### **REVIEWS OF TOPICAL PROBLEMS**

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## Investigation of the physical properties of carbon under high temperatures (experimental studies)

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### Contents

1. Introduction	1015
2. Graphite under high temperatures	1016
3. Producing carbon in the liquid state (key experiments on pulsed current heating of graphite)	1018
3.1 Carbon solid-liquid-vapor triple point; 3.2 Graphite melting at high pressures (≈ 100 kbar); 3.3 Pioneering	
studies on measuring graphite expansion and electrical resistivity under pulsed current heating	
4. Thermal expansion of graphite and liquid carbon	1021
4.1 Measuring graphite expansion under pulsed current heating; 4.2 Assessment of graphite expansion during	
melting; 4.3 Interferometric measurement of graphite and liquid carbon expansion; 4.4 Use of the interferometric	
method to determine the melting line of graphite	
5. Retention of the metallic character of liquid carbon after graphite melting	1024
6. Pulsed current heating of graphite in plates and sapphire capillaries. The first experiments	
on determining graphite and liquid carbon specific heat	1026
7. Direct measurement of specific heat at a constant liquid carbon volume	1028
8. Measuring temperature and specific heat in pulse heating processes	1029
8.1 Measurement of temperature; 8.2 Measurement of specific heat	
9. Enhanced pre-melting specific heat of rapidly heated graphite	1031
10. Electronic processes on graphite electrodes	1032
10.1 Possibility of detecting drop-like carbon particles during graphite heating under low external pressure;	
10.2 Explosive electron emission of graphite cathodes	
11. Conclusion	1034
References	1035

<u>Abstract.</u> Key experimental studies (mainly pulse heating) aimed at obtaining the physical properties of the most refractory substance — graphite — in the temperature range of 2000– 8000 K are discussed. The properties considered are enthalpy, input (Joule) energy, thermal expansion, specific heat, and electrical resistance, as well as their dependence on the level of applied pressure. The results obtained by pulsed current heating and laser pulse heating are compared. An abnormally high specific heat just before the melting point is recorded under fast (during microseconds) heating of graphite. These effects are presumably associated with the appearance of nonequilibrium defects. A connection between these anomalies and the explosive electron emission is noted.

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### 1. Introduction

It has been shown in recent decades that graphite (carbon) is the most refractory substance, having the melting temperature  $T_{\rm m} = 4800 \pm 100$  K (see reviews [1–4]) at low (~ 1 kbar) pressures.  $T_{\rm m}$  grows with increasing pressure. This finding is supported by experimental determination of the carbon solid–liquid–vapor triple point at pressures  $P \approx 107$  bar [5] and  $P \approx 120$  bar [6].

Next in order of refractivity are carbides, i.e., ceramic materials in which carbon is combined with a metallic element. For example, a highly refractory  $Ta_{0.8}Hf_{0.2}C$  composite has a melting point of 4300 K [7]. Carbides are followed by refractory metals, such as W (3693 K), Ta (3269 K), and Mo (2893 K) [8]. However, graphite undergoes intensive sublimation at growing temperature and is not very strong. For this reason, refractory metals are preferable for industrial applications taking advantage of their excellent plasticity at high temperatures and good casting properties. A combination of metal characteristics (strength, hardness, high heat conductivity, and low thermal expansion coefficient) with graphite properties (enhanced refractoriness) in

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carbides makes these compounds very promising materials for use at high temperatures, despite their relative fragility.

Layered graphite compounds finding technical application consist of graphite sheets and guest materials (metal and/ or carbide) intercalated between them to reduce brittleness and produce resistant coatings that are long-living at extremely high temperatures. For example, a nuclear fuel containing a fissionable material in the form of microspheres coated with such protective compounds (ZrC, C) ensures enhanced temperature resistance. In rocket engineering, rocket engine nozzles are coated with ceramic-based (ZrC, ZrC+C, HfC, TaC) and carbon protective layers. Carbon is characterized by high sublimation heat ( $\approx 60$  kJ g<sup>-1</sup>), and high energy needed to reach the liquid state ( $\approx 21$  kJ g<sup>-1</sup>), which makes it the main component of insulating ablative layers (graphite evaporation is accompanied by the removal of large amounts of heat).

Promising methods for the investigation of refractory substances, such as carbon, carbides, nitrides, borides, and oxides, include pulsed heating techniques (laser and current pulse heating). These methods do not require the use of hightemperature furnaces, since the high temperature is generated by Joule heating of a conducting material or laser heating of the surface layer. An advantage of the latter method is that it is the sole technique suitable for the study of nonconducting substances, e.g., oxides, whereas pulsed current heating is practically inapplicable for the purpose. Measurement of high temperature is only part of a study where both methods yield similar results. As far as bulk properties (enthalpy, thermal capacity, electrical resistance) are concerned, only pulsed current heating allows these parameters to be measured at high temperatures [9].

During the last three decades, the problem of carbon temperature measurement and investigation of its properties under melting and in the liquid phase was solved using both pulsed current heating [10–14] and laser pulse heating [15, 16] due to a better understanding of the role of sublimation in temperature measurement. However, new (still poorly explored) physical effects arose in association with short heating times.

S V Lebedev and S E Khaikin reported abnormally high electron emission from metals under the effect of pulsed current heating as early as 1954 [17]. This phenomenon observed just before melting—was supposed to be due to Frenkel pair defects (a vacancy plus an interstitial atom) [18]. The possibility of such defects in metals was substantiated by Ya I Frenkel' [19]. The cause behind their active manifestation in the fast heating process prior to melting remains unclear. Probably, one of the conditions for melting is saturation with defects, providing structural 'freedom' for the lattice. In the case of usual slow heating, the material is preferentially saturated with vacancies (having a lower formation energy than interstitial atoms) that diffuse to the bulk from the surface (from the grain surface, including the sample surface, to be precise).

In the case of fast heating, the equilibrium diffusion process has no time to saturate the bulk of the metal with vacancies. It inevitably gives rise to a competing vacancy formation process directly in the bulk, accompanied by additional energy consumption to generate pair defects. The energy needed to form Frenkel pair defects (a vacancy plus an interstitial atom) is higher than the energy of formation of two vacancies. For example, the energy of vacancy formation in copper is 1 eV and that of interstitial atom formation is 3 eV.

Equally fast heating was found to be associated with the enhanced specific heat of the substance [20, 21] in the same state domain, i.e., before melting. An important fact was the proof of independence of metal [22, 23], carbides [24], and carbon [3, 4] melting temperature of the microsecond heating rate. All studied substances showed enhanced specific heat capacity near the melting point. In other words, the measured exceedance of input energy by the onset of melting upon pulse heating is spent to enhance specific heat rather than raise temperature, i.e., to increase the lattice energy. The lattice becomes nonequilibrium for a short time. Abnormally high specific heat is observed simultaneously with anomalous electron emission [18]; hence, a natural inference that the two effects have the same underlying cause, namely the formation of nonequilibrium defects (probably Frenkel pair defects) in the bulk of a rapidly heated metal.

The present review reports results of experimental studies that confirm the hypothesis of formation of chiefly nonequilibrium defects before melting of pulse-heated graphite. As a result, their formation leads to an insignificant increase in the inserted specific energy by the onset of melting (less than 6-9% of the total input). However, it affects appreciably specific heat near the melting point, which increases several-fold within a narrow temperature region just before melting.

