Physics – Uspekhi **46** (12) 1295 – 1303 (2003)

LETTERS TO THE EDITORS

PACS numbers: **64.30.+t**, 64.70.Dv

Melting point of graphite and liquid carbon

(Concerning the paper "Experimental investigation of the thermal properties of carbon at high temperatures and moderate pressures" by É I Asinovskiĭ, A V Kirillin, and A V Kostanovskiĭ)

A I Savvatimskiĭ

DOI: 10.1070/PU2003v046n12ABEH001699

Contents

Abstract. Experimental data from various authors on the graphite melting point are reviewed and compared with the results obtained by É I Asinovskiĭ, A V Kirillin, and A V Kostanovskiĭ as presented in their paper 'Experimental investigation of the thermal properties of carbon at high temperatures and moderate pressures' (*Usp. Fiz. Nauk*. 172 931 (2002) [*Phys. Usp.* 45 869 (2002)]). It is shown that a considerable amount of available information about the heating of graphite by an electrical current or a laser pulse remained unaccounted for in that paper. A comparative analysis of the data indicates the 4800 – 4900-K range as the most reliable melting point estimate for graphite under pressures ranging from 0.1 to 3.0 kbar.

1. Introduction

The material covered in this report is a response to the article by E I Asinovskiĭ, A V Kirillin, and A V Kostanovskiĭ published in *Usp. Fiz. Nauk* **172** 931 (2002) [*Phys. Usp.* **45** 869 (2002)]. That publication contains no serious critical analysis of various investigations and exhibits a one-sided approach to the evaluation of graphite properties near the melting point.

A I Savvatimskiĭ Institute for High Energy Densities of the Joint Institute for High Temperatures, Russian Academy of Sciences
ul. Izhorskaya 13/19, 125412 Moscow, Russian Federation
Tel. (7-095) 362 57 73. Fax (7-095) 361 16 82
E-mail: savlab@iht.mpei.ac.ru

Received 23 June 2003
Uspekhi Fizicheskikh Nauk **173** (12) 1361 – 1379 (2003)
Translated by A I Savvatimskiĭ, E Yankovsky; edited by M V Chekhova

Carbon is a unique element of the Periodic Table and is the basis for a great many compounds. Organic chemistry as a science owes its existence to carbon. It is not by chance that carbon is regarded as the interface between living and nonliving matter. Graphite, a variety of carbon, is one of the most refractory materials, and this predetermined its extensive use in engineering. The construction of a complete phase diagram of carbon at high temperatures has always been an objective of researchers, because it makes it possible to predict the carbon properties that are important from the standpoint of applications. Present-day power engineering requires knowing the physical properties of carbon at high temperatures, including its liquid state. Steady-state investigation methods were no longer sufficient for solving such a problem because no crucible material exists that would be more refractory than graphite. For several decades, intensive development of unsteady-state investigation methods (fast laser or electrical heating) has been under way, first in application to metals (e.g., Ref. [1]) and then to graphite. In so doing, measurements of the true temperature of the specimen has presented the main problem. It can be regarded as proven that, for pure metals, fast heating (down to fractions of a microsecond) makes it possible to obtain equilibrium thermal properties (enthalpy at the beginning of melting, and melting heat), as well as temperature. Additional characteristic features are observed in the melting of graphite, features associated with its complex structure (anisotropy), the sublimation from the solid phase, the dependence of density on the method of preparation, the initial nonuniformity of the structure, etc.

A significant disparity of the experimental data on the melting point of graphite has been observed in recent years. The publication of Ref. [2] is a rehash, both in content and results, of earlier data published in Refs [3, 4] in *Teplofiz. Vys.*

Temp. [*High. Temp*.]. In Ref. [2] 'the parameters of a triple point are predicted to differ markedly from the current accepted values: $p_t = 1$ bar and $T_t = 4000$ K' [2, p. 869]. However, in 1978 close values of the triple point parameters were declared in Ref. [5] (0.2 bar and 3800 K), although temperature measurements in Ref. [5] appear to be unsatisfactory.

The main difference between the data published in Ref. [2] and other numerous present-day measurements is the low value of the graphite melting point (3700 or 4000 K), which almost coincides with Whittaker's data [5]. Note the basic differences observed between these data (summarized in Ref. [2]) and the majority of other data (from 4530 to 5000 K) in measuring the melting point of graphite.

2. Heating rate of graphite specimens

Asinovskiĭ et al. [2] examined only some of the studies involving the measurement of the melting point of graphite (five temperature values are given, including estimates; only three represent direct measurements). They maintain that the melting point of graphite depends on the heating time: the shorter the heating time the higher the temperature recorded. On analyzing a wider spectrum of experimental data, one is forced to admit that this inference is unjustified. For example, Table 1 lists the data of a number of experimental studies for the melting point of graphite as a function of the heating time and heating rate, with indication of the method of heating (electric current, laser pulses).

The experimental data of Vereshchagin [8] (row 2 in Table 1) are contradictory because the same method of optical pyrometry produced different results. The data listed in rows 1 and 10 were obtained from the variation of the slope of the saturation pressure temperature dependence, with the use of the same estimation method. These two results are almost the same (4765 – 5000 K), but the heating rate differs by a factor of $\sim 10^7$. Joseph et al. [18] (row 10) used high-frequency laser radiation to heat graphite in measurements of the concentration of $C_1 - C_7$ molecules by the quadrupole mass spectroscopy method. This enabled the researchers to calculate the partial pressures, whose sum was found to be roughly 100 bar at 4979 K. Thus, the independent measurements of Joseph et al. [18] produced the values of the melting point of graphite and the corresponding vapor pressure of graphite (about 100 bar).

The other data listed in Table 1 may be considered the results of direct temperature measurements. No dependence of the melting point on the heating time is observed. I I Klimovskiĭ (Institute of High Energy Densities, Moscow) proposed that there may be a dependence of the melting point of graphite on the heating rate rather than time. This dependence can be constructed using the data in Table 1. However, it also fails to demonstrate the dependence of the melting point on the heating rate (in the given range of heating rates), despite the fact that the heating rate varies by at least four orders of magnitude.

Thus, we have two groups of measurements: those with fast heating, which give the melting point of graphite in the 4530 – 5080-K range, and those with a low rate of heating (minutes and longer), which give a 3700 or 4000-K melting point. The differences between these two groups are associated with the different conditions of temperature measurements in graphite specimens, which begin subliming even in the solid phase under low ambient pressures.

