

$$\left.+\frac{(3-\beta)\theta}{2K_4}\hat{D}^2\Phi_4(R_k)\right], \qquad (17)$$

$$\varphi(a)=\sum_{k\geqslant 1}\left(R_k^4Z_k^{(220)}\hat{D}^3+\frac{Z_kR_k^2}{3}\hat{D}^2\right)\Phi(R_k), \qquad (18)$$

$$\psi(a)=\sum_{k\geqslant 1}\left[R_k^6Z_k^{(420)}\hat{D}^5+\frac{R_k^4}{2}(Z_k^{(400)}+9Z_k^{(220)})\hat{D}^4\right.$$

$$\left.+Z_kR_k^2\hat{D}^3\right]\Phi(R_k), \qquad (19)$$

$$\chi(a)=\sum_{k\geqslant 1}\left(R_k^6Z_k^{(222)}\hat{D}^5+R_k^4Z_k^{(220)}\hat{D}^4+\frac{Z_kR_k^2}{3}\hat{D}^3\right)\Phi(R_k), \qquad (20)$$

$$\Phi_{2l}(R_k)=\frac{1}{2l+1}\nabla^{2l}\Phi(R_k),\quad \hat{D}=\frac{2}{R_k}\frac{d}{dR_k}, \qquad (21)$$

$$Z_k^{(ijl)}=\frac{1}{R_k^{i+j+l}}\sum_{|\hat{A}\vec{n}|=R_k}(\hat{A}\vec{n})_x^i(\hat{A}\vec{n})_y^j(\hat{A}\vec{n})_z^l. \qquad (22)$$

Apparently for cubic crystals $Z_k^{(ijl)}=0$ if at least one of the indices i, j, or l is odd. The coefficients (22) are invarient under their permutations and possess the properties

$$Z_k^{(000)}=3Z_k^{(200)}=3Z_k^{(400)}+6Z_k^{(220)}$$

$$=3Z_k^{(600)}+18Z_k^{(420)}+6Z_k^{(222)}=\cdots=Z_k. \qquad (23)$$

Hence they can be named the partial coordination numbers. The moments $\overline{q^{2n}}$ are expressed in terms of K_2, K_4, and β.[32]

Based on the foregoing formulas as the zeroth-order approximation, we have used statistical perturbation theory which improves the contributions of the main anharmonic terms[26,30] by taking into account dynamical interatomic correlations, and also includes higher-order (fifth and sixth) anharmonic terms.[27,30] Calculations reveal that all these corrections are small excepting in the vicinity of the spinodal point

TABLE I. Properties of the fcc phase of C_{60}: the nearest-neighbor distance in Å, linear thermal expansion coefficient in 10^{-5} K^{-1}, the specific heats in cal mol K, the elastic properties in kbar, and the sound velocities in m/s. The values in the first lines have been calculated with the Girifalco potential (1) and those in the second lines with the Yakub approximation (2).

