INSTRUMENTS AND METHODS OF INVESTIGATION

# Experimental investigation of the thermal properties of carbon at high temperatures and moderate pressures

É I Asinovskiĭ, A V Kirillin, A V Kostanovskiĭ

DOI: 10.1070/PU2002v045n08ABEH001110

# Contents

1. 2.	Introduction Carbon phase diagram near the triple point	869 869
	2.1 Formulation of the problem; 2.2 Description of the experiment; 2.3 Discussing results	
3.	Carbon melting at 2.5 bar	873
	3.1 Formulation of the problem; 3.2 Description of the experiment; 3.3 Discussing results	
4.	Carbon allotropic forms	877
	4.1 Formulation of the problem;	
	4.2 Experiment No. 1; 4.3 Experiment No. 2	
5.	Conclusions	880
	References	881

<u>Abstract.</u> A consistent procedure for plotting the carbon melting and boiling coexistence curves based on published data and the authors' experimental results is proposed. The parameters of a triple point are predicted to differ markedly from the currently accepted values:  $p_t \approx 1$  bar and  $T_t \approx 4000$  K. Two types of experimental facilities were used, with laser heating of samples in one and direct ohmic heating in the other. The existence of a carbyne region (a stable linear polymer consisting of carbon atoms) in the carbon phase diagram is discussed. Results on the direct solid-phase graphite – carbyne transition are presented, and this is shown to occur under certain conditions in the form of a thermal explosion.

# 1. Introduction

The study of carbon has a history of at least three quarters of a century, but so far the differences of opinion about the data concerning the specific properties have not been resolved even in such a serious problem as the graphite-liquid-vapor triple point. This follows from the fact, known from the scientific literature, that separate groups in the scientific community have taken definitive attitudes towards the thermal properties of carbon. On this point these views are

É I Asinovskiĭ Joint Institute for High Temperatures, Russian Academy of Sciences, Institute for High Temperatures
ul. Izhorskaya 13/19, 127412 Moscow, Russian Federation
Tel. (7-095) 483 22 97
A V Kirillin, A V Kostanovskiĭ Joint Institute for High Temperatures, Russian Academy of Sciences,
Institute for High Energy Densities
ul. Izhorskaya 13/19, 127412 Moscow, Russian Federation
Tel. (7-095) 938 53 84, 362 51 23
E-mail: kirill@rfbr.ru, lai@iht.mpei.ac.ru

Received 19 September 2001, revised 26 December 2001 Uspekhi Fizicheskikh Nauk **172** (8) 931–944 (2002) Translated by E Yankovsky; edited by A Radzig very distinctive, and no tendency toward agreement is evident. Only experiments can form a basis for resolving the contradictions outlined.

The present authors, who have worked for a long time on this problem, believe it highly advisable to give a consistent account of their experiments in this field and to present the main ideas used in interpreting the results of these experiments. The experimental studies were carried out at installations that employed dissimilar methods of sample heating:

• by irradiating the sample with steady-state laser radiation;

• by sending an electric current directly through the sample, and

• by using the property of thermal conductivity of the sample.

Employing the various methods of sample heating provides additional possibilities for bringing out the peculiarities by which the thermal properties of carbon manifest themselves.

In the course of our research we collected a vast set of microphotographs taken by various electron diffraction apparatuses which belong to several scientific institutions. Some of these photographs will be presented in this article. On the whole, the exposition of the material follows the real history of studying this problem, so that the logic in choosing the various steps in our research becomes more obvious.

# 2. Carbon phase diagram near the triple point

# 2.1 Formulation of the problem

At present, the number of papers in which the results of original studies into carbon melting, the phase equilibrium coexistence curves, and the triple point parameters (pressure  $p_t$  and temperature  $T_t$ ) are presented is several dozen [1–21]. Nevertheless, the carbon  $T_t$  can only be specified with an error of about 1000 K, which differs dramatically from the situation with metals, where this error does not exceed several kelvins.

Notice that the dominant part of the studies has been carried out by highly qualified specialists from leading scientific centers and the experimental results are certainly authoritative. Hence, after carefully considering the situation we have come to the conclusion that, rather than criticize the methodical errors of the individual studies, it would be wiser to describe, basing our reasoning on the indisputable facts, the framework (of the portion) of the carbon (p, T) diagram and, as a result, to choose the directions of investigations that would make it possible to determine the parameters of a triple point with the proper accuracy.

Let us turn to Fig. 1 where we have depicted the portion in question of the carbon (p, T) diagram. The data have been gathered by researchers who have studied the carbon melting parameters [1-12], the triple point parameters (solid–liquid–vapor) [13–15], and the solid–vapor (sublimation) and liquid–vapor (boiling) coexistence curves [16-19]. The solid and dot-and-dash curves represent the calculated results of the total pressure of carbon atoms and molecules above the carbon's surface at proper temperatures [13, 20]. Here we will not do a comprehensive review of the literature data, since this has been done very professionally and completely in Refs [22, 23]. However, to make the understanding of the results depicted in Fig. 1 easier, we note that they were obtained by three different experimental methods.

In the first method [1-7], an electric current is passed through the graphite rod placed in a high-pressure chamber (HPC), with a characteristic heating time of about 1 s. The melting temperature  $T_m$  is determined at a pressure equal to that in the HPC. In the second method [14-19], the graphite sample is heated in the HPC by irradiating the sample with high-power laser radiation. Here the characteristic time in the experiments also amounts to about a second. The thermogram recorded in the experiment is used for finding the temperature corresponding to the liquid–vapor saturation curve (the boiling curve) or the sublimation curve at a known pressure.

In the third method of determining the parameters of the phase transitions in carbon [8, 9, 11, 12, 21], a thin wire



**Figure 1.** Carbon (p, T) diagram (review of literature data): 1 - [1, 3-6, 10]; 2 - [2]; 3 - [7]; 4 - [8]; 5 - [9]; 6 - Shaner [11]; 7 - Pottlacher [12]; 8 - triple point [13]; 9 - critical point [13] and solid line [12]; 10 - [14], and 11 - [15] and [16] (dashed line), [17-19] (vertical hatching), and [20] (dot-and-dash line). (Pressure is measured in bars.)

specimen is heated by sending a very short  $(10^{-3}-10^{-6} \text{ s})$ , high-density current pulse through the wire (electric explosion). The melting parameters of carbon are also usually found by the thermogram method from the characteristic plateaus corresponding to the phase transitions. While discussing the results, we would like to note that usually a dependence of the measured temperature  $T_{\rm m}$  on the characteristic sample heating time is quite evident. Some results of the above-cited works are compiled in Table 1, and the viewpoint of the present authors concerning this problem will be discussed in Section 4.