In the case of graphite, fast heating is preferable because the specimen is at a high temperature for only a short period

Table 1

No.	Heating time	Heating rate, K s^{-1}	Melting point T, K (method)	Pressure P, bar	Reference
1	10 s	5×10^2	5000 ± 200 (laser)	100	[6, 7]
2	Several seconds	1×10^3	4650 (1963) (current) 4040 (1968) (current)	100 (in gas, using a solid-state light guide); 100 (with specimen embedded in transparent NaCl)	[8]
3	20 – 30 ms	1.6×10^5	4800 ± 150 (laser)	110— 2500*	[9]
4	15 ms	3×10^5	4530 ± 150 (current)	140 – 200**	[10]
5	2 ms	2.3×10^6	> 4700 (current)	1000	[11]
6	1.7 ms	3×10^6	5080 ± 70 (current)	1000 – 2000	[12]
7	0.7 ms	6.8×10^6	4750 ± 150 (laser)	150	[13, 14]
8	~ 20 μs	2.4×10^8	4900 ± 200 (current)	3000	[15]
9	1 μs	4.8×10^9	4800 ± 200 (current)	$\geqslant 1000$	[16, 17]
10	8 ns × 1000 (averaged over 1000 pulses)	$\geqslant 4.8 \times 10^9$	$(4765 - 5000) \pm 200$ (laser)	Sum of measured values of partial pressures yields ~ 100 bar at 4979 K	[18]

* According to the data of Ref. [9], the variation of pressure from 110 to 2500 bar had no effect on the measured melting point.
** Input of oxygen to the high-pressure chamber (for transforming graphite to an optically transparent gas CO or CO_2) resulted in an increase in the temperature being measured (the partial oxygen pressure of 40 bar produces an 80-K rise in temperature).

of time, with the result that the amount of evaporated graphite is minimized. One can conceive that the slower the heating the larger the amount of carbon vapor (and, consequently, condensate) that forms before the optics of the pyrometer. This may cause an underestimation of the measured temperature, which could be the case in Refs [2–4]. In fact, the results of measurements of the melting point of graphite depend solely on the experimental conditions, in particular, on the presence of condensed vapor, which affects the recording of temperature by a pyrometer not equipped with a solid-state optical fiber.

3. Role of condensed graphite vapor

Although Vereshchagin [8] arrived at contradictory results (at a pressure of about 100 bar) for the melting point of graphite (4650 and 4035 K), he noted the need to use a solid-state optical fiber in pyrometric measurements at high pressures and temperatures. This makes it possible to avoid convective flows, which lead to a nonuniform vapor density, which in turn inhibits reliable temperature measurement [8].

The temperature measurements in Ref. [2] were conducted for pressures not only lower than 100 bar but also higher than 100 bar. Asinovskiĭ et al. [2] used steady laser heating to determine the melting point of MPG-6 graphite under a pressure of 223–277 bar. 'The melting point was found from the temperature value corresponding to the horizontal section of the thermogram in the specimen heating or cooling mode.' And also 'a horizontal section . . . can be identified as the level of crystallization from the liquid phase.' [2, p. 871, Fig. 2]. According to Asinovskiĭ et al. [2], the temperature found in this manner (4000 ± 100 K) is the melting point. However, there exists another viewpoint supported by experimental data.

Under conditions of slow heating of graphite in Refs [2–4], a pyrometer registered the glow of condensed vapor rather than the glow of a solid surface. That is just what Basharin et al. [13, 14] observed in their experiments (in the time interval of roughly 4 ms), where the optical axis of the pyrometer was oriented along the surface of the graphite specimen heated by laser light. The temperature of the condensed vapor over the graphite surface was 3400–4200 K, which is approximately the temperature level referred to by Asinovskiĭ et al. [2–4] as the graphite melting point (3700 and 4000 K).

This fact forced Basharin et al. [13, 14] to limit the free volume above the surface of the graphite specimen (a quartz plate was secured above the graphite surface at a distance of 20–150 μm). This ensured the transparency of the thin vapor layer covering the surface and no release of laser pulse energy in the vapor condensing over the surface. As a result, the value of 4750 ± 150 K for the graphite melting point was obtained in Refs [13, 14] under a pressure of 150 bar.

A detailed review of the experimental studies of the heating of graphite specimens in 1914–1981 was published in 1981 by Sheĭndlin [19]. The review gives evidence of the difficulties encountered by various researchers '... in measuring temperatures close to the melting point because of the emergence of carbon vapor, which caused a substantial underestimation of temperature' [19, p. 637]. Apparently, the paper by Asinovskiĭ et al. [2] also bears an imprint of previous approaches to graphite investigations because the researchers did not discuss the sublimation of solid graphite at high temperatures and the effect of vaporization on the pyrometer. Senchenko and Sheĭndlin [20] believe that 'the amount of vapor abruptly increases as the sublimation point of graphite, i.e., $T \geqslant 3000$ K, is approached. The pyrometer's signal attenuation in the layer of condensed vapor leads to a hard-to-take-into-account underestimation of the radiance temperature, which increases with temperature' [20, p. 496].

4. Detecting traces of liquid carbon at 1 bar and in a vacuum

Asinovskiĭ et al. [2] claim a pressure of 1–2 bar for the triple point of graphite. In the majority of pulsed measurements (Table 1), the temperature plateau during the melting of graphite was recorded only at pressures no less than 100 bar. In Ref. [7] it is pointed out that 'traces of melt are reliably observed only at pressures above 150 bar' [7, p. 704]. Basharin et al. [13, 14], after their experiment, observed solidified crystals of up to 200 μm in size only under pressures above 100 bar. No such crystals of fused graphite were observed at lower pressures.

Asinovskiĭ et al. [2] provided arguments in favor of the triple point being at a low pressure, especially the detection of solidified droplets of fused graphite in experiments with an electric arc at atmospheric pressure. Such droplets were also observed in the case of electric discharges in a vacuum [21]. The investigation of the latter fact by Mesyats and Proskurovsky [21] and Koval' et al. [22] revealed that a high pressure (up to 400 bar) develops in the cathode zone even in solid graphite. 'The conditions for the melting of graphite develop both in the emission zone and at a distance of tens of micrometers from this zone' [21, p. 106]. The temperature of the graphite cathode in this zone is estimated in Refs [21, 22] as being 5500 K. Obviously, solidified droplets of graphite may be observed at a low ambient pressure as well. Such droplets were also observed at a low pressure in Whittaker's experiments [5] with laser heating of a rapidly rotating graphite rod. One can assume that thermoelastic stresses in the rod could develop (by analogy with [21, 22]) a pressure higher than 100 bar at isolated points.