In other words, investigation of the graphite melting region encompasses such critical issues as refractory substance melting proper, as well as ionic lattice-electronic subsystem interaction, leading to unexpected and far-reaching implications for fast heating processes.

### 2. Graphite under high temperatures

Fast current heating of graphites of low initial density  $\gamma$  (from 1.6 to 1.9 g cm<sup>-3</sup>) at a pressure of  $\ge 2$  kbar leads to their compaction, even in the solid phase [25]. Moreover, a pulsed electrical current creates pinch pressure in a sample that provokes compression work [26]. Compaction of porous systems may cause cracking in the solid phase and a local arc-discharge, i.e., the development of further inhomogeneous heating.

It was shown in 1998 [27] based on results of numerous experiments with low-density graphites (including those described in [26]) that current heating of grade UPV-1T graphite samples with a high initial density and near-zero porosity may contribute to the investigation of liquid carbon, more specifically to the measurement of thermal expansion of graphite. Implementation of such a research program with the use of solid-state light guides in [11] provided data on melting temperature (4800  $\pm$  200 K), enthalpy at the onset of melting (10.5 kJ  $g^{-1}$ ), melting heat (10 kJ  $g^{-1}$ ), and the specific heat of liquid carbon at constant pressure  $C_P$  (4.2 J g<sup>-1</sup>K<sup>-1</sup>) up to a temperature of 12,000 K (on the assumption of invariable emissivity). In addition, electrical resistivity of liquid carbon was measured: 730  $\mu\Omega$  cm (±7%) for a density of 1.8 g cm<sup>-3</sup> and pressure up to ten kbar. The thermal expansion of graphite during melting was estimated at 70% [11, 28] (pressure  $P \le 1$  kbar), 45% [29], and 50% [30].

All recent studies have usually been carried out using either highly ordered pyrolytic graphite (HOPG) and highly annealed pyrolytic graphite (HAPG) with density  $\gamma =$ 2.25 g cm<sup>-3</sup> or Japanese-made grade MF-307 isotropic graphite with initial density  $\gamma = 2.0$  g cm<sup>-3</sup>. Inhomogeneous heating of low-density ( $\approx 1.83$  g cm<sup>-3</sup>) graphite is exemplified by interesting important experiments described in [31]. The authors failed to assess graphite expansion by the start of melting because of the instability of the specimen volume during registration of its diameter (the sample underwent disintegration in the melting region). A merit of this work is the reliable measurement of graphite melting temperature ( $4900\pm200$  K) at an external pressure of 3 kbar and obtaining (for the first time) a temperature curve exhibiting the whole melting plateau (from beginning to end).

A breakthrough event in carbon research was the demonstration (in 1988) of the temperature dependence of solid-state carbon enthalpy [32] up to  $\approx 10$  kJ g<sup>-1</sup> at 4500 K (Fig. 1a). The experiment included pulsed current heating of high-density (over 2 g cm<sup>-3</sup>) pyrolytic graphite for 2 ms. This study related results of continuous and pulsed measurements and revealed excellent agreement among the data obtained.

It follows from Fig. 1a that enthalpy at 4500 K equals 9.1 kJ  $g^{-1}$  (pulsed current heating). To recall, steady-state measurements up to 3800 K and estimates for higher temperatures [35] give an enthalpy of 9.2 kJ  $g^{-1}$  at 4500 K. Moreover, both studies ([32] and [35]) demonstrated accelerated growth of specific heat with temperature for the solid



Figure 1. (a) Temperature dependence of pyrolytic graphite enthalpy *H*. Solid line — measurements in [32] (1988). Black dots — results of steady-state measurements [33] (1984). Hollow dots — steady-state measurements by the mixing method [34] (1972). (b) Experimental measurement of graphite triple point pressure [6] (1976). Squares indicate graphite solid phase, circles are carbon liquid phase. The triple point temperature ( $\approx$  4100 K) was not the subject of research in [6], the authors being dubious about its true value. JANAF — Joint Army Navy Air Force. Tables of thermodynamic properties of various materials are issued under the auspices of JANAF.

phase of graphite, i.e., a nonlinear H(T) dependence (Fig. 1a).

Measurements in [32] give  $C_P = 2.8 \text{ J g}^{-1} \text{ K}^{-1}$  for 4200 K,  $C_{\rm P} = 3.08 \text{ J g}^{-1} \text{ K}^{-1}$  for T = 4500 K. The rise in enthalpy with temperature in Fig. 1a reflects an increase in specific heat  $C_{\rm P}$  with growing T. The maximum melting temperature of graphite, 4700 K, was achieved at a heating rate up to  $2 \times 10^7$  K s<sup>-1</sup> [32]. According to the authors of [32], this value, obtained in five experiments, corresponds to the lower level of the graphite melting temperature. The data presented in Fig. 1a were published as national standard reference data [36] and those for temperatures 4100, 4200, 4300, 4400, 4500 K as information data. The pulsed current heating time in [32] was 0.5–2 ms at a pressure of 100 MPa in the gaseous atmosphere of Ar or He. The enthalpy measurement error did not exceed 2.5% at 4500 K. The temperature measurement error was  $\sim 2\%$  and the error of specific heat measurement  $C_{\rm P} \sim 5\%$  at 4500 K. This temperature at a corresponding enthalpy of 9.1 kJ g<sup>-1</sup> was used by certain researchers as the calibration point for input energy measurements to create a temperature scale.

Table 1 illustrates graphite properties (enthalpy and specific heat) up to the melting point (4900 K). Stationary experiments were carried out at temperatures up to 3800 K; the data for higher temperatures were calculated taking into account all contributions to enthalpy and specific heat (formation of equilibrium vacancies, anharmonicity, etc.).

Thus, both steady-state measurements of the H(T) dependence for graphite up to 4500 K [35] and pulsed millisecond heating up to 4500 K [32] yielded practically

Table 1. Properties of UPV-1T graphite (HOPG analog) revealed instationary experiments [35]. For comparison, NSRDS data [36] arepresented in parentheses for pyrolytic graphite in a temperature rangefrom 3800 to 4400 K. (NSRDS—National Standard Reference DataSystem.)

Т, К	H(T) - H(0), kJ mol <sup>-1</sup>	$C_{ m P},$ J mol <sup>-1</sup> K <sup>-1</sup>
200.15	1 0000	0.404
298.15	1.0098	8.606
300	1.026	8.67
400	2.062	11.95
500	3.398	14.70
600	4.982	16.87
700	6.758	18.56
800	8.680	19.86
900	10.72	20.88
1000	12.85	21.68
1200	17.32	22.85
1400	21.97	23.65
1600	26.76	24.25
1800	31.65	24.70
2000	36.63	25.07
2200	41.68	25.38
2400	46.78	25.68
2600	51.95	25.99
2800	57.19	26.37
3000	62.51	26.86
3200	67.94	27.54
3400	73.54	28.47
3600	79.35	29.73
3800	85.46 (84.06)	31.38 (30.83)
4000	91.93 (90.16)	33.48 (33.36)
4200	98.88 (97.5)	36.07 (37.0)
4400	106.41 (105.4)	39.18 (42.1)
4600	114.60	42.84
4800	123.58	47.04
4900	128.40	49.35



**Figure 2.** Linear thermal expansion of pyrolytic graphite along two axes [37] in comparison with reference values [38] (solid lines): upper line (1) and symbols (3)—normal to the base plane; lower line (2) and symbols (4)—parallel to the base plane. The dashed line denotes averaging of experimental data.

identical results. Experiments conducted by other authors after the H(T) (Fig. 1a) dependence was published confirmed the results of [32, 35]. In other words, no melting-related peculiarities in the graphite behavior were documented up to a temperature of 4500 K.