T-LL-	1
i anie	
I HOIC	

Heating time, s	$T_{\rm m}, {\rm K}$	<i>p</i> , bar	References
$4 \times 10^{-5}$	4800	_	[11]
$3.5  imes 10^{-5}$	5000		[12]
$5 \times 10^{-3}$	4530	100	[9]
$2  imes 10^{-3}$	4600		[21]
1	4035	100	[1, 2, 4-7]

Figure 1 shows that the low-pressure range (p < 100 bar) has been studied the least in experiments.<sup>1</sup> The reason is apparently the result of the idea adopted earlier [13] that the triple point of carbon corresponds to a pressure of 100 bar and  $T_{\rm t} \sim 5000$  K. To corroborate or refute this idea, one must have the experimental data on the  $p \sim f(T)$  dependence for the carbon melting and boiling within a broad range of variation of these parameters. Then, in accordance with the thermodynamic approach, the triple point can be found as the point of intersection of two coexistence curves: the melting curve and the boiling curve. It is important here that the coexistence curves must be obtained in the same conditions. However, the analysis of the known experimental data has shown that usually only one phase transition was studied, while the methods of investigation often differed. Hence, a possible 'ideal experiment' for refining the parameters of the triple point of carbon can be envisioned as follows. In one experiment, say involving steady-state laser heating, on the thermogram we identify a plateau corresponding to the boiling curve  $T_b$ , and a plateau corresponding to the melting point  $T_{\rm m}$ . If we carry out such an experiment at different pressures,  $T_{\rm b}$  and  $T_{\rm m}$  can be extrapolated in pressure up to the triple point, where the curves intersect. Conducting an 'ideal experiment' was our first goal.

#### 2.2 Description of the experiment

In this section we describe an experiment resembling that discussed in Refs [10, 14–19] and being close to 'ideal'. The carbon phase diagram in the neighborhood of the assumed triple point was studied over the 150-310-bar range using steady-state laser heating at a facility modified according to the requirements of the 'ideal experiment' (a detailed description of the facility can be found in Ref. [24]). The thermal source was a CO<sub>2</sub> laser with a peak output power of about 800 W and a 10.6-µm wavelength of emitted light. The experimental sample was placed in an HPC rated at a working pressure of 400 MPa, and the laser beam entered the HPC horizontally. The optical scheme of the facility ensured the irradiation of any part of the sample's surface by the laser

<sup>&</sup>lt;sup>1</sup> The results of the respective research done by Whittaker and Kintner [16] and Pirani [42] are discussed in detail later in this review.

radiation, where it was focused to a spot of 1.5-2 mm in diameter. A protective KCl glass was placed in front of the sample at a distance of 2-4 mm for reducing the effect of convection.

The sample temperature at the heating spot was measured by a high-speed micropyrometer [25] incorporated into the data acquisition system built around an HP 9845 minicomputer. The pyrometer operated in the color-temperature mode at wavelengths equal to 0.604 and 0.804 µm. This mode guarantees smaller errors in temperature measurements compared to the brightness-temperature mode in the cases when the spectral emissivity of the material under investigation remains almost constant [26]. More than that, the color-temperature mode is preferable when the temperature is nonuniformly distributed over the surface of the heated sample, and when the crater emission is absorbed by the vapor and by the optical elements of the facility [27]. The temperature scale of the pyrometer was calibrated according to the blackbody model [28] (for graphite material) up to 3700 K with subsequent extrapolation to the 3700-6000-K range.

The dense isotropic graphite used in the experiments was of the MPG-6 brand in the shape of a  $4 \times 4 \times 1$ -mm plate of 99.9 purity, and it was positioned perpendicularly to the laser beam.

Here is a brief description of the investigation procedure. First, the thermograms of the sample heating were recorded at a fixed pressure of the buffer gas (high-purity argon) and a fixed intensity of the incident laser radiation. Then, with the pressure constant but with an increased intensity of the laser radiation, the recording of the thermogram was repeated. The experiment was terminated after it became evident that a further increase in the radiation intensity had no effect on the measured maximum temperature. This was the way in which the boiling temperature of the material was determined at a given pressure. The melting point was found from the temperature value corresponding to the horizontal section of the thermogram in the sample heating or cooling mode. Since the duration of the experiment was no less than 1 s, the possibility of correctly recording the full thermogram (heating and cooling) in a single experiment turned out to be hardly realizable due to convective flows in the gas layer. Therefore, the recording of the cooling thermograms was done at the same gas pressure and with the same sample, but with the sample preheated by laser radiation of an intensity of about  $(0.8-1.0) \times 10^5$  W cm<sup>-2</sup>.

Typical thermograms for sample heating and cooling at 223-277 bar are shown in Fig. 2. For instance, Fig. 2a depicts the heating thermogram at p = 277 bar. Noteworthy is the horizontal plateau at level A and a section with the maximum attainable temperature at a given pressure (level B [19]). The cooling curve (Fig. 2b) relating to p = 223 bar also has a horizontal section (level C) which can by identified as the level of crystallization from the liquid phase.

Note that the level A in the heating curve (4000  $\pm$  100 K) and the level C in the cooling curve agree with each other. The very fact that the melting point remained practically constant as the pressure was increased from 223 to 277 bar is a consequence of the weak pressure dependence of  $T_{\rm m}$ . Such behavior of this dependence is typical of many other pure substances.

Thus, as a result of recording the heating and cooling thermograms for steady-state laser heating of graphite, both phase transitions (solid–liquid and liquid–vapor) were



Figure 2. Fragments of (a) the heating thermogram at p = 277 bar, and (b) the cooling thermogram at p = 223 bar for carbon samples.

shown (for the first time) to exist under the same experimental conditions.

## 2.3 Discussing results

We believe that it is natural to assume that the triple point of carbon occurs at the intersection of two groups of experimental data in Fig. 1: the first group comprises the data gathered in Refs [1–7, 10, 15], where the melting point of graphite is found to be close to 4000 K (45-degree hatching) at a pressure that varies by a factor of 10 (melting curve), and the second group comprises the data of experimental studies (vertical hatching) [16–19] in steady-state laser heating (boiling curve) that agree with calculated results produced in Refs [13, 20].

Figure 1 shows that the melting curve must be extrapolated to lower pressures, i.e. the parameters of a triple point occur in the horizontally hatched region. In this case the position of the triple point contradicts the statement (e.g., see Ref. [15]) that traces of melting at the edges were observed only at  $p \ge 100$  bar. The contradiction can be resolved if we assume that traces of graphite melting at the edges in laser heating (p < 100 bar) simply cannot be observed after the experiment: the melt fully evaporates. Obviously, the higher the pressure, the thicker the melt film at the heating spot, with the result that many researchers have observed traces of



**Figure 3.** (*p*, *T*) diagram of carbon (experimental data): 1 - [1]; 2 - [2]; 3 - [3]; 4 - [4, 5]; 5 - [6]; 6 - [7]; 7 - [10]; 8 - [15]; 9 - [16]; 10 - [17, 18], 11 - [19]; 12 - authors' data on melting, and 13 - authors' data on boiling.

melting at the edges at pressures p > 100 bar [1, 2, 10, 15, 19]. Possibly, if special measures hindering the evaporation of the melt film are taken (say, the configuration of the crater in the sample is made more complicated), traces of melt could also be observed at pressures below 100 bar.

We believe that the data depicted in Fig. 3 seriously support the above assumption. In this figure we have gathered the results of studies on carbon melting [1-7, 10, 15] and the boiling curve [16-19] together with our findings discussed in Section 2.2. Clearly, our experimental values are in good agreement with the results of other studies for the liquid – vapor phase transition as well as for the solid – liquid phase transition. This pertains equally both to the functional dependence of the coexistence curves and the scatter of experimental points.