T	261.4	300	400	600	800	1000	1200	1400	1600	1800	1900
a	10.067	10.071	10.082	10.106	10.132	10.161	10.194	10.233	10.282	10.354	10.426
	10.060	10.064	10.076	10.100	10.127	10.157	10.192	10.233	10.289	10.387	
α	1.070	1.084	1.126	1.223	1.347	1.512	1.745	2.103	2.763	4.710	12.713
	1.090	1.106	1.151	1.256	1.394	1.581	1.852	2.296	3.220	8.729	
C_V	92.70	112.60	160.55	231.39	273.20	297.82	312.99	322.83	329.48	334.11	335.86
	92.69	112.59	160.54	231.37	273.17	297.79	312.96	322.78	329.42	334.00	
C_p	93.09	113.06	161.17	232.35	274.55	299.63	315.41	326.09	334.17	342.68	359.44
	93.10	113.07	161.19	232.38	274.61	299.73	315.58	326.41	334.97	349.96	
B_T	140.51	137.25	128.89	112.88	97.54	82.73	68.22	53.71	38.61	21.11	7.40
	143.28	139.73	130.73	113.49	97.06	81.23	65.72	50.12	33.55	11.34	
B_s	141.11	137.80	129.39	113.34	98.02	83.24	68.75	54.25	39.16	21.65	7.91
	143.93	140.33	131.25	113.99	97.57	81.76	66.27	50.69	34.12	11.88	
C_{11}^T	218.95	215.43	206.38	188.84	171.69	154.67	137.35	119.20	99.14	73.93	52.69
	223.72	219.85	210.01	190.99	172.50	154.19	135.57	115.89	93.49	60.28	
C_{12}^T	101.29	98.16	90.15	74.90	60.46	46.77	33.65	20.96	8.33	−5.32	−15.28
	103.07	99.67	91.08	74.74	59.34	44.75	30.79	17.23	3.58	−13.16	
C_{44}	111.77	110.01	105.48	96.37	87.00	77.16	66.56	54.76	40.93	22.61	7.02
	114.08	112.15	107.17	97.19	86.99	76.29	64.70	51.62	35.69	10.64	
C_{11}^S	219.55	215.98	206.87	189.31	172.18	155.17	137.89	119.74	99.69	74.47	53.21
	224.36	220.45	210.54	191.49	173.01	154.72	136.12	116.45	94.05	60.83	
C_{12}^S	101.89	98.71	90.64	75.36	60.94	47.27	34.18	21.50	8.88	−4.78	−14.76
	103.71	100.27	91.61	75.24	59.85	45.28	31.35	17.80	4.14	−12.62	
v_1	3638.2	3610.7	3539.6	3397.9	3253.0	3101.4	2937.8	2753.5	2530.4	2210.2	1887.7
	3674.1	3644.2	3567.4	3414.4	3258.4	3095.1	2918.0	2715.6	2460.3	2007.0	
v_t	2595.8	2577.0	2527.5	2424.4	2312.4	2187.0	2041.1	1862.0	1621.5	1217.9	685.8
	2619.9	2599.3	2545.2	2432.5	2310.5	2173.3	2011.8	1808.2	1515.5	839.2	

T_s where contributions of the fifth and sixth terms to elastic coefficients (13)–(15) rise steeply.

The CUSF enables one to consider the quantum corrections to lattice properties of strongly anharmonic crystals.[28] However, as pointed out above, they are negligible for the fcc fullerite C_{60}. In contrast, its intramolecular vibrations[19–22] are governed by quantum theory, since their characteristic temperatures $T_j = \hbar\omega_j/k$ are from 391.3 to 2302 K. Their contributions to the internal energy (9) and specific heat (10) are included using exact formulas.

The linear thermal expansion coefficient, the adiabatic elastic moduli, and the isobaric specific heat can be calculated from familiar thermodynamic relations:

$$a = \frac{\Gamma}{3B_T}, \quad B_S - B_T = C_{11}^S - C_{11}^T = \frac{9TV\alpha^2 B_T^2}{C_V},$$

$$C_{44}^S = C_{44}^T, C_p = C_\nu B_S / B_T, \tag{24}$$

with B_T, Γ, C_V, and $C_{\alpha\beta}^T$ containing corrections of the perturbation theory.

In spite of the apparent awkwardness of the formulas, especially for the elastic constants (13)–(20), a personal computer is sufficient to carry out all calculations, with little computer time being required.

IV. RESULTS AND DISCUSSION

In our computations we have used both the Girifalco intermolecular potential (1) and the Yakub approximation (2). To include contributions of the intramolecular degrees of freedom we have used the data of Raman and infrared scattering experiments performed by Martin *et al.*[19] and by Dong *et al.*[20] which are close to the results of first-principles calculations by Wang, Wang, and Ho.[22]

At $P = \text{const}$, the equation of state (8) has two roots $a_1(T) < a_2(T)$ which coalesce at some temperature T_s, $a_1(T_s) = a_2(T_s)$ above which this equation has no real roots. On the lower branch $B_T > 0$, while on the upper one $B_T < 0$, meaning thermodynamic instability. At the temperature T_s, $B_T = 0$ and it is the spinodal point of the investigated phase (if on the lower branch of the isobar, other stability coefficients are positive up to T_s). At normal pressure, the intermolecular potentials (1) and (2) give $T_s \approx 1916$ and 1834 K, respectively. Scaling T_s for typical van der Waals crystals like rare-gas solids[27] and their experimental melting points T_m, a possible melting temperature of the C_{60} fullerite has been estimated at 1400 K.[17] However, when it is considered that the intermolecular forces in the fullerite have more short-range character than in simple van der Waals crystals, this estimation can increase to about 1500 K. Note also that the possibility of a liquid phase of C_{60} is debated.[32–34]

We have calculated the complete set of thermodynamic properties for the fcc modification of the C_{60} fullerite on the lower branch of its normal isobar. Results are listed in Table I. Both potentials (1) and (2) lead to close values at all but high temperatures, at which the differences increase, especially in the vicinity of the spinodal point T_s.