5. Beginning of graphite melting recorded by enthalpy

In the studies of the melting of graphite, the specific energy input corresponding to the beginning of melting has repeatedly been recorded. Table 2 lists the data on the enthalpy and heat capacity of the solid phase of graphite prior to melting and at the melting point obtained by different authors (in chronological order).

An analysis of the data in Table 2 shows that the specific energy input (10.4–10.5 kJ g^{-1}) corresponding to the beginning of melting of graphite is a quantity that has been reliably determined in experiments. Assuming that the average heat capacity of solid graphite at high temperatures is $C_p \sim 3.0-3.2$ J g^{-1} K^{-1} (Table 2) and knowing that the temperature of 3500 K corresponds to an enthalpy of 6.3 kJ g^{-1} or that 3800 K corresponds to 7.1 kJ g^{-1} (according to the data of steady-state measurements done at the Graphite Research Institute [24]), we can calculate the melting point of graphite. The result is something like $T_{\mathrm{melt}} = 4900-4600$ K, but certainly not 3700–4000 K, as claimed by Asinovskiĭ et al. [2–4], who did not perform their own measurements of the specific energy input.

Table 2

No.	Author, year, Ref.; method, type of graphite, density	Enthalpy at the beginning of melting (specific energy input) H_{solid}, kJ g^{-1}	Corresponding pressure, kbar	Melting point T_{melt}, K; heat capacity
1	Bundy, 1963 [23]; current pulse (several ms), spectroscopic graphite, 1.6 g cm^{-3}	10.45 12.2 (H_{solid} is determined by the drop in electrical resistivity at the beginning of melting)	9 – 31 and 67 – 97 50 – 60	Not determined
2	Buchnev et al. 1984 [24]; steady-state investigation of UPV-1T graphite and glassy carbon	7.1 ($T = 3800$ K)	0.1	4890 K (estimate). The temperature was measured by an EOP-66 standard optical pyrometer up to 3818 K in argon at atmospheric pressure. C_p(3800 K) = 2.5 J g^{-1} K^{-1} (measured); C_p(4500 K) = 3.3 J g^{-1} K^{-1} (extrapolation)
3	Lebedev and Savvatimskiĭ 1986 [25]; current pulse (tens of μs), UPV-1T (2.26 g cm^3), pyrolytic graphite (density of about 2 g cm^{-3})	10 (estimate) Experiments in water, rosin, and fused silica capillary tubes. Uniform heating of graphite of different densities was analyzed. For an energy input of 18 kJ g^{-1} the specimen expansion amounted to 68%	~ 1	
4	Sheĭndlin et al. 1988 [11]; current pulse (1 – 2 ms), pyrolytic graphite (density of about 2 g cm^{-3}) [11], presumably UPV-1T graphite (density 2.14 – 2.17 g cm^{-3}) [26]	9.1 ($T = 4500$ K) Pyrometer was focused onto the *c* plane of a square anisotropic specimen	1	At 4700 K graphite still does not melt (five experiments). The temperature dependence of enthalpy (with 2.5% error) is obtained. C_p = 3.1 J g^{-1} K^{-1} (at 4500 K)
5	Baitin et al. 1990 [12]; current pulse (2 ms), UPV-1TMO graphite (density of 2.26 g cm^{-3})	10.4 Beginning of the temperature plateau of melting was registered (on the *a* plane)	1 – 2	5080 ± 70 K (measured for an emissivity of liquid graphite equal to 0.6)
6	Korobenko et al. 1998 and 1999 [27, 28]; current pulse (1.5 μs), UPV-1T graphite	(a) 12 (inaccurate value), recorded by pyrometer on the *a* plane. (b) 10.5, with the melting plateau registered by pyrometer on the *c* plane (a)	~ 1 tens of kilobars	5000 ± 500 C_p(solid) = 3.2 J g^{-1} K^{-1}; C_p(liquid) = 4 J g^{-1} K^{-1} (measured)
7	Kerley and Chhabildas 2001 [29]; equation of state for graphite is constructed for the 0 – 10^8-K range	9 (estimate obtained in simulating different experiments)	Pressure at triple point is 170 bar (estimate)	Temperature at triple point is 4660 K (estimate)
8	Korobenko and Savvatimskiĭ 2003 [16] and Korobenko 2001 [17]; current pulse (1.5 μs), UPV-1T graphite	(a) 10.5, with the melting plateau recorded by pyrometer on the *a* plane at about 1 kbar (correction for cooling of the surface layer in the case of a close contact with glass was introduced) (b) melting of graphite blackbody model with calibration with respect to the melting of tungsten blackbody model at 3690 K (embedded in resin)	~ 1 ~ 1	C_p(liquid) = 4.2 J g^{-1} K^{-1} (measured) T_{melt} = 4800 ± 200 K (measured)

6. Electrical heating of low-density graphite

Lebedev and Savvatimskĭ [25] have demonstrated that, in the case of electrical heating of low-density (lower than 2 g cm^{-3}) graphite (as well as graphite annealed below 3000 K), the electrical resistivity of the specimen in the initial stage of heating decreases. This leads to an increase in the nonuniformity of graphite electrical heating because a higher power begins to be released in microdomains with lower electrical resistivity.

Therefore, uniform electrical heating requires a high density of the initial graphite specimens and their deep annealing. The initial electrical resistivity of dense graphite after such preparation is 50 μΩ cm. For example, consider Fig. 1 from [30], which demonstrates the results previously obtained by Lebedev and Savvatimskiĭ [25]. Measurements of the electrical resistivity of graphite specimens may serve as an additional check on whether the heating is uniform and the melting region is reached. As Figure 1 shows, the use of a limited volume diminishes the inhomogeneity in the heating of low-density graphite.