Figure 3 implies that the results of different studies are grouped around unified dependences: a linear dependence for the melting curve, and an exponential (or second-degree polynomial) for the boiling curve. Extrapolation of these curves to their intersection determines the parameters of a triple point of carbon. We also see that the pressure at the solid – liquid – vapor triple point of carbon is noticeably lower than the earlier accepted value of  $p_t \sim 100$  bar.

Figure 4 depicts some experimental data for the boiling curve plotted in the  $(\lg p, 1/T)$  coordinates which are standard for such investigations [29]. Clearly, the curve approximating the experimental data differs from a straight line, which is to be expected if we take into account the range of pressure variations (five orders of magnitude) and the variability of the vapor composition over the surface of liquid carbon (C, C<sub>2</sub>, C<sub>3</sub>, ..., C<sub>n</sub>) [20, 29].

Figure 5 shows a section of the boiling curve, which is described by a quadratic dependence on the reciprocal of the temperature:

$$\lg p = 1.259 + 3.479 \left(\frac{10^4}{T}\right) - 1.596 \left(\frac{10^4}{T}\right)^2, \tag{1}$$

and a section relevant to the melting curve, which is expressed by a linear dependence of *p* on *T*:

$$p = \frac{T - 4044}{0.08678} \,. \tag{2}$$



**Figure 4.** Experimental data on the boiling curve: 1 - [16]; 2 - [17, 18]; 3 - [19], and 4 - authors' data. (Pressure is measured in bars.)



Figure 5. Averaging boiling (1) and melting (2) curves (corresponding to the equations given in the text).

The latter dependence is extrapolated to the lowerpressure region. The intersection of the above curves determines the parameters of a triple point:  $p_t = 1$  bar,  $T_t = 4000$  K. The parameters of a triple point found in this manner contain not only the results of many experimental studies but also correspond to the thermodynamic approach, according to which the solid-liquid and liquid-vapor phase transitions belong to the same type, namely, a first-order phase transition.

These parameters agree with the experimental findings of Whittaker and Kintner [16]. The very fact that the parameters obtained of a triple point differ (especially in a pressure value) from the results of other cited investigations (which assume that  $p_t = 100$  bar) is related, as noted earlier, with the absence of traces of the liquid phase on the cooled sample. Hence it is reasonable to assume that new experiments should be aimed at finding the traces of melting at the edges at  $p_t < 100$  bar.

In our opinion, the main outcomes of this part of our work are that in investigating the thermal properties of carbon we substantiated the need for a detailed study in the low-pressure region (p < 100 bar) and also proposed and realized the method of an 'ideal experiment' that strives for a thermodynamically justified solution to the problem of finding the parameters of the triple point. It was the joint processing of the measurement data providing the basis for the construction of boiling and melting curves obtained under the same conditions that corroborated the hypothesis of the need to study the lower-pressure region more thoroughly. However, the 'ideal experiment' has been conducted at pressures above 100 bar. Therefore, the next stage in our research reduced to the investigation of carbon melting at essentially lower pressures, which was conducive to the maximum approach to the region established for the triple point of carbon.

# 3. Carbon melting at 2.5 bar

## 3.1 Formulation of the problem

In Section 2 we proposed a version of the carbon phase diagram near the triple point (see Fig. 1) that differs substantially from the commonly accepted version. The main distinctions are that the triple point temperature is roughly 4000 K instead of 5000 K and that the triple point pressure is 1 bar instead of 100 bar. The crucial arguments in favor of the revision reduced, in particular, to the idea that one must allow for the data of only those experiments in which the characteristic heating time was no less than  $\sim 10^{-2}$  s. By the time of arranging the experiments described in the present section, the mechanism explaining the shift of the temperature relevant to the characteristic plateau in the thermogram as a function of the heating rate in experiments on electric explosions of thin wires (see Table 1) had not received a conclusive explanation. Hence we decided to conduct the experiments of a given set at fairly low heating rates

Thus, to verify the validity of our version of the carbon phase diagram we were forced to carry out the graphite melting experiment at low heating rates and moderate pressures. Strictly speaking, earlier such experiments were conducted twice and both times the results were wholly satisfactory. In 1925, Alterthum, Fehse, and Pirani [30] were first to find experimentally that a graphite rod 37 mm in diameter partially melted in the course of 1/2 hour of slow ohmic heating under a buffer gas pressure of 1.06 bar. According to their experiments, the melting point was  $3760 \pm 65$  K.

The second experiment was performed by Whittaker, Kintner, Nelson, and Richardson in 1977 [31]. A graphite cylinder 3.2 to 6.4 mm in diameter was rotated at a rate of about 40,000 revolutions per minute and at the same time was locally heated by a focused laser beam. The pressure in the system was varied from  $2.6 \times 10^{-5}$  to 11 bar. As a result of heating, a narrow band of liquid carbon formed on the target surface. The fact of melting was corroborated by photographs of liquid drops (that had broken away from the surface of the sample) in their collisions with cooled targets. From these photographs one can readily perceive a similarity with the well-known experiment that studied the deformation and destruction of solder droplets when they fell to the floor [32].

Thus, from the results presented in Refs [30, 31] it follows that the carbon phase diagram proposed in Section 2 is meaningful. In both works the two above-specified conditions, i.e. the relatively low rate of heating and the low pressure of the buffer gas, were maintained when an electric current was sent through the sample and when the sample was heated by laser radiation. The goal of the present stage in our research is to experimentally verify the proposed version of the carbon phase diagram, i.e. the presence of a liquid phase at low pressures.

## 3.2 Description of the experiment

The experimental setup resembled that used earlier by Alterthum, Fehse, and Pirani [30]. We employed a facility (Fig. 6) that had a chamber with a rated pressure up to 200 bar. The maximum power consumption reached 20 kW. To measure temperatures, we employed a micropyrometer MP-6000 developed at the Institute for High Temperatures of the Russian Academy of Sciences [25] and calibrated by reference to the high-temperature blackbody model [33] and a standard pyrometer (electrooptical converter) ÉOP-66. The maximum working temperature amounted to 3700 K.

Two types of active sections in the phase diagram were used. The first was actually an analog of a safety fuse (Fig. 7a). This provided a simple way to observe the sample melting,



**Figure 6.** Schematic of the setup with ohmic heating: 1 — chamber; 2 — sample; 3 — window; 4 — standard optical pyrometer ÉOP-66; 5 — micropyrometer MP-6000; 6-8 — digital voltmeter V7-38; 9 — current meter UTT-6M; 10 — current transformer OSU-80, and 11 — temperature controller VRT-2.



**Figure 7.** Experimental samples: (a) in the shape of a safety fuse, and (b) in the form of a high-temperature blackbody model.

Table 3.

since as a result of the experiment the fuse is 'blown' and the electric circuit is broken. However, certain difficulties with determining the characteristic temperature emerged. The difference in temperatures on the axis of the cylinder, where apparently the melting begins, and at the sample surface may be substantial [23]. So in addition we used an active section in the model form given by a blackbody radiator (Fig. 7b). It was assumed that the central partition of the radiator, which has the maximum temperature, is the place where the melting emerges. At the same time, this partition was used to determine the temperature. Thus it was expected that the temperature measured would be as close to the melting point as possible. More than that, the blackbody model makes it possible to determine the true temperature, which means an increase in the accuracy of finding the melting point in comparison with the accuracy of measuring it in the coloror brightness-temperature mode.