Before comparing with experimental data, we emphasize that they are few in number. As previously discussed,[17] our results differ from experimental data for the lattice parameter $d=a\sqrt{2}$ available between 295 and 1180 K,[3] by about 0.8%. Based on these data, the average linear thermal expansion coefficient in this range has been estimated at 1.567×10^{-5} K,[3] which is just between the values in Table I for such temperatures. The result of Gugenberger *et al.*,[35] $\alpha\approx10^{-5}$ K, obtained for the fcc phase between the orientational melting point and 300 K is also in agreement with our values. Our results for B_T are close to the experimental datum of Fischer *et al.*[36] at room temperature, ≈ 144 kbar, but not to that of Duclos *et al.*[37] ≈ 180 kbar. Recently, Ludwig *et al.*[38] have measured the isothermal bulk modulus of the C_{60} fullerite at 70, 170 (sc phase), and 300 K. Their result for the fcc modification, $B_T=134$ kbar, differs from the value calculated using the Girifalco potential by only about 2.5%. Comparing with our previous results[39] one can see that the intramolecular vibrations provide the dominant contributions to the specific heats, being one to two orders of magnitude greater than the contribution of the lattice vibrations and molecular rotations. The excepton is C_p near the spinodal point. Owing to rather high values of the characteristic temperatures for the intramolecular vibrations, the specific heats increase considerably with temperature. Our results for C_p are in good agreement with experimental data available below 300 K.[40,41] Note also that there are experimental indications about the orientational-dependent part of the intermolecular forces in the fcc phase,[42] but the available data do not enable us to estimate their contributions to thermodynamic properties.

It is known[43,44] that a given phase is stable (or metastable) when its stability determinant and its principal minors are positive. For cubic crystals, the stability conditions take the form

$$B_T>0, \quad C^T_{11}>0, \quad C_{11}-C_{12}>0, \quad C_{44}>0, \quad T/C_v>0. \tag{25}$$

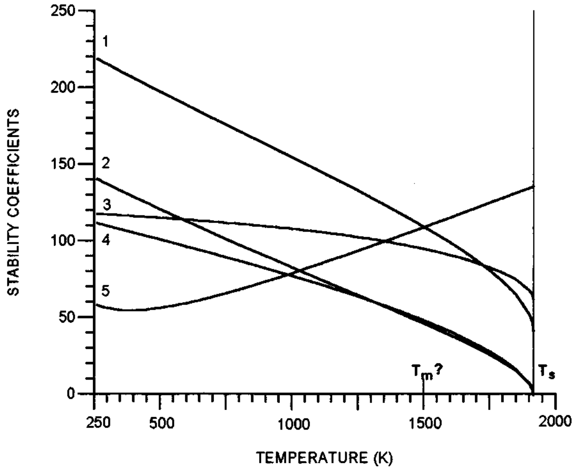

FIG. 1. The stability coefficients of the fcc phase of the fullerite C_{60}: (1) C^T_{11} (2) B_T, (3) $C_{11}-C_{12}$, (4) C_{44} (all in kbar), and (5) $100T/C_V$ (in mol K^2/J).

In Fig. 1 the stability coefficients of the fcc phase of C_{60} are plotted versus the temperature. One can see that all isodynamical stability coefficients, but the last [values given by (25)], decrease with increasing temperature, most notably near the spinodal point T_s at which B_T goes to zero. As this takes place, the thermal expansion coefficient a and the isobaric specific heat tend to infinity. Unlike the case of familiar van der Waals crystals with the fcc lattice, the elastic constant C_{44} goes to zero as well. Other stability coefficients remain finite and positive.

Thus we have calculated the complete set of thermodynamic properties for the fcc modification of the C_{60} fullerite at normal pressure up to the instability point. Our results are in good agreement with available experimental data. We hope that the present work can provide the incentive for further measurements, especially at high temperatures.

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*Address for correspondence.

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