Note that Asinovskiĭ et al. [2] used electrical heating of cylindrical graphite rods. However, the researchers failed to provide data on the density of the employed specimens, on their annealing, and on the initial electrical resistivity; neither did they perform measurements of the electrical resistivity in the vicinity of the assumed region of melting. Nevertheless, Asinovskiĭ et al. [2] assumed that the interruption of current in the electric circuit implies the melting of the specimen of MPG-7 graphite (whose initial density was 1.65 – 1.85 g cm^{-3}, according to the data of the Graphite Research Institute). Therefore, it is possible that a failure of the specimen was identified with melting.

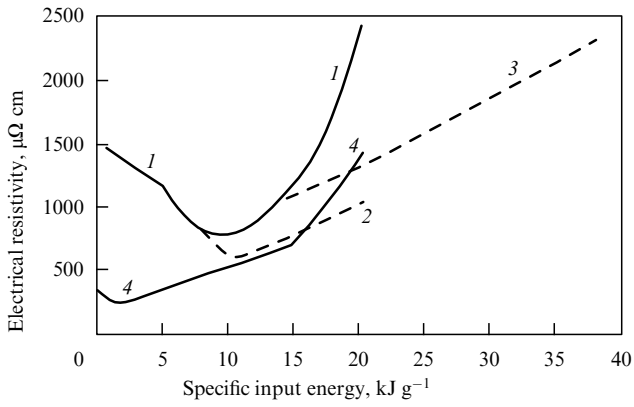

Figure 1. Resistivity of pyrolytic graphite specimens of different initial density versus specific energy input (according to the data of [25] (1986) and [30] (1998)): *1* — pyrolytic cylindrical unannealed graphite (density 1.9 g cm^{-3}), pulse heating in water; *2* — an identical specimen in a glass capillary tube ($V_{\text{tube}}/V_{\text{graphite}} = 1.19$, where V_{tube} is the inner volume of the tube, and V_{graphite} is the volume of the graphite specimen). The beginning of the heating is along curve *1*, and then, as graphite fills the tube, along curve *2* (dashed curve); *3* — an identical specimen in a glass capillary tube with $V_{\text{tube}}/V_{\text{graphite}} = 1.45$. The beginning of the heating is along curve *1*, and then, after graphite has filled the tube, along dashed curve *3*; *4* — pyrolytic plane graphite (volume density 2.15 g cm^{-3}), pulse heating in solid rosin. The slight drop in resistivity at the beginning of heating is due to the insufficient annealing of the specimen.

The reader will recall that graphite is a complicated material with different expansion coefficients in the *a* and *c* planes. The majority of present-day experimenters have long been using square specimens of highly oriented graphite (density 2.26 g cm^{-3}), whose electrical heating involves independent expansion along two axes [11, 12, 16, 17, 27, 28]. Therefore, the assertion by Asinovskiĭ et al. [2] that one of the methods of 'determining the parameters of the phase transitions in carbon' (here the researchers give various references) is that in which 'a thin wire specimen is heated by sending a very short ($10^{-3}-10^{-6}$ s) high-density current pulse through the wire (electric explosion)' [2, p. 870] is erroneous.

In 1998, after numerous experiments with low-density graphite (including those reported in Ref. [25]), it was pointed out in Ref. [30] that it is the electrical heating of specimens of graphite of only high initial density UPV-1T (whose porosity is close to zero [26]) that can lead to success in investigating liquid carbon and, in particular, in measuring the thermal expansion of graphite. This program was implemented, and Korobenko et al. [16, 17, 27, 28] using solid-state optical fibers obtained results on the melting point (4800 ± 200 K), the enthalpy at the beginning of melting (10.5 kJ g^{-1}), the melting heat (10 kJ g^{-1}), and the heat capacity (4.2 J g^{-1} K^{-1}) of liquid carbon. The electrical resistivity of liquid carbon was also measured and found to be 730 μΩ cm (±7%) at a density of 1.8 g cm^{-3} (the pressure was tens of kilobars). According to various researchers, the thermal expansion of graphite in melting was estimated at 70% [16] (pressure $P \leqslant 1$ kbar), 45% [9], and 50% [29].

An example of nonuniform expansion of a cylindrical graphite specimen with an initial density of 1.83 g cm^{-3} under conditions of pulsed electrical heating can be found in Ref. [15]. For the specific energy input of 8.5 kJ g^{-1}, i.e., even before melting, two values of V/V_0 were obtained: 1.69 in one experiment and 2.47 in another experiment. In other words, the volume of graphite even in the solid phase seemed to increase significantly (the results were obtained by illuminating the cylindrical specimen in a certain cross section). Thus, low-density graphite may fail without reaching the melting stage. If this is so, even before melting, solid graphite of low initial density may develop microcracks in which additional energy may be released due to the burning of electric arcs. This will lead to an intensification of nonuniform heating and may also produce a high pressure (above 100 bar) at isolated spots of the failing specimen [22]. In this case the specimen will not melt as an integral whole. However, in some spots melting may be observed. Therefore, the visual observation by Asinovskiĭ et al. [2] of 'traces of graphite melting' does not give sufficient grounds to state that the pyrometer recorded the temperature of the melting graphite specimen.

Pottlacher et al. [15] presented a photograph of a cylindrical graphite specimen with isolated spots brightly glowing on the surface as evidence of nonuniform electrical heating of graphite of low initial density. It is not by chance that the researchers maintain that this graphite is not suitable for studying the liquid state. A reference to the study of Pottlacher et al. [15] was cited in Ref. [2], but the results apparently were disregarded.

Note that the slow electrical heating used in Ref. [2] leads to a lower recorded melting point than for laser heating. For the blackbody model 'the destruction temperature and, hence, the melting point proved to be in the 3630–3740-K range' (with an error of ±150 K) [2, p. 875]. Asinovskiĭ et al. [2] failed to record a temperature plateau under conditions of slow electrical heating of specimens of MPG graphite (with an 'available porosity' of 20% [26]). The pyrometer signal showed only a continuous rise to the above-noted temperatures [2, Fig. 10], while previously, under a faster electrical heating, the melting plateau was repeatedly recorded [10, 12, 15–17, 27, 28] at high temperatures (4530–5080 K), including the case of low-density graphite (4900 K) [15] (of poorer quality, however). By way of example, we present some figures (Figs 2–7) from various works (in chronological order), which show the graphite melting plateau under