The samples were fabricated from MPG-7 graphite, with an impurity content not exceeding  $10^{-3}$ % (see Technical Specification TU48-01-70-71).

Five experiments were conducted during the progress of the research. Out of these, experiments Nos 1, 2, and 5 used samples in the form of the blackbody model, while experiments Nos 3 and 4 used samples in the shape of safety fuses. In all experiments the chamber was pre-evacuated to  $10^{-1}$  Pa, after which it was filled with high-purity argon up to a pressure of 2.5 bar. Each of the experiments was carried out as follows. The temperature was measured with the input power slowly increasing, and the characteristic time between the two modes varied from 0.25 to 5 min.

**Experiment No. 1.** The sample was fabricated in the model form given by a blackbody radiator (Fig. 7b), with the degree of perfection of this model close to 0.99. The temperature was measured at an emission wavelength equal to  $0.65 \mu m$ . The diameter of the pyrometer sighting spot was 0.6 mm. And, finally, the sample was heated several times.

Table 2 lists the values of the true temperature measured at the bottom of the model black radiator. Note that the power was limited in such a way that the maximum temperature was sure to be below the melting point. A test of the power unit of the setup showed that the power reserve was sufficiently high to attain the parameters needed to melt the sample. This experiment also demonstrated that the measuring system was capable of recording the temperature within necessary limits.

#### Table 2.

Time, min	40	45	50	55	60	65	70
Temperature, K	2685	2737	2814	2936	2993	3093	3200

**Experiment No. 2.** Here, a new sample in the blackbody model form was heated. The goal of the experiment was to determine the highest temperature that the sample can endure. Notice that the blackbody model was designed in such a way [33] that the central partition (where the temperature is measured) is heated due to thermal conductivity rather than by electric current passing directly through the partition. Hence, the destruction of the partition occurs not in its central part but at the place where the partition is tight against the central part of the radiator. This aspect was taken into account in measuring the temperature, which was done according to the scheme

Time, min	Temperature, K
30	2193
35	2265
40	2330
45	2415
50	2512
55	2571
60	2620
65	2691
70	2739
75	2811
80	2897
85	2963
88	3052
91	3144
94	3191
97	3271
100	3343
103	3480
105	Destruction of the sample

adopted in experiment No. 1. The thermogram data are compiled in Table 3. In the course of this experiment a result was obtained that proved important for further analysis: the temperature of sample destruction differs from the expected melting point by an amount close to the temperature measurement error.

**Experiment No. 5.** Here again we used a sample in the blackbody model form. However, in contrast to experiments Nos 1 and 2, we increased the thickness of the cylindrical wall of the radiator by 20%. The temperature was measured at wavelengths of emitted light amounting to 1.2 and 0.88  $\mu$ m, with the diameter of the pyrometer sighting spot being 0.3 mm. The data from the respective thermogram are listed in Table 4.

Table	4.
-------	----

Time, min	$T_{\text{Wien}} (\lambda = 1.2 \ \mu \text{m})$	$T_{\rm Wien} \ (\lambda = 0.88 \ \mu { m m})$
20	1825	1803
25	1905	1895
30	1986	1991
35	2068	2082
40	2119	2131
50	2211	2229
55	2287	2298
60	2358	2371
65	2434	2448
70	2525	2539
75	2601	2612
80	2658	2663
85	2706	2706
90	2781	2789
95	2873	2867
100	3001	2981
105	3062	3037
110	3125	3105
115	3243	3202
120	3314	3266
123	3407	3359
125	3446	3373
126	3446	3401
126.5	3632	3548
126.75	3744	3626
Destruction of the same	ple	



Figure 8. Melt at the partition surface of the blackbody model.

Inspection of the sample after the experiment showed that there had been local melting, since traces of melting at the edges were found at the place where the partition failed (Fig. 8). The destruction temperature and, respectively, melting point proved to be in the 3630-3740-K range. According to our estimates, the error in measuring the temperatures amounted to  $\pm 150$  K.

**Experiment No. 3.** The sample had the shape of a safety fuse (Fig. 7a). The goal of the experiment was to find the optimal conditions for exposure of traces of graphite melting at the edges. First the sample was buried in graphite powder to improve thermal insulation. This meant that temperature measurements had to be abandoned. During experimentation it was established without doubt that the sample destruction is accompanied by the appearance of melt on the cylinder axis (Fig. 9). After that the same sample was heated but without a graphite covering. The color temperature was measured at two emission wavelengths: 0.80 and  $1.0 \mu$ m. The diameter of the pyrometer sighting spot amounted to  $0.65 \mu$ m.



**Figure 10.** Thermogram of the heating of a sample in the shape of a safety fuse, when the sample is not covered by graphite powder.

temperature was measured at the central part of the safety fuse on the outer cylindrical surface. Figure 10 shows the thermogram from which it follows that the highest color temperature at which the sample fails is about 3500 K. Notice that due to the absence of high-temperature data on the ratio between spectral emissivities, the true temperature of the sample could not be calculated.

**Experiment No. 4.** The sample was in the shape of a safety fuse. Here the goal was to measure the temperature in the melt zone and, in particular, the temperature of the draining liquid film (Fig. 11). The experiment was carried out twice, with the results listed in Table 5. Unfortunately, we were unable to offer a clear explanation for such low values of the measured color temperature of the liquid film, viz.  $\sim 3040-3090$  K. There is only one plausible explanation: the graphite melting occurred above the point at which the measurements were taken, so that the pyrometer measured not the temperature of the liquid (which proved to be quite transparent) but the lower temperature of the wall under the draining film.

#### 3.3 Discussing results

The results of a comparative analysis for the main body of research are as follows: two experiments, Nos 1 and 5 (the partition heating via thermal conductivity), and experiment



**Figure 9.** Carbon melt at the surface after heating a sample in the shape of a safety fuse buried in graphite powder.



Figure 11. Draining film of carbon melt on the lateral surface of the safety fuse.

Table 5.

Time, min	<i>T</i> <sub>c</sub> , K
6	1511
8	1531
11	1552
12	1552
14	1608
15	1608
16	1680
18	1705
19	1731
21	1976
22	1992
22.5	2887
23.5	3085
Experiment was terminated	
15	2421
15 16	2421 2370
15 16 17	2421 2370 2502
15 16 17 18	2421 2370 2502 2530
15 16 17 18 19	2421 2370 2502 2530 2502
15 16 17 18 19 20	2421 2370 2502 2530 2502 2588
15 16 17 18 19 20 21	2421 2370 2502 2530 2502 2588 2649
15 16 17 18 19 20 21 22	2421 2370 2502 2530 2502 2588 2649 2681
15 16 17 18 19 20 21 22 23	2421 2370 2502 2530 2502 2588 2649 2681 2746
15 16 17 18 19 20 21 22 23 24	2421 2370 2502 2530 2502 2588 2649 2681 2746 2780
15 16 17 18 19 20 21 22 23 24 25	2421 2370 2502 2530 2502 2588 2649 2681 2746 2780 3043
15 16 17 18 19 20 21 22 23 24 25 26	2421 2370 2502 2530 2502 2588 2649 2681 2746 2780 3043 2925
15 16 17 18 19 20 21 22 23 24 25 26 27	2421 2370 2502 2530 2502 2588 2649 2681 2746 2780 3043 2925 2780
15 16 17 18 19 20 21 22 23 24 25 26 27 27.75	2421 2370 2502 2530 2502 2588 2649 2681 2746 2780 3043 2925 2780 2887

No. 3 with samples in the shape of safety fuses (heating by passing the current through the specimen) revealed that under a pressure of 2.5 bar the temperatures at which the samples of different shapes, heated by principally different methods, fail are approximately the same. The fact that for a safety fuse the destruction temperature proved to be somewhat lower than for a sample in the form of a blackbody model is in order since the measurements of the temperature for the safety fuse are done at the surface of the cylinder, while the melting begins on its axis, where the temperature is sure to be higher. The spread in the different experimental data is within the estimated error of the temperature measurements.