Relatively slow millisecond heating of graphite enabled the author of [37] to obtain expansion coefficients of pyrolytic graphite with an initial density of 2.18 g cm<sup>-3</sup> in the solid state practically up to the melting temperature (Fig. 2). The experiments were carried out under a static argon pressure of 1000 bar. The samples were heated to the melting temperature for ~ 1.5 ms; the start of the melting plateau was registered on thermograms. The mean melting temperature of pyrolytic graphite in six experiments was  $4800 \pm 100$  K. Graphite linear expansion was estimated from photographs of the luminance of a heated sample taken by a CCD camera. An insulating K-8 glass was used to avoid distortion of sample dimensions caused by active graphite sublimation at high temperatures.

The data presented in Fig. 2 were used to calculate the density of pyrolytic graphite in the solid state at temperatures up to the melting point [37]. The relative density of pyrolytic graphite by the onset of melting was  $\gamma/\gamma_0 = 0.83$  (where  $\gamma_0 = 2.18 \text{ g cm}^{-3}$  is the initial density).

### **3.** Producing carbon in the liquid state (key experiments on pulsed current heating of graphite)

#### 3.1 Carbon solid-liquid-vapor triple point

The problem of measuring the graphite melting temperature could not be solved until it was shown that graphite actively sublimates in the solid state at high temperatures (especially higher 3000 K). The cooled soot-like sublimate in front of a measuring device is the main obstacle to the accurate measurement of graphite temperature. The development of pulsed heating methods ensured reliable measurement of temperature under conditions of intense graphite sublimation. It was further promoted by determining the carbon triple point (solid–liquid–vapor) parameters using indirect methods and in direct experiments [6]; the pressure at the

carbon triple point was shown to be at least 120 bar) (Fig. 1b).

The majority of recent experiments do not confirm graphite melting under atmospheric pressure (see, for instance, Ref. [2] overviewing the relevant literature published in the last 40 years).

In 1976, D M Haaland of Sandia National Lab., USA, undertook experiments [5, 39] on laser pulse heating of graphite for fractions of a second and observed a pressure of  $107 \pm 2$  bar at the triple point. The author concluded that "results presented in this report remove all doubts about the possibility for graphite to melt at pressures below 100 bar under the equilibrium conditions" [39]. Haaland paid great attention to temperature measurements. He found out that sublimation of a specimen close to the melting temperature has a marked adverse effect on temperature measurements (a fact frequently neglected by later researchers, including authors of on-going studies). Haaland emphasized the wide dispersion of measured temperature values in the graphite melting region (from 4000 to 5500 K) and their dependence on the presence of small dense vapor jets before the optics of a pyrometer under high pressure (147 bar). The author ascribed this observation to rapid cooling of the jets and their condensation into soot that blocks emission from the sample.

Steady-state measurements of graphite thermophysical properties were performed in 1987 [35]. An X-ray structural analysis of the samples was carried out as temperature increased. The authors arrived at an important conclusion: "Heating of both quasi-monocrystalline graphite and glassy carbon up to 3818 K did not change main characteristics of the crystal lattice in these materials." In other words, the samples did not melt. A temperature of  $\approx$  3800 K appears to be the highest possible in graphite studies by stationary methods. Further development of pulse methods markedly extended the temperature range for graphite investigation.

### 3.2 Graphite melting at high pressures ( $\approx$ 100 kbar)

F Bundy, a recognized authority in carbon high-pressure research [40], measured the electrical resistance of graphite specimens together with enthalpy and stationary pressure (up to 100 kbar) under current heating during milliseconds [40–43]. He studied pyrolytic graphite with density  $\gamma = 2.2$  g cm<sup>-3</sup>, as well as less dense graphites. Bundy assessed the state of the samples after current heating experiments from the results of thin-section analyses. One of the main conclusions from his studies is the reduced post-melting electrical resistance of graphite under high pressure. It was confirmed in the majority of subsequent experiments.

It is worthwhile to mention another, less known, inference of Bundy to the effect that graphite melting at high pressure in all probability occurs from the diamond phase in response to a further input of energy (Fig. 3). To recall, diamond forms before the liquid phase of carbon. This fact tends to be overlooked in the literature, although it can open up a new area of experimental studies, e.g., diamond synthesis in graphite pulse heating processes. For this purpose, the heating current must be sharply reduced at high pressure and input energy of 8-9 kJ g<sup>-1</sup> with exposure at a proper temperature.

Figure 3 shows results of two experiments with low and high input energies (dashed line with triangles and solid line, respectively). The diamond phase is formed in the former case and liquid carbon in the latter case. The diamond reaction



**Figure 3.** Electrical resistance *R* versus input energy for boron-doped graphite. Pressure: 140 kbar. Total heating time: 6 ms. Numerical designation: *1*—the total input energy, 8.5 J (up to the vertical dashed line), 2—a dense diamond disk formed during this period in a low input energy experiment, 3—the onset of the diamond reaction, 4—the central part of the previously formed diamond disk melts during this period while a new diamond grows in the direction of piston butt-ends, 5—the total input energy of 22.8 J. (From Ref. [40].)

begins (see Fig. 3) when the input energy is around 6 J. For a 1.02-mm-long sample 0.76 mm in diameter with a density of 1.6 g cm<sup>-3</sup> (as for spectroscopic graphite), it corresponds to a specific energy of 8.1 kJ g<sup>-1</sup> and marks the beginning of diamond phase formation. The solid curve maximum at 7.5 J appears to correspond to the onset of melting (of diamond or graphite) and the specific energy of 10.14 kJ g<sup>-1</sup> (in work with microsecond electrical heating, graphite melting begins at 10.5 kJ g<sup>-1</sup>). In [40], melting ended at  $\approx$  20 J, i.e., before the growth of resistance terminates according to Fig. 3. It will be shown below that the melting of dense anisotropic graphite subjected to microsecond heating ends at a specific energy of  $\approx 20.5-21$  kJ g<sup>-1</sup>.

The resistivity calculation in accordance with the data in Fig. 3—taking into account the initial parameters of the sample (diameter 0.76 mm, length 1.02 mm, electrical resistance  $R = 0.0233 \Omega$ )—gives  $\rho = 1035 \mu\Omega$  cm for the liquid phase of carbon (at energy E = 20 J; see the righthand part of region 4; this value is obtained for boron-doped graphite!). A close value of  $\approx 1000 \mu\Omega$  cm for liquid carbon (up to a temperature of 6000 K) was reported by J W Shaner [44] for microsecond pulsed heating of graphite having an initial density of 1.83 g cm<sup>-3</sup> at a gas pressure in the chamber equaling 4 kbar.