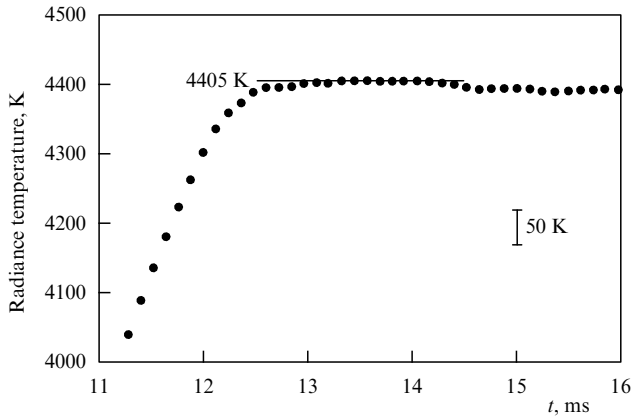

Figure 2. Beginning of the temperature plateau for the melting of a polycrystalline graphite surface (POCO grade; [10], 1990). The radiance temperature was determined at a wavelength of 655 nm. Argon pressure in the chamber was 140–200 bar. The influx of oxygen into the high-pressure chamber (for transforming graphite vapor into the optically transparent gas CO_2) increased the temperature being measured (a partial oxygen pressure of 40 bar produces a rise in temperature by 80 K). $T_{\text{melt}} = 4530 \pm 150$ K [10] if the emissivity of 0.8 is taken into account.

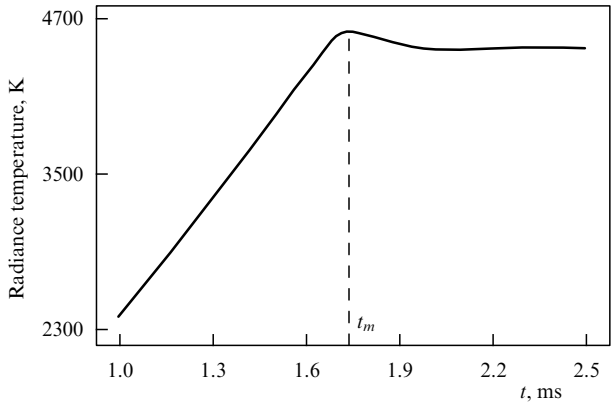

Figure 3. Beginning of the temperature plateau for the melting of a highly oriented pyrolytic graphite surface *a* (grade UPV-1TMO; [12], 1990): gas pressure 1–2 kbar. $T_{melt} = 5080 \pm 70$ K [12]. Emissivity ε was measured at 4000 K ($\varepsilon = 0.71$); at the melting point ε was assumed to be equal to 0.6.

electrical heating or only the beginning of the phase transition from the solid to the liquid state.

7. Selectivity of the authors of Ref. [2] in citing works with different results

Note that Asinovskiĭ et al. [2-4] believe the results of studies performed in 1925–1939, e.g., by Pirani [31], to be reliable, despite that in those years, sophisticated equipment for experimental investigations of graphite on a high technical level was absent and the problems associated with the sublimation of solid graphite were not treated at all. Pirani makes no comments in Ref. [31] on the pyrometry of graphite. He gave the result on the melting point of graphite (3500 °C) in the expectation that the procedure applied in [31] to metals at low ambient pressures would produce a valid result for carbon at low pressures (800 mmHg) as well. In fact, Pirani [31] observed the bulging of graphite from a side drill-hole (3 mm in diameter) in a graphite rod 37 mm in diameter slowly heated by alternating current. The pyrometer recorded the temperature of this bulged region. Naturally, the entire rod (37 mm in diameter) did not melt. Such an experiment can hardly be called successful (as Asinovskiĭ et al. [2] claim) in relation to the melting of graphite in Ref. [31].

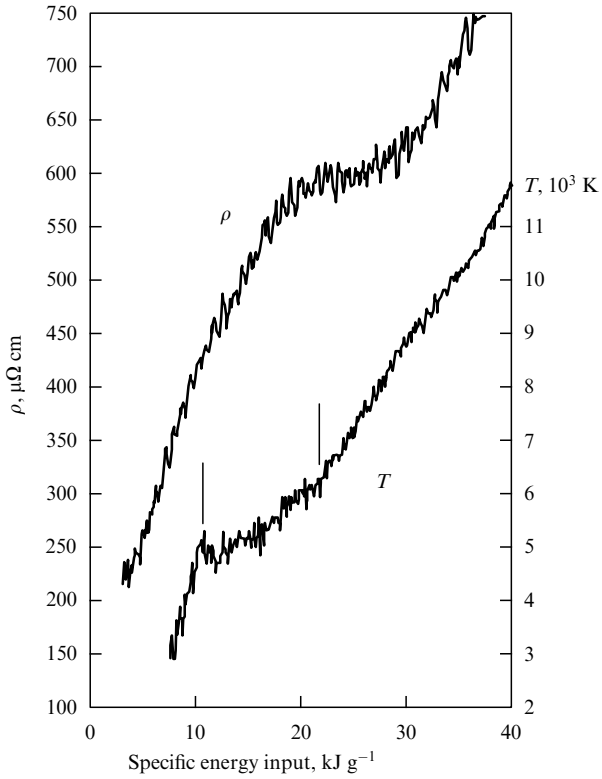

Figure 5. Inclined temperature plateau (marked with vertical lines) in the melting of a UPV-1T graphite specimen in a thick-walled sapphire capillary tube under high (tens of kilobars) pulse pressure ([28], 1999). At the beginning of melting $H_{solid} = 10.5$ kJ g^{-1}. The temperature was fixed at the *c* surface through the sapphire wall of the tube and through a glass plate cemented (with optical cement) on top of the tube. Temperature calibration ($E = 9.14$ kJ g^{-1} corresponds to 4500 K) was done according to Ref. [11]. The temperature at the beginning of melting should be somewhat lower than 5000 K (by 200 K, according to estimates), since the pressure at the melting point is high. The graphite surface in contact with the sapphire cooled off very slowly, since there was high heat conductivity between graphite layers (along the *a* plane).