It is principally important that the samples failed as a result of local melting. This is corroborated, first, by the fact that the two temperatures coincide ( $T_d \approx T_m$ ) and, second, by the results of subsequent analyses.

Below we briefly discuss the results of the local X-ray spectroscopic and structural analyses made at Laboratory No. 773 of the TIV Scientific Center of the Joint Institute for High Temperatures, RAS. The four samples that were ohmically heated to the melting stage (experiments Nos 3 and 4) were subjected to X-ray diffraction (XRD) studies. Here are some of the common features discovered in the course of such studies.

Firstly, XRD analysis made it possible to estimate the purity of the samples. No impurity elements in quantities exceeding the concentrational sensitivity (0.05%) of the analysis were discovered in the relatively cold (in the course of heating) zones far from the melt zone. Studies of the material of the crater that formed in the melt zone of one of the samples revealed the same situation.

Impurity elements were discovered directly in the melt zones of the four samples studied. These were mainly potassium and chlorine (in approximately equal quantities) and a small amount of aluminium. For instance, for the sample depicted in Fig. 11, according to the record of the XRD measurements: "... only K and Cl were observed in the sample, and those were localized in separate inclusions on the surface with a transformed structure. Sometimes such inclusions with typical linear dimensions of  $5-8 \ \mu m$  form chains, but in other cases their distribution is of a discrete nature. The average mass content of potassium in the surface layer with a transformed structure is  $\sim 0.87\%$ , and that of chlorine is  $\sim 0.8\%$ ". Apparently, potassium and chlorine impurities got onto the surface of the sample together with the graphite powder enclosing the sample. In further studies the samples were covered with graphite powder after the graphite had been treated with distilled water and dried. Then, after treating the graphite powder, it was analyzed for the purpose of discovering the above-mentioned impurities. The measurements were taken in the flame of a propane-air burner, and the emission and absorption spectra of the flame were taken with graphite particles injected into it. It was found that the average value of the specific mass concentration of potassium does not exceed  $10^{-4}$ . As for the effect of impurities in the melt layer on the melting point, the estimates based on Raoult's law revealed that their presence, with the mass content discovered in the experiment, should affect the value of the sought melting temperature no more than by 20-30 K [34].

Obviously, the impurities discovered through XRD analysis can also randomly land onto the sample's surface in the course of preparing the sample, of adjusting the entire chamber and during the experiment itself (in experiment No. 4, the sample was not covered with graphite powder). What is important, however, is that the partial melting of samples was observed in the entire range of impurity concentrations discussed here, but at practically the same temperature  $T \sim 3700$  K.

Secondly (and this is principally important), XRD analysis verified the fact of graphite melting. Here is a quotation from the XRD report: "Analysis showed that far from the heating zone the graphite has the following lattice parameters:  $a = 2.463 \pm 0.001$  Å, and  $c = 6.772 \pm 0.001$  Å; in the heating zone at the top of the convex part of the sample graphite lattice parameters are as follows: the  $a = 2.461 \pm 0.001$  Å, and  $c = 6.746 \pm 0.001$  Å. Thus, while the parameter *a* is practically the same in the heating zone and the cold part, the parameter c is smaller in the heating zone." In other words, according to estimates, the parameter  $(p_3)$  of the three-dimensional lattice ordering is  $p_3 = 0.53$  in the heating zone, and  $p_3 = 0.39$  in the cold part of the sample. The changes in the graphite lattice are sure to be related to melting and subsequent recrystallization of the zone under investigation.

We note that some of the experimental material used in the present work have been previously published in Refs [35, 36].

Thus, the results of XRD analysis confirm the presence of melting of the material under investigation. Hence, the goal — to melt graphite at 2.5 bar — has been successfully reached. All the experiments run with the samples in the form of a blackbody model and in the shape of a safety fuse have shown that the destruction temperature  $T_d = 3500 \text{ K}$  (color)-3700 K (true) proves to be slightly below 4000 K, i.e. the temperature defined in Section 2 as the carbon triple

point temperature. This is logical, since in such experiments the destruction temperature may serve only as the lower bound for the melting point. It is principally important here that the traces of partial melting were observed at such a low pressure. This is an additional proof of the ideas discussed in Section 2 in favor of the carbon phase diagram proposed.

# 4. Carbon allotropic forms

## 4.1 Formulation of the problem

In the previous sections we consciously used the more general concept of 'carbon', both in discussing the phase diagram and in studying the experimental findings. The fact that carbon can exist in different modifications and that these states differ considerably in structure is well known [37]. With this in mind we intentionally used the term 'framework' to describe their version of the carbon (p, T) diagram, understanding that the real diagram may be much more complex. More than that, when describing the boiling curve we intentionally departed from the linear dependence  $[\lg p \sim a + b(1/T)]$  commonly accepted for many pure substances and replaced it with a more complex one, viz. a second-degree polynomial. In this way the data processing of the two phase transitions, solid liquid and liquid-vapor, has made it possible to determine the parameters of a carbon triple point, while remaining within the thermodynamic approach. More than that, the selected dependence for the boiling curve assumes that this fairly smooth function can, if necessary, be replaced by a piecewise-linear dependence that would correspond more fully to the exact shape of the carbon phase diagram.

Of all the allotropic forms of carbon we were interested only in those that exist within the range of parameters discussed in this article: relatively low pressures and high temperatures. Hence, our primary goal was to experimentally expose such allotropic forms and to understand to what extent these forms acquire significance for influencing the shape of the carbon phase diagram.

There is an opinion that carbyne (a stable linear polymer consisting of carbon atoms) constitutes an independent form of carbon (in addition to diamond and graphite) [37]. But while the modern configuration of the carbon phase diagram, which incorporates diamond and graphite, is undeniable (except for some minor details), the possibility of positioning carbyne in this diagram is still being debated [38].

The first, and to our knowledge the only, attempt to build the carbon phase diagram with allowance made for carbyne (see Fig. 12) was made by Whittaker [39]. Its salient feature is the assumed parameters of the (carbyne) triple point: T = 3800 K, and  $p = 2 \times 10^4$  Pa. The fact that carbyne has still not been detected in experiments was explained by Whittaker [40] on the assumption of the relatively low rate of the graphite–carbyne solid-phase transition, i.e. for rapid heating with a characteristic time of  $10^{-3}$  s the abovementioned transition may not have enough time to occur, which results in the melting of graphite proper (the graphite triple point).