In Ref. [26], liquid carbon resistivity was estimated at 700  $\mu\Omega$  cm for graphite of a high starting density (referring to the initial size of the sample) using analog oscilloscopes. In a later study [45], the value of 600–640  $\mu\Omega$  cm was obtained by digital oscilloscopy for the case of high (but unmeasured) pressure in sapphire capillaries. This result coincides with M Togaya's measurements ( $\approx 630 \ \mu\Omega$  cm [46] at a pressure of  $\approx 14 \ \text{kbar}$ ).

It follows from Fig. 3 that the diamond reaction began at the same input energy (i.e., temperature). It is worthwhile to mention Bundy's remark: "there is practically no doubt that liquid carbon originates from the melting of diamond rather than graphite." Indeed, Fig. 3 shows that diamond forms before the liquid phase. It gave Bundy reason to conclude that "the formation of liquid carbon requires much more energy than diamond formation."



**Figure 4.** Bundy's carbon phase diagram [47] (1989) showing fast heating pathways. The dashed line indicates calculated *P*, *T*-trajectories of graphite specimen heating that undergoes expansion of a different degree upon energy input. ' $0\Delta V$ ' stands for heating at a constant volume. When temperature increases after energy input so that 0.5 of the possible thermal expansion is realized, such *P*, *T*-trajectory is designated ' $0.5\Delta V'$ . A—the region of catalytic synthesis of diamond from graphite, B—the region of fast spontaneous transition of graphite into diamond, C—the region of martensitic transition of hexagonal graphite into hexagonal diamond, E—the putative nonmetallic state postulated by Bundy (unconfirmed in experiment). The straight solid line denotes experimental data [48] obtained under a constant pressure of 2.5 kbar. This line falls into the graphite melting line just in the metallic liquid carbon region somewhat above the E region.

Bundy deserves special credit for the construction of several carbon phase diagrams. The best known of them is presented in Fig. 4.

Bundy himself used in his experiments in 1963 [40, 41] pulsed current heating for 5 ms. He used Gustafson's data from 1986 [49] on graphite expansion depending on pressure and temperature. Bundy defined in 1989 [47] the 'thermal pressure' generated in a sample for different bulk expansions  $\Delta V$ . For example, Fig. 4 shows that thermal expansion under the effect of heating at 300–4500 K can be stopped by compaction at 240 kbar needed for the case of  $\Delta V = 0$ , i.e., for heating at a constant volume, meaning the possibility of constructing the dependence P-T corresponding to  $\Delta V = 0$ ,  $\Delta V = 0.5$ , etc.

Realization of 0.9 of the possible thermal expansion gives the pathway to the P-T dependence indicated by the  $0.9\Delta V$ curve. The microsecond experiments by Shaner [48] presented in the diagram at 2.5 kbar intersect the graphite melting curve near the postulated boundary between nonmetallic and metallic liquid carbons (see Fig. 4).

The heat transfer pathway for graphite in the case of its fast homogeneous current heating in microsecond experiments can be shown in a carbon phase diagram. The trajectory of microsecond graphite heating [11, 45, 50] (melting at a pressure of  $\approx 10-15$  kbar) passes near the  $0.7\Delta V$  line shown in Fig. 4. As far as liquid carbon electrical resistance is concerned, Bundy emphasized that it was measured more accurately in the studies by M Togaya [46, 51–54] than in his own.



**Figure 5.** (a) Electrical resistivity  $\rho$  (referring to the starting size) of a pyrolytic graphite specimen having a high initial density of  $\approx 2.2 \text{ g cm}^{-1}$  [54].  $\rho$  scale is indicated at the top right of the figure. (b) Electrical resistivity of liquid carbon at the melting line depending on static pressure for pyrolytic graphite (initial density  $\approx 2.2 \text{ g cm}^{-1}$ ) [54]. The dashed line denotes data obtained in the absence of heating (at room temperature).

Bundy's pioneering studies were extended by Togaya [46, 51–54], who also investigated electrical resistivity  $\rho$  of graphite with a different density, depending on the input energy at different pressures. This author more clearly identified the dependences of resistivity  $\rho$  (referring to the initial dimensions) on enthalpy and steady-state pressure. Togaya's method records the start of melting from the highest resistivity  $\rho$  values of both high-density ( $\gamma = 2.2 \text{ g cm}^{-3}$ ) pyrolytic graphite and low-density spectroscopic graphite.

In 2002, Togaya published in [54] useful information on pyrolytic graphite resistivity at high pressures (from 14 to 94 kbar) (see Fig. 5a). Although these data were presented without regard for thermal expansion, they allowed important conclusions to be reached about the physical properties of liquid carbon.

The data presented in Fig. 5 were obtained in experiments on millisecond pulsed current heating under stationary pressure. The arrows  $(J_e)$  indicate the moment melting is completed at different pressures (from 25 to 94 kbar). Resistivity reference points on each curve are displaced. The energy needed for the formation of the liquid phase  $(J_e)$  decreases with growing pressure, which reduces melting heat at a high pressure (on the assumption that the energy at the onset of melting is unrelated to the pressure). The major physical effect reported by Togaya was determination of the moment at which the pressure dependence of electrical resistivity  $\rho$  for liquid carbon changed;  $\rho$  decreased at pressures below  $\approx 50$  kbar and increased at higher pressures (Fig. 5b) [54]. It should be remembered that Togaya could not measure expansion; in other words,  $\rho$  in his work is resistivity without regard for expansion. Figure 5b is published also in Ref. [46].

Togaya's experimental results can be summarized as follows.

1. Electrical resistivity of liquid carbon at the melting point decreases from 630 to 470  $\mu\Omega$  cm with increasing pressure (from 14 to 40 kbar); thereafter, it grows from 490 to 560  $\mu\Omega$  cm as pressure further increases from 56 to 94 kbar.

2. Carbon resistivity is higher than that of highly resistant metals, such as Ba and Eu. Therefore, liquid carbon can be regarded as a "poorly conducting metal" (Togaya).

3. Electrical resistivity of liquid carbon tends to change from the metal-like behavior  $d\rho/dT > 0$  to that of semiconductors  $d\rho/dT < 0$  under pressures in the 40–56 kbar range (Fig. 5b). It is a very important conclusion, because the temperature dependence of resistivity is related to the structural factor of a fluid [55].

4. The available data on liquid carbon resistivity and its dependence on pressure and temperature suggest a structural liquid-liquid transition in liquid carbon. It appears that the structural transition of this type in liquid carbon at a pressure of  $\approx 50$  kbar occurs with a change of the sign of the d $\rho/dP$  derivative from negative to positive (Fig. 5b).

M Togaya argued after his early experiments that liquid carbon can hardly be viewed as a conductor. However, the low electrical resistivity of this material (630  $\mu\Omega$  cm) reported by him in 2010 [46] made him maintain that it is a "poorly conducting metal."

## **3.3** Pioneering studies on measuring graphite expansion and electrical resistivity under pulsed current heating

Participants in early academic seminars used to discuss the possibility of graphite expansion (up to a two-fold volume increase) after melting at low pressures in the absence of published experimental evidence of this phenomenon. In 1986, an experiment on the heating of a pyrolytic graphite rod in a thick-walled glass capillary tube with the inner diameter somewhat larger than that of the rod was conducted [26]. The starting pressure was equivalent to atmospheric pressure and grew only by virtue of graphite sublimation in the closed volume, possible evaporation of the glass surface, and enlargement of the sample volume. The pressure significantly increased as soon as the expanding rod came into contact with the tube wall, which was registered from a change in electrical resistivity (Fig. 6, right-hand arrow).