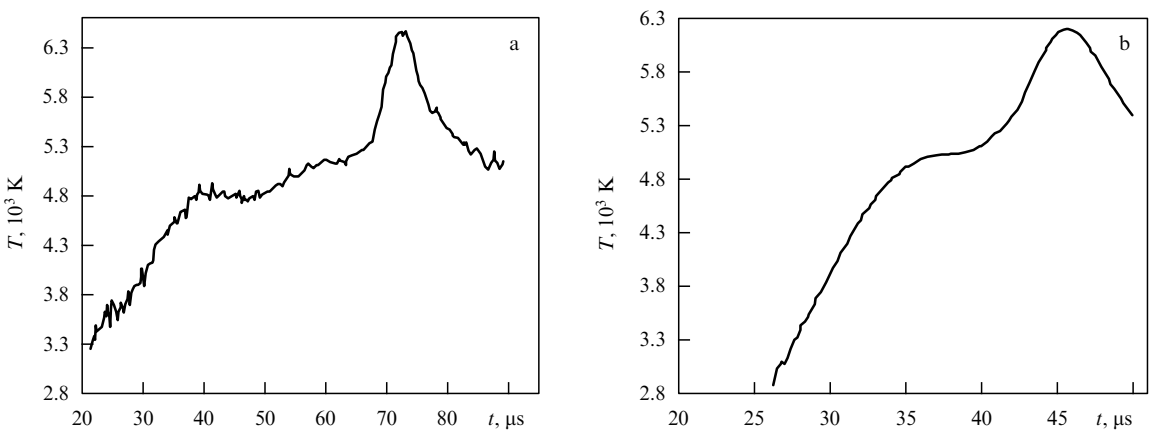

Figure 4. Temperature plateau for the melting of POCO graphite of low density (1.83 g cm^{-3}) ([15], 1993): (a) experiments in Graz (Austria), and (b) experiments in Los Alamos (USA) with the same graphite specimens. Pressure was 3 kbar, $T_{melt} = 4900 \pm 200$ K [15]. Emissivity ε was assumed to be equal to 0.8 according to Ref. [10].

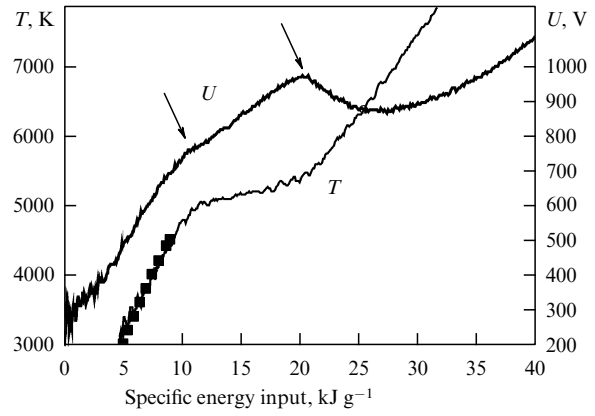

Figure 6. Melting of a highly oriented pyrolytic graphite of high density UPV-1T (placed in a glass cell) under heating for 1.5 μs ([16, 17], 2001). A graphite strip (1 × 10 mm, thickness 0.3-mm) is fixed between two thick glass plates. The beginning and the end of melting are indicated by arrows on the voltage curve U. The calculated pressure (modelling by A D Rakhel) at the melting point varies from 5 kbar (surface layer) to 15 kbar (inner layer). The specific energy input for the solid state under melting, E_{solid}, was 10.5 kJ g^{-1} at the melting point of 4900 K (with allowance for $dP/dT = 54$ bar K^{-1} [8] for the surface layer). Temperature measurements were conducted at the a surface. The graphite layer in contact with the glass cools off due to the low heat conductivity between graphite layers (along the c plane). The surface graphite layer (roughly 2-μm thick) loses about 12% of its energy due to the contact with the glass for 1 μs. Taking this correction into account makes inflection points on the temperature plateau and the voltage curve U coincide at the melting point. The experimental data of V N Senchenko (Institute for High Temperatures of the Russian Academy of Sciences, Moscow; PhD thesis, 1987) are indicated by small black squares. The calibration of the pyrometer temperature in Refs [16, 17] was carried out with the data from Ref. [11] ($E = 9.1$ kJ g^{-1} corresponds to the true temperature of 4500 K). The error in temperature measurements amounts to 2%, and in specific energy input the error is no greater than 5% [11]. The emissivity in Refs [16, 17] is assumed constant at temperatures above 4500 K.

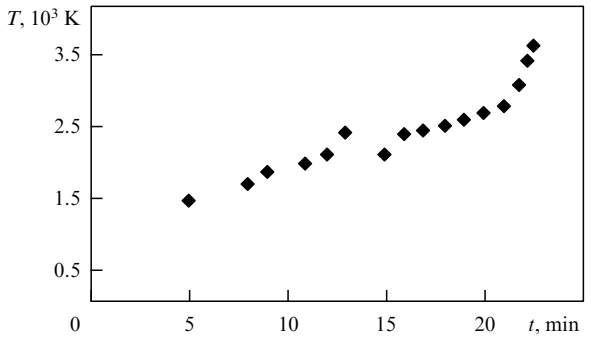

Figure 7. Thermogram of slow electrical heating of a low-density graphite specimen ([2], 2002). The color temperature 'was measured at the central part of the safety fuse on the outer cylindrical surface' [2, p. 875]. A limiting fixed temperature was identified with the melting point (~ 3700 K [2]). The argon pressure in the chamber was 2.5 bar.

Asinovskiĭ et al. [2] make no references to many recent studies in which the measured high-melting point of graphite lies in the 4800 – 5000-K range. We will give only one example: the 1992 study by the team of Ronchi (Ref. [32]) is cited ($T_{melt} = 4100$ K) and its data are included in the figures in Ref. [2]. However, no references are made there to the subsequent 1998 study by the same group [9] with improved temperature measurements ($T_{melt} = 4800 \pm 200$ K). Their skillfully performed study in pulsed laser heating of graphite revealed the absence of the melting plateau in the stage of heating of a low-density (1.55 g cm^{-3}) graphite specimen (only an inflection point is observed on the growing signal of the pyrometer). In order to obtain a temperature plateau in heating, one must use a laser with an extremely uniform heat release over the heating spot. In the Musella et al. [9] study, this uniformity was within 5%, and in the study of Basharin et al. [13, 14] the uniformity was even higher. Basharin et al. [13, 14] obtained a temperature plateau by heating highly oriented graphite (density 2.25 g cm^{-3}); in so doing, a gently sloping crater with a flat bottom was observed after the experiment, which is an indication that the heat release over the area of the heating spot is uniform. Nevertheless, Asinovskiĭ et al. [2, p. 871, Fig. 2], who make no comments at all on the heat release over the heating spot, show a melting plateau in the region of heating of low-density graphite (at a temperature of about 4000 K), which contradicts the results and conclusions of Refs [9, 13, 14].