Let us again turn to the research done by Whittaker et al. [31, 32]. The essence of their experiment has been discussed in Section 3. A graphite cylinder rotated with a rate of roughly 40,000 revolutions per minute was heated by a focused laser beam under pressures close to atmospheric pressure. A band of liquid carbon formed as a result of the sample heating. This fact was corroborated by photographs of liquid drops that



Diamond

Figure 12. Whittaker's version of the carbon state diagram.

had broken away from the sample's surface. The photographs clearly show spheroidlike formations, which Whittaker and Kintner [32] named 'spherulas', with characteristic asperities. According to the authors of Ref. [32], these asperities are formed in the process of cooling of the liquid drop. Since the fluid density is lower than that of the solid phase inside the drop, the pressure begins to grow as the shell hardens. This results in the formation of local bulges of the shell, which can be clearly seen in the photograph. Carbynes and diamondlike structures were detected in the spherulas. In our opinion, Whittaker and Kintner were very careful when mentioning the presence of diamondlike structures.

Note that spherulas containing diamondlike structures were also detected in experiments on shock compression of preheated graphite [41].

A weak point of work [32] is the absence of data on the melting point. This determines the methodical advantage of the essentially earlier research (1925) done by Alterthum, Fehse, and Pirani [30]. In their experiment carbon was melted at a low pressure due to ohmic heating of a graphite cylinder. A system of axial and radial openings made it possible to record the onset of melting by registering the appearance of liquid in the radial opening. Notice that a similar method was used by Pirani [42] to determine the tungsten melting point, and the result was quite reasonable. Unfortunately, Pirani [42] gave no data on the phase composition of the remelted carbon. Probably, this composition was not studied or the cooling rate was such that complete graphitization occurred in the sample.

We found it interesting not only to reproduce Pirani's experiment but also to compare our data on phase composition with those presented by Whittaker and Kintner [32], primarily the data on carbyne and diamondlike structures [43].

## 4.2 Experiment No. 1

**Description of the experiment.** We introduced two changes into the scheme of the experiment first conducted by Alterthum, Fehse, and Pirani [30]. The first change amounted to replacing hydrogen as the buffer gas by argon. We did this because the interaction between carbon and

p, Pa

hydrogen at high temperatures could affect the 'purity' of interpreting the experimental results. The second change amounted to not making a radial opening and to extending the axial opening to the massive lower part of the sample. In this way we constructed a trap for liquid carbon (an accumulating reservoir). Unfortunately, in this case there is a difference in the temperatures of the liquid carbon in the reservoir and of the micropyrometer sighting spot on the surface of the sample (estimates fix this difference at 200–300 K). Therefore, we used the results of Ref. [36] (see Section 3), where the carbon melting point at p = 2.5 bar was set at  $T_{\rm m} \approx 3700$  K.

**Discussion.** Figure 13 is a photograph of the surface of a solidified carbon mass and a fragment of the cylindrical wall of the reservoir, while Fig. 14 presents a photograph of the material microstructure in the ring zone. An analysis of the



Figure 13. Solidified graphite mass in the accumulating reservoir and a fragment of the cylindrical wall of the latter.



**Figure 14.** Microstructure of the material on the surface of the ring zone *A* (see Fig. 13).

microstructure has shown that here the material comprises rounded formations. The surface of these formations contains mainly the crystals in the shape of thin plates with a thickness of roughly 0.1  $\mu$ m and linear dimensions of 0.2– 0.6  $\mu$ m. The lamellar shape of the crystals is a typical feature of the hexagonal graphite.

The phase composition has also been analyzed for other zones of the heated section and for the cold part (far from the place where the surface was heated) of the sample [44].

We found that the material in the cold part of the sample consists of graphite and a small amount of X-ray amorphous substance. The graphite in its turn is represented by two modifications: the hexagonal and the rhombohedral, with the first being predominant. The hexagonal graphite involves two components with different degrees of graphitization. Both components have the same lattice parameter  $a = 2.461 \pm 0.001$  Å. The value of the period c for the component with the higher degree of three-dimensional lattice ordering ( $p_3 = 0.566$ ) amounts to  $c = 6.740 \pm 0.001$  Å, while the second component has  $c = 6.777 \pm 0.001$  Å ( $p_3 = 0.366$ ). The graphite in the sample is textured: a major portion of the grains possess crystallographic planes (001) which are oriented perpendicularly to the sample's axis.

A small diffuse halo in the vicinity of Bragg angles  $2\theta = 9-17^{\circ}$  (CuK<sub> $\alpha$ </sub> radiation) with a maximum corresponding to the interplanar spacing d = 6.6 Å (see Fig. 15) suggests the presence of a small amount of X-ray amorphous substance.

In the sections of the heated sample's surface that are visually brighter than the other sections, the degree of texturing in the surface layer about 250-µm thick is much higher than in the initial (unheated) sample, which explains the enhanced luster of the material in these zones.

The graphite in the lustrous sections consists of three components with the different degrees of three-dimensional lattice ordering. The predominant component is the one with  $p_3 = 0.607$  (c = 6.734 Å), while the other less-abundant components have the following parameters of three-dimensional lattice ordering:  $p_3 = 0.253$  (c = 6.806 Å) and  $p_3 = 0.009$  (c = 6.851 Å). The value of the parameter *a* for all three components is identical to that recorded in the cold part of the sample. Thus, the lustrous sections contain graphite with a structure that can be more or less ordered than the hexagonal graphite in the cold part of the sample.



**Figure 15.** Fragments of the diffraction spectrum of the sample's material over the region far from the thermally treated section: I — hexagonal graphite; 2 — rhombohedral graphite, and 3 — amorphous graphite.

We observed that the black sections only contain hexagonal graphite with a crystal structure less ordered than that of graphite from the cold part. The graphite components have the following parameters of three-dimensional lattice ordering:  $p_3 = 0.495$  (c = 6.752 Å),  $p_3 = 0.324$  (c = 6.786 Å),  $p_3 = 0.107$  (c = 3.845 Å), and  $p_3 = 0.069$  (c = 6.857 Å). The *a* parameter of the crystal lattice has a value greater than the initial value  $a = 2.465 \pm 0.002$  Å.

All the thermally treated surface exhibits an increase in the amount of X-ray amorphous substance as compared to that in the cold part. The diffuse halo indicating the presence of an X-ray amorphous substance takes up position in the diffraction spectrum within the same angular interval as in the spectrum taken from the cold part of the sample. However, its peak intensity is approximately twice as high as that in the spectrum from the cold part.

The rhombohedral graphite content in the thermally treated region is similar to that registered in the cold part of the sample.

The diffraction spectra of silvery, lustrous, and dark-gray sections of the thermally treated surface contain, in addition to lines characteristic of the above-mentioned phases, peaks corresponding to the interplanar spacings d = 2.058, 1.262, 1.073, and 0.866 Å. This set of lines corresponds to a cubic structure with a lattice period  $a = 3.566 \pm 0.001$  Å (see Fig. 16).

An elemental analysis of the material making up the surface of the ring zone has shown that, within the sensitivity of the X-ray spectroscopic (XRS) analysis, the material under investigation is free of impurities of chemical elements with atomic number  $Z \ge 12$ . Note that the sensitivity of this method applied to surfaces whose relief is close to that of the region under investigation amounted to  $10^{-2}$  mass.%.