The left-hand arrow indicates on curve 3 (Fig. 6) the start of the accelerated growth of resistivity, associated, in the opinion of the authors, with accelerated expansion of graphite. The right arrow shows the moment at which the resistivity growth rate drops abruptly, depending on the specific input energy. At this moment, the inner cavity of the tube is completely filled with expanding graphite, the relative volume  $V_c/V_0 = 1.68$ , and the specific input energy



**Figure 6.** Resistivity of pyrolytic graphite (referring to initial sample dimensions) under fast heating in boiled water (*I*), colophony (*2*), and a capillary tube (*3*). *E*—the input (Joule) energy. For curve 3: graphite specimen of  $0.22 \times 0.26$  mm in cross section (cross section spread along the length  $\pm 4\%$ ) in a glass capillary (inner diameter d = 0.349 mm, outer diameter D = 5.2 mm, length l = 13.7 mm,  $V_c/V_0 = 1.68$ , where  $V_c$  is the internal volume of the tube,  $V_0$  is the initial volume of the graphite specimen [26].

approaches ~ 18.5 kJ g<sup>-1</sup> (it amounts to 20.5 kJ g<sup>-1</sup> by the completion of melting). Thus, according to [26], at low external pressure the total graphite expansion in the solid phase and during melting is roughly 70% of the initial volume.

At the moment when the internal volume of the tube is filled with graphite (at low external pressure), resistivity referring to original dimensions is  $\rho^0 = 890 \ \mu\Omega$  cm (Fig. 6, right-hand arrow).

Figure 6 shows the moment the tube is filled with graphite; its expansion before this moment is relatively free. Therefore, the pressure in the gap between the glass and graphite is negligibly small and depends only on the sublimate state in the gap. It is unlikely to significantly increase during shortterm (5 µs) heating. Graphite expansion is sharply limited after it fills the entire capillary volume. Note that in long-term (several microseconds) experiments and at a tube length to diameter ratio equaling 40, graphite outflow can be ignored, the more so that the tube is closed at both ends with massive electrodes. The initial volume of the capillary  $V_{\rm c}$  and graphite  $V_0 (V_c/V_0 = 1.68)$  being known, it is possible to determine graphite density in the state in which it fills the entire cavity of the tube (the right-hand arrow pointing to curve 3 in Fig. 6). The density is  $\sim 1.25 \text{ g cm}^{-3}$  when the input energy is 18.5 kJ g<sup>-1</sup> (initial graphite density is  $\approx 2.2$  g cm<sup>-3</sup>). Resistivity  $\rho$  can be calculated taking into consideration thermal expansion for the case of low external pressure. This value is  $\rho = \rho^0 V_c / V_0$ , where  $V_c / V_0 = 1.68$ . Thus, graphite resistivity with regard for expansion is  $\rho = 890 \times 1.68 \approx$ 1500 μΩ cm if the input energy E = 18.5 kJ g<sup>-1</sup> (see Fig. 6). It should be emphasized that this resistivity value taking account of the expansion (1500  $\mu\Omega$  cm) holds for low external pressure (roughly 200 bar).

# 4. Thermal expansion of graphite and liquid carbon

## 4.1 Measuring graphite expansion under pulsed current heating

The authors of [26] were the first to measure relative expansion of graphite with an initial density of 2.1-



**Figure 7.** Graphite melting temperature plotted against pressures up to 40 kbar. The first five points at low temperature were obtained in a gaseous atmosphere [57].

2.2 g cm<sup>-3</sup> undergoing current heating in a glass capillary tube for a few microseconds. It proved to be  $V_c/V_0 = 1.68$ before melting was completed (see Fig. 6). The moment the tube was filled with carbon was registered from a well apparent change in electrical resistance after energy input (the steep dependence sharply turned into a smoother one). The results presented in Fig. 6 refer to low external pressures (of the order of 200 bar).

In 2003, the authors of [28] calculated a change in the graphite volume upon melting based on experimental findings and the Clausius–Clapeyron equation

$$\frac{V_{\rm l}}{V_{\rm s}} = 1 + \frac{E_{\rm m}}{V_{\rm s}T_{\rm m}\left({\rm d}P/{\rm d}T\right)} \,,$$

where  $V_1$ ,  $V_s$  are the specific volumes of the liquid and solid phases, respectively,  $E_m$  is the melting heat,  $T_m$  is the melting temperature, dP/dT is the derivative at the melting point, and  $V_1/V_s$  was found to be  $\approx 1.7$ . Graphite proved to markedly expand (by  $\sim 70\%$  for the time of melting at low pressure).

To calculate  $V_1/V_s$ , the following quantities were used:  $V_s$ —the solid phase volume at the melting point (~ 1.2 $V_0$  the literature data),  $E_m = 10 \text{ kJ g}^{-1}$ —previous estimates [26] confirmed in later experiments,  $T_m = 4800 \pm 200 \text{ K}$ —measurements during current heating,  $4800 \pm 100 \text{ K}$ —measments during laser pulse heating with homogeneous energy heat liberation over the heating spot [56],  $dP/dT \approx 50 \text{ bar K}^{-1}$ according to measurements in [57] (Fig. 7).

Experiment [57] was conducted with graphite encased in rock salt except the starting points (the gaseous medium). However, the authors of [57] believe that it did not affect measurements of temperature, because it was determined from the ratio of intensities of two spectral lines.

It follows from Fig. 7 that the derivative  $dP/dT \approx 10$  and  $\approx 50$  bar K<sup>-1</sup> at pressures ranging from 0 to 15 and from 15 to 40 bar, respectively. At low pressures, much lower melting temperatures of graphite (on the order of 4600 K) were obtained in experiment [57] (see Fig. 7). In our experiments including pulse heating of graphite clamped between glass plates [27], the pressure was somewhat elevated as appears from measured melting temperature values amounting to 4800–5000 K.

### 4.2 Assessment of graphite expansion during melting

Certain publications report marked graphite expansion at a pressure of several kilobar. In 1998, the authors of [29] heated HOPG (2.24 g cm<sup>-3</sup>) and RW1 (1.55 g cm<sup>-3</sup>) graphites with a pulsed laser for 20–30 ms. They recorded a melting temperature of  $4800 \pm 150$  K that did not vary appreciably over a pressure range from 300 to 2500 bar. The volume of graphite after cooling of the sample was estimated to increase by 45%.

It can be expected that at low pressures (immediately after melting), the carbon melting temperature will be minimal and the liquid phase maximally expanded (see Fig. 7). At higher pressures (several kilobar), a higher melting temperature (4800–5000 K) is invariably recorded during both pulsed current heating [10, 45] and laser pulse heating [56]. In Ref. [11] (graphite heating in sapphire capillary tubes), the measured graphite melting temperature was 6200 K, while the pressure was roughly estimated at  $\sim 50$  kbar.