8. Does the graphite – carbyne solid-phase transition exist?

In concluding their article, Asinovskiĭ et al. [2] discussed the possibility of transforming graphite into carbyne at temperatures in the 2800 – 3500-K range (which requires a finite time). This would make it possible to examine the hypothesis that they had detected the melting of carbyne at ~ 3700 – 4000 K at low pressures rather than the melting of graphite. For this hypothesis to be true, one must prove that there exists a phase transformation of solid graphite into carbyne, i.e., that the traces of carbyne detected by Asinovskiĭ et al. [2] are not the result of condensation of vapor. This scenario would make it possible to bring into accord the high melting point of graphite (4800 – 5000 K) obtained in the majority of experiments and the low temperature (3700 and 4000 K) recorded in Ref. [2] at low pressures as the melting point (presumably) of carbyne. Unfortunately, Asinovskiĭ et al. [2] failed to convincingly solve this problem. As to the very idea of a graphite – carbyne transition, it was discussed in publications made in 1975 [5], because Whittaker's experiments [5] also revealed traces of carbyne. In 1981 a detailed and useful review was made by Sheĭndlin [19], which covered virtually all aspects of graphite investigation starting from 1914, including the difficulties with identifying carbyne when electron microdiffraction is used to analyze trace amounts of matter. As noted by Bundy et al. [33] (1996), the existence of a graphite – carbyne transition on the phase diagram (below the melting point) remains controversial and unresolved.

It would be appropriate to add that, according to Buchnev et al. [24], who performed steady-state investigations of graphite in argon at atmospheric pressure, 'The results of X-ray structure analysis of the investigated specimens have demonstrated that the heating of both quasi-single-crystal graphite and glassy carbon up to 3818 K does not lead to a variation in the basic parameters of the crystalline structure of these materials' [24, p. 1110]. Thus, apparently no graphite – carbyne solid-phase transition is realized, at least below 3818 K. Nevertheless, Asinovskiĭ et al. [2] conclude that, in their case, in the vicinity of 3500 K, 'a thermal explosion in a carbon sample has been realized, and it is highly probable that

this explosion was caused by a graphite – carbyne transition' [2, p. 880]. They also conclude that the thermogram in Fig. 19 of Ref. [2] is most likely caused by a so-called thermal explosion. This thermogram shows an almost constant temperature level (near 3500 K) in the course of heating for ~ 40 s with a temperature dip at the 8th second and temperature peaks at the 30th and 40th seconds. Such a thermogram only supports the assumption that the heat release over the volume of the graphite specimen studied in Ref. [2] is inhomogeneous.

A 'thermal explosion' may be nothing more than the result of heat release during the equalization of temperature from the more heated core of the specimen to the less heated surface (owing to the nonuniformity of heat release over the volume). The facts mentioned above (and in Sections 6 and 7) are indications that the heat release under conditions of electrical heating of low-density ($1.65 - 1.85$ g cm^{-3}) graphite specimens in [2] is inhomogeneous.

9. Conclusion

Nowadays, pulse heating of substances (by laser radiation or electric current) has become the main method for obtaining trustworthy scientific information

— about standard thermophysical properties under high temperatures and pressures [1, 9, 12, 14, 16, 30]; and

— about new physical effects that emerge in the very short time interval of heating [34, 35].

For example, picosecond laser heating of the *c* surface (anisotropic graphite) leads to homogeneous melting of the subsurface layer during a time interval shorter than 3 ps (3×10^{-12} s) [35]. As noted by Agranat et al. [35], the typical time for the existence of a liquid state and its hardening into a homogeneous amorphous state is $\sim 10^{-10}$ s. This is accompanied by the generation of a periodic structure on the surface, its period being of the order of the wavelength of the heating laser pulse.

Figure 8 (taken from Ref. [34]) presents the equilibrium phase diagram for the trace of heating of a highly oriented pyrolytic graphite (grade HOPG) specimen by a femtosecond laser pulse. During heating there is no expansion and, hence, the pressure rises from the beginning of heating. Investigations of the equilibrium thermophysical properties are problematic under fast heating of this kind not only because it is difficult to make heating equilibrium but also because it is hard to make it homogeneous.

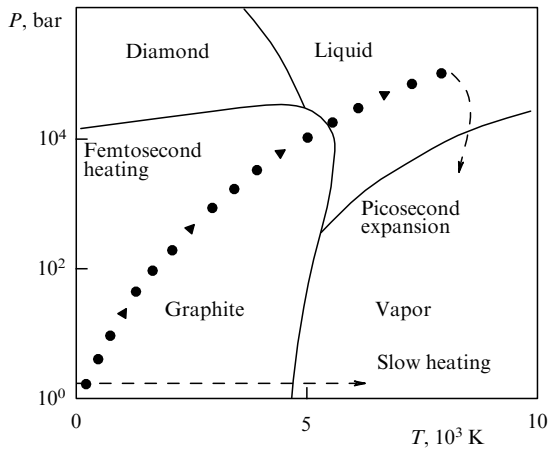

Figure 8. Equilibrium phase diagram of carbon accessible in a short pulsed laser heating experiment ([34], 1993) with a HOPG graphite specimen.

Note that under pulse electrical heating of HOPG graphite [16, 17, 27, 28], heat is released in the entire volume of the specimen, which gives this method an advantage over surface laser heating. It is a well-known fact that the time of transfer of the energy input (from the electron subsystem to the metal lattice) is about 1 ps (the theoretical estimates of Allen [36] coincided with the experimental results of Brorson et al. [37]). The value of the resistivity of carbon in the liquid states at high pressures is about 600 μΩ cm [27, 34], which is close to the resistivity of expanded liquid metals at elevated pressures [30]. Hence pulse heating of graphite (during times much longer than 1 ps) may correspond to the equilibrium phase diagram. For microsecond heating of HOPG graphite by a current pulse (with the pressure at melting amounting to 5 – 15 kbar), the trace of heating of carbon in our case (see Refs [16, 17, 27, 28]) was close to that shown in Fig. 8.