The data gathered from phase and elemental analyses suggests that the above-mentioned sections of the thermally treated surface contain cubic diamond rather than a random impurity. The diamond phase content in an approximately 0.35-µm thick layer is 2-2.5 mass.% (1.3-1.6 vol.%). Traces of cubic diamond are found down to layers at a depth of about 0.5 mm from the surface. The diamond crystals are located in a random manner, without a preferred orientation of the crystallographic planes in relation to the sample's axis. Since the diffraction lines belonging to this phase are not blurred, we conclude that the crystallite sizes are larger than 0.1 µm.

XRS analysis detected no carbynes in the accumulating reservoir. Neither were they detected by Raman scattering of light from the surface of samples, whose spectra were taken in conditions close to those described earlier.



Figure 16. Fragments of the diffraction spectrum of the material constituting the ring zone: I — hexagonal graphite; 2 — rhombohedral graphite; 3 — amorphous graphite, and 4 — cubic diamond.

## 4.3 Experiment No. 2

Description of the experiment. Our next step was to alter the thermal conditions of the experiment [45]. The sample in the blackbody model form was heated up to 2800-3500 K, i.e.to temperatures higher than the temperature of the graphitecarbyne phase transition ( $T_{ph.t} = 2600$  K). Then the surface of the sample was rapidly cooled with a rate comparable to the cooling rate ( $\sim 10^5$  K s<sup>-1</sup>) in the experiments of Whittaker et al. [31, 32]. The idea was that such a rapid cooling is needed to preserve, at least partially, the changes in the structure of the sample that emerged because of the graphite-carbyne phase transition. Detailed information about the given experiment can be found in Ref. [43]. The most important result was the discovery of carbynes in the cooling zone thanks to the characteristic band in the Raman spectrum (Fig. 17). Curiously, the spherulas were also found in this zone, and they were similar to those discussed earlier (see Fig. 18).

**Discussion.** Thus, in our opinion we were able to corroborate the results of Whittaker and Kintner [32] concerning the formation of carbynes from graphite at a temperature in the 3000–3500-K range and the possibility of



Figure 17. Raman spectrum of the graphite surface subjected to thermal treatment at  $T \approx 2800 - 3000$  K.



**Figure 18.** Microstructure of the graphite surface after thermal treatment at  $T \approx 2800 - 3000$  K. It is assumed that the large spheroidlike formations (spherulas) contain the carbyne phase.

preserving them (at least partially) under rapid cooling. An important point is that all the experiments were conducted at pressures close to atmospheric pressure.

Now let us go back to the diagram proposed by Whittaker [39]. It is our opinion that to confirm its validity directly one must prove the existence of a graphite-carbyne solid-phase transition. To this end we turn to the current data on the thermodynamic properties of carbyne. We first note the research done by Kudryavtsev et al. [37] and Lebedev et al. [46]. The results of their research suggest (and this is important for our further analysis) that the difference in the graphite-carbyne enthalpies is

$$\Delta_f H^0 = -37.03 \text{ kJ mol}^{-1}, \qquad (3)$$

i.e. a sizable amount of heat is liberated in the graphitecarbyne solid-phase transition. All this means that under certain conditions this transition proceeds as a thermal explosion.

The theory of thermal explosion can be found in monograph [47], and it amounts to solving the problem of the stability of a temperature field in the presence of heat sources with a volume strength of the form

$$Q = Q_0 \exp\left|\alpha(T - T_0)\right|,\tag{4}$$

where  $\alpha = E/T_0^2$ , with *E* being the activation energy.

We assume, following Whittaker's data [40], that the characteristic time of the graphite–carbyne phase transition at  $T_0 = 3500$  K is about 25 s. Then, setting the graphite density at  $\rho \approx 2$  g cm<sup>-3</sup> [48], we find that

$$Q_0 = 0.25 \times 10^3 \text{ J cm}^{-3} \text{ s}^{-1}.$$
 (5)

Using the data from Ref. [40], we can estimate the activation energy E. It proves to be

$$E = 112.6 \times 10^3 \text{ K}.$$
 (6)

According to Landau and Lifshitz [47], the minimum size of the site of a thermal explosion is given by the formula

$$l^2 = \lambda_{\rm cr} \, \frac{\chi}{Q_0 \alpha} \,, \tag{7}$$

where  $\chi$  is the thermal conductivity, and  $\lambda_{cr} = 2$  (for a cylinder). This yields l = 0.5 cm.

It is quite possible that the linear polymers (carbynes) [37] created by the thermal explosion form the above-mentioned spherulas, which with all necessary reservations are similar to globules [49]. This is apparently followed by formation, after melting, of liquid clusters and drops. The possible ways in which spherulas may form have been discussed by Kleiman et al. [41]. What is important is that by selecting the proper cooling rate for the spherulas one can ensure the preservation of carbynes in them and the creation of diamondlike structures.

Thus, the goal of our experiment was to corroborate the existence of a thermal explosion and the phase transitions caused by this explosion. We used the blackbody model for our experiment (see Ref. [36]). In agreement with the abovecited estimates, we set the initial temperature equal to 3500 K. Notice that at 3000 K the value of  $Q_0$  decreases by three to four orders of magnitude, i.e. there can be no thermal explosion in such conditions.





The results of the experiment in the form of a time dependence for the temperature of the transverse wall of the radiator are depicted in Fig. 19.<sup>2</sup> We believe that they corroborate the version of a thermal explosion and thus support the hypothesis that there is a graphite–carbyne solid-phase transition.

The experimental data given in this section confirm the possibility of the existence of carbon allotropic forms in the range of parameters under investigation and undoubtedly are of much interest. However, the body of data is not large enough to affect the phase diagram in the way discussed in Section 2. Nevertheless, we do not exclude the possibility that further studies will lead to the necessity of refining and specifying the region of the carbon phase diagram we are discussing here.

In some cases transparent crystalline formations were observed in a solidified graphitized mass (see Fig. 20). Possibly, these were the carbyne crystals. We are presently trying to identify these formations.

We would like to complete Section 4 by a short list of our concrete results, as we did in the preprint [44]:

• the results of Whittaker and Kintner [32] have been corroborated by an entirely new experimental method;

• it has been shown that it is possible to build an accumulating reservoir for liquid carbon, and

• 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.

## 5. Conclusions

There were many reasons why we believed that the problem of refining the carbon phase diagram for the region of fairly low pressures is interesting. Firstly, little attention has been paid traditionally to this region. Secondly, preliminary analysis of the experimental and theoretical studies in this field showed that the triple-point pressure may be much lower than is commonly assumed. It is our opinion that not only numerous experiments but also those differed dramatically in the methods used have made it possible to broaden our ideas about the thermal properties of carbon. In many respects the scientific literature of the last two years has corroborated the main conclusions and experimental findings that formed the basis of our research.

<sup>&</sup>lt;sup>2</sup> Notice here that we give only one thermogram. At present we are analyzing several thermograms that represent the heating of carbon samples under the same conditions. The results will be published as a separate article in *Teplofizika Vysokikh Temperatur* [English translation: *High Temperatures*].



Figure 20. Safety fuse after heating.