## 4.3 Interferometric measurement of graphite and liquid carbon expansion

Technical aspects of interferometric measurement are discussed in Refs [58, 59]. Laser interferometry for measuring graphite expansion under conditions of its fast electric pulse heating has been intensely developed lately [60].

To measure the expansion of a graphite specimen placed between two sapphire plates, interference between two beams of light was used, with one of them reflecting from the graphite surface and the other from the outer side of the sapphire plate. The displacement of interference fringes caused by expansion of the clamped sample was registered by a high-speed photodetector, the signal of which was recorded by a digital oscilloscope. Processing of the oscillogram thus obtained permits deducing the time dependence of graphite-sapphire interface movements and their speed. Further calculations based on a number of assumptions give the time dependence of pressure in the specimen.

An essential feature of the method is that it makes use of the fact that the refraction index of the transparent material of the plates (sapphire) is a linear function of density (in the case of uniaxial high-pressure compaction). Because heat transfer from the specimen into sapphire can be disregarded according to [59], sapphire compression is isentropic. Under these conditions and with due regard for the relevant reference data, it is possible to calculate pressure at the graphite-sapphire interface and specific work done by the specimen on the sapphire plates. The internal energy of the graphite specimen is determined as the difference between the Joule energy scattered inside the sample and the specific work.

The use of this interferometric method in 2016 [60] allowed determining the relative specific volume  $V/V_0$ , enthalpy H, and pressure P for graphite with an initial density of  $\approx 2.26$  g cm<sup>-3</sup> and liquid carbon at the melting line (Table 2). In this study, the graphite plate was clamped between sapphire or quartz plates. Thin quartz plates were glued on the cell sides so as to cover only their small parts [60] and keep the cell fully assembled. The cell was  $10 \times 10$  mm in size, the graphite specimen (thickness  $\approx 0.03$ )  $\times 10$  mm.

The input energy recorded at the onset and at the end of graphite melting was 10.5 and 20.5 kJ  $g^{-1}$ , respectively, in agreement with similar measurements at the graphite melting point reported by other authors.

It follows from Table 2 that graphite expansion from the initial to liquid state is 60% at a pressure of 7 kbar (the lower line in Table 2). In other words, the data from Ref. [60] give evidence that graphite expansion is significant even at high pressures.

Reference [60] emphasizes the necessity to satisfy many conditions, the most rigorous one being the assumption of one-dimensionality of graphite plate expansion only in the direction perpendicular to the specimen plane. The unidimensionality suggests that the expansion of the graphite plate and the respective contraction of the sapphire plates occur in **Table 2.** Enthalpy and pressure dependence of expansion and electrical resistivity of pyrolytic graphite [60];  $V_0$ —initial graphite volume, V—resulting graphite volume.

$V/V_0$	P, kbar	H, kJ g <sup>-1</sup>	$ ho$ , $\mu\Omega$ cm		
Graphite					
$\begin{array}{c} 1.18 \pm 0.01 \\ 1.21 \pm 0.01 \end{array}$	$\begin{array}{c} 9\pm2\\ 4\pm1 \end{array}$	$\begin{array}{c} 11.3 \pm 0.2 \\ 11.0 \pm 0.2 \end{array}$	$\begin{array}{c} 480\pm20\\ 460\pm20\end{array}$		
Liquid carbon					
$\begin{array}{c} 1.45 \pm 0.02 \\ 1.60 \pm 0.02 \end{array}$	$\begin{array}{c} 14\pm2\\ 7\pm1 \end{array}$	$\begin{array}{c} 22.0\pm0.3\\ 20.7\pm0.3\end{array}$	$\begin{array}{c} 810\pm30\\ 970\pm30\end{array}$		

a plane-parallel mode in the absence of edge effects. However, unidimensionality may be disturbed at high pressure in the middle of the cell and if the glued rims of the cell (sapphire, quartz) are strongly fixed. In the presence of edge effects, sample expansion is not unidimensional.

The duration of sample heating up to the melting temperature is not specified in [60]. The current buildup time is reported to be 0.5  $\mu$ s. A plot of current strength versus specific heat scattered in the sample is presented. The current buildup area is registered for energies from 0 to 5 kJ g<sup>-1</sup>, which are much lower than the energy at the end of melting, 20.5 kJ g<sup>-1</sup>. It may be supposed that the time of sample heating to the melting temperature is much longer than current buildup time.

## 4.4 Use of the interferometric method to determine the melting line of graphite

In 2019, the method in question was employed in HOPG melting experiments [61] using a densely packed (thickness 0.02 - 0.04) × (width 4.5 - 5.0) × 10 mm graphite plate clamped between  $(3-5) \times 10 \times 10$  mm sapphire and quartz plates. The authors [61] do not report the heating time. They used two beams to obtain the interference fringe pattern, one reflecting from the plate outer surface of the cell, the other from a dielectric mirror sprayed over the central part of the inner surface of the same plate in contact with the specimen. Sample expansion was measured by the interferometric method at a single (central) point far from the edges.

Let us summarize the results of experiments [61] with reference to the graphite melting curve (Fig. 8).

On the whole, the slope of the graphite melting curve in [61] (Fig. 8, line 7) agrees with other measured parameters. The main difference is due to overestimated melting temperature values (given that pressure measurements are correct), which must be  $\approx$  5000 K in accordance with previous reports (see Fig. 8). The difference between 6400 K at 3 kbar found in [61] and 4800 K reliably measured at 1 kbar in [37] suggests much higher pressures in [61]. Another difference is due to underestimated pulsed pressure values (given that temperature measurements are correct) that must be as high as tens of kilobar (35–50 kbar). Both pressure and temperature measurements may be incorrect. The results of [61] presented in Fig. 8 suggest that temperature near the carbon triple point is not 4800–5000 K (as found in numerous experiments) but actually amounts to  $\approx$  6300 K.

A thorough analysis of Ref. [61] is complicated by the absence of a detailed description of the cell and experimental conditions. The following remarks concerning measurements in [61] are in order:

1. Pressure measurement. Pressure was calculated but not measured directly in [61] under assumptions, the validity of



**Figure 8.** Graphite melting curve. The main part of the figure from Ref. [61] is presented to demonstrate the deviation of the results obtained in [61] from the known data (largely experimental) about the graphite melting curve). 1—data from [61] for two specimens placed in a quartz cell, 2—the same in a sapphire cell, 3—results of steady-state measurements [57], 4—Togaya's data [52] (1997), 5—calculated data [30] (2001), 6—Bundy's data [43], 7—result of experiment [61] for graphite specimens in cells.

which needs confirmation. To calculate pressure in the specimen from the sample-sapphire interface displacement rate, the formula for estimating pressure in a simple wave for a one-dimensional case and an infinite medium [58] was used. The specimen described in [61] had finite dimensions and the cell size in its plane was of the same order as the specimen size, making possible the influence of edge effects responsible for the disturbance of unidimensionality of the graphite expansion and accordingly for the expected uniaxial compaction of sapphire.

2. Temperature measurement. Temperature calibration was performed in [61] at a single point according to NSRDS 1991 [36] for the solid phase (4160 K at an enthalpy value of 8 kJ g<sup>-1</sup>). The authors of [61] do not discuss emissivity in the melting region; it accounts for some uncertainty of temperature measurements in the liquid phase (calibrated against the solid one). Calibration of temperature was also possible at T = 4500 K (Fig. 1a) and higher temperatures (Table 1).