Since 1963, in only two (Whittaker [5] and Asinovskiĭ et al. [2 – 4]) out of ten research centers in various countries has a low melting point of graphite (3700 – 4000-K) been obtained (we leave out the study of Vereshchagin [8] as indeterminate because of its dual result). The majority of other studies give a substantiated melting point in the 4530 – 5080-K range. This difference is larger than the experimental error, and the conclusions by Asinovskiĭ et al. [2], based on incomplete information, may give an incorrect view of graphite melting.

References

1. Lebedev S V, Savvatimskiĭ A I *Usp. Fiz. Nauk* **144** 215 (1984) [*Sov. Phys. Usp.* **27** 749 (1984)]
2. Asinovskiĭ É I, Kirillin A V, Kostanovskiĭ A V *Usp. Fiz. Nauk* **172** 931 (2002) [*Phys. Usp.* **45** 869 (2002)]
3. Asinovskiĭ E I, Kirillin A V, Kostanovskiĭ A V *Teplofiz. Vys. Temp.* **35** 716 (1997) [*High Temp.* **35** 704 (1997)]
4. Asinovskiĭ E I, Kirillin A V, Kostanovskii A V, Fortov V E *Teplofiz. Vys. Temp.* **36** 740 (1998) [*High Temp.* **36** 716 (1998)]
5. Whittaker A G *Science* **200** 763 (1978); *Nature* **276** 695 (1978)
6. Kirillin A V, Malyshenko S P, Sheindlin M A, Evseev V N *Dokl. Akad. Nauk SSSR* **257** 1356 (1981) [*Sov. Phys. Dokl.* **26** 422 (1981)]
7. Kirillin A V, Kovalenko M D, Sheindlin M A, Zhivopistsev V S *Teplofiz. Vys. Temp.* **23** 699 (1985)
8. Vereshchagin L F *Tverdoe Telo pri Vysokikh Davleniyakh*: *Izbrannye Trudy* (Solids under High Pressure: Selected Works) (Moscow: Nauka, 1981)
9. Musella M, Ronchi C, Brykin M, Sheindlin M *J. Appl. Phys.* **84** 2530 (1998)
10. Cezairliyan A, Müller A P *Int. J. Thermophys.* **11** 643 (1990)
11. Sheĭndlin M A, Senchenko V N *Dokl. Akad. Nauk SSSR* **298** 1383 (1988) [*Sov. Phys. Dokl.* **33** 142 (1988)]
12. Baitin A V et al. *High Temp.-High Press.* **22** 157 (1990)
13. Basharin A Yu, Fortov V E, in *14th Symposium on Thermophysical Properties, June 25 – 30, 2000, Boulder, CO, USA*, Abstracts (Eds W M Haynes, B A Stevenson) (Boulder, CO: National Institute of Standards and Technology, 2000) p. 159
14. Basharin A Yu, Lipgart I G, Marin M Yu *Tr. Inst. Teplofiz. Ekstremal'nykh Sostoyaniĭ* OIVT RAN (3) 79 (2000)
15. Pottlacher G et al. *Thermochim. Acta* **218** 183 (1993)
16. Korobenko V N, Savvatimskiy A I, in *Temperature*: *Its Measurement and Control in Science and Industry* Vol. 7 (AIP Conf. Proc., Vol. 684, Ed. D C Ripple) (Melville, NY: AIP, 2003) p. 783
17. Korobenko V N "Eksperimental'noe issledovanie svoĭstv zhidkikh metallov i ugleroda pri vysokikh temperaturakh" ("Experimental investigation of liquid metals and carbon properties at high temperatures"), Author's Abstract of Thesis for Candidate of Physico-Mathematical Sciences (Moscow: Joint Institute for High Temperatures of the Russian Academy of Sciences, 2001)

18. Joseph M, Sivakumar N, Manoravi P *Carbon* **40** 2031 (2002)
19. Sheindlin M A *Teplofiz. Vys. Temp.* **19** 630 (1981)
20. Senchenko V N, Sheindlin M A *Teplofiz. Vys. Temp.* **25** 492 (1987)
21. Mesyats G A, Proskurovskii D I *Impul'snyĭ Elektricheskiĭ Razryad v Vakuume* (Pulsed Electrical Discharge in Vacuum) (Novosibirsk: Nauka, 1984) [Translated into English (New York: Springer, 1989)]
22. Koval' B A et al. *Pis'ma Zh. Tekh. Fiz.* **5** 603 (1979)
23. Bundy F P *J. Chem. Phys.* **38** 618 (1963)
24. Buchnev L M et al. *Dokl. Akad. Nauk SSSR* **278** 1109 (1984)
25. Lebedev S V, Savvatimskii A I *Teplofiz. Vys. Temp.* **24** 892 (1986)
26. Virgil'ev Yu S *Neorg. Mater.* **30** 353 (1994) [*Inorganic Mater.* **30** 336 (1994)]
27. Korobenko V N, Savvatimskii A I, Cheret R *Teplofiz. Vys. Temp.* **36** 725 (1998) [*High Temp.* **36** 701 (1998)]
28. Korobenko V N, Savvatimski A I, Cheret R *Int. J. Thermophys.* **20** 1247 (1999)
29. Kerley G I, Chhabildas L, Sandia Report Sand2001-2619 (2001) p. 50
30. Savvatimski A I, Fortov V E, Cheret R *High Temp.-High Press.* **30** 1 (1998)
31. Pirani M, in *Elektrothermie; die elektrische Erzeugung und technische Verwendung hoher Temperaturen* (Ed. M S Pirani) (Berlin: J. Springer, 1930) [Translated into Russian: 'Issledovatel'skie raboty po elektrotermii' ('Research in electrothermics'), in *Elektrometriya. Elektricheskie Metody Polucheniya Vysokikh Temperatur i Ikh Ispol'zovanie v Tekhnike* (Electrometrics. Electrical Methods of Attaining High Temperatures and Their Use in Engineering) (Ed. D L Orshanskiĭ) (Moscow: GONTI, 1938)
32. Ronchi C et al. *Int. J. Thermophys.* **13** 107 (1992)
33. Bundy F P et al. *Carbon* **34** 141 (1996)
34. Downer M C et al. *Int. J. Thermophys.* **14** 361 (1993)
35. Agranat M B et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **66** 661 (1997) [*JETP Lett.* **66** 699 (1997)]
36. Allen P B *Phys. Rev. Lett.* **59** 1460 (1987)
37. Brorson S D et al. *Phys. Rev. Lett.* **64** 2172 (1990)