We would like to thank many colleagues who actively participated in our research: V E Fortov for the support he gave to our research as a whole and for the useful discussion concerning our results, S É Asinovskii for experimentally verifying the carbyne model, T I Borodin for the XRD analysis, V Yu Davydov and N N Mel'nik for the Raman spectroscopic analysis, and G E Val'yano for the photographic work.

# References

- 1. Basset M J J. Phys. Radium 10 5 (1939)
- Noda T, in *High-Temperature Technology* (Ed. I E Campbell) (New York: Wiley, 1956) [Translated into Russian (Moscow: IL, 1962) p. 471]
- 3. Bundy P P J. Chem. Phys. 38 618 (1963)
- Vereshchagin L F, Fateeva N S Zh. Eksp. Teor. Fiz. 55 1145 (1968) [Sov. Phys. JETP 28 597 (1969)]
- Fateeva N S, Vereshchagin L F Pis'ma Zh. Eksp. Teor. Fiz. 13 157 (1971) [JETP Lett. 13 110 (1971)]
- 6. Schoessow G J Phys. Rev. Lett. 21 738 (1968)
- Diakonis N S et al. "Graphite Melting Behavior", U.S. Report. General Electric Co. AD 727064. AFMLTR 119 (1971)
- 8. Baitin A V et al. High Temp.-High Press. 21 157 (1990)
- 9. Cezairliyan A, Miller A P Int. J. Thermophys. 11 643 (1990)
- 10. Ronchi C et al. Int. J. Thermophys. 13 107 (1992)
- 11. Shaner J W et al. J. Phys. (Paris) 45 (11) 235 (1984)
- 12. Pottlacher G et al. *Thermochim. Acta* **218** 183 (1993)
- 13. Leider H R, Krikorian O H, Yong D A Carbon 11 555 (1973)
- 14. Haaland D M, in 12th Biennial Conf. on Carbon: Pittsburgh, PA, 1975, Abstracts, p. 54
- 15. Gokcen N A et al. High Temp. Sci. 8 (2) 81 (1976)
- 16. Whittaker A G, Kintner P L, in *12th Biennial Conf. on Carbon: Pittsburgh, PA, 1975*, Abstracts, p. 37

- 17. Kirillin A V et al. Dokl. Akad. Nauk SSSR 257 1356 (1981)
- Evseev V N, Kirillin A V, Sheĭndlin M A Promyshl. Teplotekh. 4 87 (1982)
- 19. Kirillin A V et al. *Teplofiz. Vys. Temp.* **23** 699 (1985)
- JANAF Thermochemical Tables (United States National Bureau of Standards. National Standard Reference Data Series, NSRDS – NBS 37, Project Directors D R Stull, H Prophet) 2nd ed. (Washington, DC: NBS, 1971)
- 21. Togaya M, Sugiyama S, Mizuhara E AIP Conf. Proc. 309 255 (1994)
- 22. Sheĭndlin M A Teplofiz. Vys. Temp. 19 630 (1981)
- 23. Scheindlin M A Sov. Tech. Rev. Sec. B. Therm. Phys. 1 139 (1987)
- Kirillin A V, Kostanovskiĭ A V, Vinogradov V L Teplofiz. Vys. Temp. 22 1200 (1984)
- 25. Sheĭndlin M A et al. Teplofiz. Vys. Temp. 19 839 (1981)
- Izluchatel'nye Svoĭstva Tverdykh Materialov (Radiative properties of Solid Materials) (Ed. A E Sheĭndlin) (Moscow: Énergiya, 1974)
- Kirichenko I I Metrologicheskie Osnovy Opticheskoĭ Pirometrii (Metrological Bases of Optical Pyrometry) (Moscow: Izd. Standartov, 1976)
- Kostanovskii A V, Nefedkina L B, Miroshnichenko V I "Model" absolyutno chernogo tsveta" ("Perfectly black color model"), Russian Patent No. 1124682 recorded in the State Register on October 22, 1992
- Kirillin V A, Sychev V V, Sheĭndlin A E *Tekhnicheskaya Termodi-namika* (Engineering Thermodynamics) 3rd ed. (Moscow: Nauka, 1979) p. 479 [Translated into English (Moscow: Mir Publ., 1981)]
- 30. Alterthum I I, Fehse W, Pirani M Z. Elektrochem. 31 313 (1925)
- Whittaker A G et al. Rev. Sci Instrum. 48 632 (1977) [Prib. Nauch. Issl. (6) 52 (1977)]
- 32. Whittaker A G, Kintner P L Carbon 23 255 (1985)
- Kostanovskii A V, Nefedkina L B, Kostanovskaya M E *Teplofiz*. Vys. Temp. 35 122 (1997) [High Temp. 35 119 (1997)]
- Kostanovskii A V, Zhilyakov L A Inzh. Fiz. Zh. 73 198 (2000) [J. Eng. Phys. Thermophys. 73 198 (2000)]

- Asinovskii É I, Kirillin A V, Kostanovskii A V Teplofiz. Vys. Temp. 35 716 (1997) [High Temp. 35 704 (1997)]
- Asinovskii É I et al. Teplofiz. Vys. Temp. 36 740 (1998) [High Temp. 36 716 (1998)]
- 37. Kudryavtsev Yu P et al. Izv. Akad. Nauk SSSR Ser. Khim. (3) 450 (1993)
- 38. Bundy F P et al. Carbon 34 141 (1996)
- 39. Whittaker A G Science 200 763 (1978)
- 40. Whittaker A G Nature 276 695 (1978)
- 41. Kleiman J et al. J. Appl. Phys. 56 1440 (1984)
- 42. Pirani M S, in Elektrothermie; die elektrische Erzeugung und technische Verwerdung hoher Temperaturen (Ed. M S Pirani) (Berlin: J. Springer, 1930) [Translated into Russian "Issledovatel'skie raboty po élektrotermii" ('Research in electrothermics'), in Élektrometriya. Élektricheskie 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 Orshanskii) (Moscow: GONTI, 1938)
- Asinovskii E I et al., in ADC/FCT Joint Conf. 1999: 5th Intern. Conf. on the Application of Diamond Films and Related Materials. 1st Intern. Conf. on Frontier Carbon Technology, Tsukuba, Japan, 1999, pp. 558-562
- 44. Asinovskii É I et al., Preprint No. 1-449 (Moscow: Joint Institute for High Temperatures, Russian Academy of Sciences, 2000)
- Asinovskii S É Poluchenie Karbinov Omicheskim Nagrevom Grafita (Carbyne Production Through Ohmic Heating) (Moscow: Moscow Physicotechnical Institute Press, 1999)
- Lebedev B V, Tsvetkova Z Ya, Zhogova K B Thermochim. Acta 299 127 (1997)
- Landau L D, Lifshitz E M *Gidrodinamika* (Fluid Mechanics) (Moscow: Fizmatlit, 1986) [Translated into English (Oxford: Pergamon Press, 1987)]
- Fizicheskie velichiny. Spravochnik (Handbook of Physical Quantities) (Eds I S Grigor'ev, E Z Meĭlikhov) (Moscow: Énergoatomizdat, 1991) [Translated into English (Boca Raton: CRC Press, 1996)]
- Vol'kenshteĭn M V *Biofizika* (Biophysics) (Moscow: Fizmatlit, 1981) [Translated into English (Moscow: Mir Publ., 1983)]