The authors of the earlier study [60] observed the start of melting at  $\approx 10.5$  kJ g<sup>-1</sup> and its finish at  $\approx 20.5$  kJ g<sup>-1</sup> under a pressure of 4–14 kbar (thin quartz plates were glued to cover only a small part of the cell sides). In [61], melting under 3–17 kbar began at 13 kJ g<sup>-1</sup> and ended at 23 kJ g<sup>-1</sup>, i.e., a 2.5 kJ g<sup>-1</sup> shift of these points took place, Ref. [61] does not explain the cause of the discrepancy between the data from the same authors. To recall, the mode of 'packing' a graphite plate in a glass cell determines both the level of pressure attained and its distribution over the entire graphite plane. However, the authors of [61] do not present concrete data on the mode of packing, nor do they clarify how densely packed the 'sandwich' specimen was in which the graphite plate was clamped: on two or four sides.

Reference [61] contains some inaccuracies. Specifically, it points out that "...Pulsed heating of graphite samples placed in thick-walled capillary tubes with gauged openings enabled the authors of [17]... (see reference [11] in the present work) to observe a well apparent melting plateau at temperatures 5400–6000 K. However, neither the volume of samples nor



Figure 9. (Color online.) Temperature dependence of graphite input energy E [61]: 1—two curves for quartz glass plates, 2—two curves for sapphire plates. See [61] for references to JANAF.

pressure in experiments [17] was measured while enthalpy, density, and pressure were evaluated with certain not entirely clear errors..." [61, p. 175702-1, 175702-2].

It is worth mentioning that calibrated sapphire tubes were used in [11] to register the moment at which expanding graphite (initial density  $\gamma = 2.26$  g cm<sup>-3</sup>) came into contact with the tube wall, which allowed the direct measurement of graphite density at the instant of filling without any assumptions (the measured density at this instant was  $\gamma =$ 1.82 g cm<sup>-3</sup> [11]). The enthalpy, volume, and density of graphite were not estimated but measured directly in [11]. Temperature measured at the onset of melting was 5000 K and amounted to 6200 K upon its completion at elevated pressure (see Fig. 14b). Only pressure was estimated from  $dP/dT \approx 50$  bar K<sup>-1</sup> (Fig. 7), which gives a few dozen kilobar (up to 50 kbar).

It is worthy of note that the authors of [61] cite only those data that confirm their conclusions. For example, Fig. 9 (Fig. 3a in [61]) shows the temperature dependence of the specific input energy of graphite. In this figure, the authors of [61] do not indicate important details of their own experiment or of the cited publications.

Here are essential details necessary for the correct interpretation of this figure.

1. Baitin et al. [10] registered the melting plateau at 5000 K for an argon pressure of 2 kbar(!) (green circles) absent in the figure in Ref. [61].

2. The authors of [61] believe that the straight line of calculated JANAF data up to 6000 K in Fig. 9 gives evidence of preservation of the solid phase up to 6000 K. JANAF calculations are presented for a pressure of 1 bar, i.e., lower than the triple point pressure. The authors of [61] fail to account for these important features mentioned in items 1, 2.

An analysis of the data presented in Fig. 9 gives the impression that the authors of [61] obtained the melting plateau for the first time at  $\approx 6400$  K (for quartz plates *I* in Fig. 9) for the pressure at the onset of melting of approximately 3 kbar (curve 7 in Fig. 8), and all the remaining data presented in Fig. 9 confirm their result.

Let us compare measurements of the specific input energy E in [61] and those of Bundy made under high pressure. To recall, Bundy obtained in [41] the input energy value for the beginning of melting E = 13.2 kJ g<sup>-1</sup> at 48 kbar! The specific input energy at the onset of melting is presented for quartz (*I* in Fig. 9) and sapphire plates (2 in Fig. 9) as E=13 kJ g<sup>-1</sup> and E = 15 kJ g<sup>-1</sup>, respectively (*E* was determined by the authors of the present review from magnified Fig. 9). These estimates give evidence that the pulsed pressure reported in [61] is comparable to that in Bundy's experiment [41] and equals 40–50 kbar during a short heating time (about 1  $\mu$ s). It should be mentioned that the authors of [61] obtained data on

the beginning of graphite melting at  $11-11.3 \text{ kJ g}^{-1}$  and 4-9 kbar (Table 2) in their earlier study [60], where temperature was not measured.

However, Ref. [61] reports the calculated pressure as varying from 3 to 18 kbar (curve 7 in Fig. 8), which confirms the computational error resulting from the faulty measurement of graphite plate expansion. Moreover, the authors of [61] calculated that the velocity of sound in liquid carbon monotonically increases along the isobar P = 10 kbar with decreasing density ([61, p. 4]). This conclusion also alerts the reader with regard to the reliability of calculating total sample density in the case of measuring expansion at a single (central) point.

The results of an investigation of carbon properties using the interferometric method being considered are significantly different from those obtained in all other experimental studies. For example, the authors of [61] observed;

1. A metal-nonmetal transition at the carbon melting point [64] (discussed in Section 5 below).

2. An unreasonably low calculated pressure ( $\approx 3$  kbar) at a graphite melting temperature of  $\approx 6400$  K [61] (see Fig. 9), at odds with the results of previous multi-year research by various authors aimed at elucidating the graphite melting line and carbon triple point. It appears appropriate to mention measurements of the pyrolytic graphite melting temperature made in 2017 in experiments on millisecond current heating of pyrolytic graphite:  $4800 \pm 100$  K for the accurately measured pressure of 1 kbar in a gaseous medium [37]. The pulsed current heating experiment [10] revealed a graphite melting plateau at 5000 K under a gaseous pressure of 2 kbar. The melting temperature of  $\approx 6400$  K at  $\approx 3$  kbar reported in [61] should be ascribed exclusively to an erroneous calculation of pressure and disregard of other reliable data.

Unfortunately, the authors of [61] no longer use direct measurement of pulsed pressure from ruby spectral line displacement that they successfully performed in the preceding period (see, for instance, [58, 62, 63]). Such control measurements could remove the above contradictions.

# 5. Retention of the metallic character of liquid carbon after graphite melting

At two scientific conferences held in 2018–2019, young researchers from the Joint Institute for High Temperatures, Russian Academy of Sciences, delivered reports [65, 66] on

graphite properties at a stationary pressure of 0.2–6 kbar under conditions of laser pulse heating. In these studies, the moment at which the graphite melting temperature was reached was recorded by direct observation of the liquid state surface tremor. In other studies with laser pulse heating, the same approach was employed to register oscillations of a laser beam reflected from the surface of a molten specimen (a high-frequency signal), as exemplified in Ref. [7]. The moment of liquid carbon formation was visualized in [65, 66] by means of high-speed photography with the use of a powerful diode laser as the illuminator. A steady-state pressure from 200 to 6000 bar was maintained throughout the experiment.

The authors of a graphite laser heating study [65] calculated the dependence of graphite expansion during melting by an applied external pressure (Fig. 10a). 'Hardening' of laser-molten graphite during its crystallization allowed the relative volume of cavities formed in solidified drops of liquid carbon to be determined. The value of this result, notwithstanding the use of an indirect method for the assessment of graphite expansion, is in the confirmation of significant expansion at small pressures. Reference [65] shows that graphite expansion during melting is inversely proportional to pressure, i.e., the lower the pressure, the greater the expansion (up to  $\Delta V = 1.9$ ). The degree of expansion at as low a pressure as 200 bar,  $\Delta V \approx 1.9$  (Fig. 10a), is close to the experimental value  $\Delta V > 1.70$  obtained in [26]. At the same time, it was shown in [57] (see Fig. 7) that the lower the pressure, the lower the graphite melting temperature (up to 4500 K).

The authors of [65] argue that "according to the scarce available data (see the work of Bundy published in 1963 [41]), liquid carbon is nonconductive up to the pressures of several kilobar.... In other words, the laser heating of graphite is the sole alternative." The hypothetical region of nonconducting liquid carbon appears in Bundy's phase diagram [47] proposed in 1989 (region E in Fig. 4). It might be a response to calculations published at that time that gave reason to postulate the existence of a mixture of two fluids, conductive and nonconductive, in the liquid carbon region near the melting point. The long history of carbon research overviewed in detail in Refs [1–4] disproves this statement of the authors of [65]. Pyrolytic graphite is readily melted by pulsed current at a pressure above the triple point and heated along deposition planes in the liquid state, because its electrical resistance remains low enough. The conclusion of V N Koro-





benko's thesis (2001) reads as follows: "It is shown for the first time that resistivity of liquid carbon weakly increases with temperature near the melting point, i.e., it has a metallic character" [50].

Here are proofs of the perfect conductivity of liquid carbon after melting and in the liquid state up to 8000 K obtained in our experiments. Figure 10b presents the result of 5-µs-long pulsed current heating of an approximately 30-µmthick sample of anisotropic HAPG graphite placed in a silica glass cell (sandwich). Pressure slightly increases during melting, which leads to a rise in temperature by the end of melting (from  $\approx 4750$  K at the onset to  $\approx 4900$  K at the termination of melting). Because dP/dT = 10 bar K<sup>-1</sup> (the initial part of the curve in Fig. 7), the rise in temperature during melting by 150 K (4900 - 4750) corresponds to the rise in pressure (1.5 kbar). Evidently (Fig. 10b), electrical resistivity in the base plane of HAPG graphite with a density of 2.26 g cm<sup>-3</sup> referred to the starting sample size changes during melting from 450 to 630  $\mu\Omega$  cm. A further rise in temperature is accompanied by a gradual increase in resistivity, which eventually reaches 900  $\mu\Omega$  cm at 8000 K. This means that current-induced melting of graphite is associated with a slight change in its resistivity.

The graphite surface was not covered with a glue (Fig. 10b), and temperature was measured on the clean surface through a silica glass layer. The melting of a thin silica glass plate does not affect its optical transmission, in contrast to that of sapphire  $Al_2O_3$ .

Accurate registration of melting completion during measurement of graphite resistivity (Fig. 10b) is even more precise fixing than that provided by an optical pyrometer. The absence of any peculiarities in the resistivity curve up to 8000 K in Fig. 10b appears to suggest that the boiling point of liquid carbon in this experiment lies above 8000 K (probably due to enhanced pressure in the cell at later stages of pulse heating). In these experiments, pressure was not measured, but it was not as high as during pulsed heating in thick-walled sapphire capillary tubes (Fig. 11).

A high-pressure experiment is exemplified by that of Korobenko [50, 67], in which grade UPV-1T anisotropic graphite of high density was subjected to pulse heating. Rods produced from anisotropic graphite of a square section by pulling through diamond dies were placed in thick-walled sapphire capillary tubes with the inner diameter somewhat larger than the diameter of the rods. At a certain instant close to the melting point, the expanding graphite filled the entire tube lumen. After that moment, isochoric heating of liquid carbon occurred with a sharp rise in pressure.

Carbon density at and above the melting point was calculated from the  $V_c/V_0$  ratio, where  $V_c$  is the tube volume and  $V_0$  is the initial volume of the graphite specimen. Figure 11 demonstrates unstable electrical resistivity at the start of heating due to the fast current growth after its onset. A peculiarity of this experiment is illustrated by Fig. 11, showing electrical resistivity with regard for thermal expansion after the input of Joule energy E 20 kJ g<sup>-1</sup>. The experiment (see Fig. 11) provides data for a conclusion about the influence of pressure on the behavior of liquid carbon resistivity.

Liquid carbon resistivity at the melting point with due regard for expansion decreases as density increases (arrows indicate 800–700–640  $\mu\Omega$  cm on curves *1–3*, respectively, with a growth of density). High carbon density implies high pressure in the capillary tube; therefore, it can be assumed



**Figure 11.** Specific input energy dependence of high-density UPV-1T graphite resistivity  $\rho$  with regard for expansion in the region of a fluid [50]. Arrows indicate the onset of the liquid state. Isochoric heating of graphite is registered starting from the liquid state (as indicated by the arrows). Graphite specimens of initial density  $\approx 2.2 \text{ g cm}^{-3}$  were placed in sapphire capillaries. *I*—carbon density in the liquid state  $\gamma = 1.1 \text{ g cm}^{-3}$ ,  $V_c/V_0 = 2.0$  (low pressure),  $2 - \gamma = 1.76 \text{ g cm}^{-3}$ ,  $V_c/V_0 = 1.25$  (moderate pressure),  $3 - \gamma = 1.88 \text{ g cm}^{-3}$ ,  $V_c/V_0 = 1.17$  (maximum pressure).

that the pressure derivative of resistivity for liquid carbon at the melting point  $d\rho/dP < 0$ . Liquid carbon resistivity at the melting point falls with increasing pressure to  $\approx 50$  kbar (see Fig. 11), in agreement with Togaya's measurements [52] (Fig. 5b). After melting, resistivity decreases at low pressures (curve 1 in Fig. 11) and remains unaltered at high pressures (curve 3). The weight of evidence suggests that resistivity must increase as pressure continues to grow, as was observed by Togaya at pressures in excess of 50 kbar [54]. Transition to the new dependence begins when the pressure amounts to 40 kbar (Fig. 5b). It is not unlikely that such a pressure level is reached in experiment (Fig. 11, curve 3), because resistivity of liquid carbon ceases to fall and the transition to the right branch probably occurs as resistivity increases (Fig. 5b).

It follows from Fig. 11 that, for curves *I* and *2* describing the  $\rho(E)$  dependence,  $d\rho/dE < 0$  immediately after the melting point is reached. Because temperature increases after the input of energy,  $d\rho/dT < 0$ . Hence, a question arises about the possible cause of post-melting reduction in liquid carbon resistivity (curves *I* and *2* in Fig. 11), i.e., of the negative temperature coefficient of resistivity (TCR),  $d\rho/dT < 0$ . It may be connected with the role of the structural factor [55] rather than additional ionization by heating. According to [55], negative TCR can be due to the increase in the coordination number in response to structure compaction, leading to the appearance of additional free electrons.

There is no reason to regard negative TCR at low pressures (curves *I* and *2* in Fig. 11) as indicating a metalnonmetal transition owing to its smallness and because carbon retains the property of conductivity (with a resistivity similar to that of a semimetal). At high pressures, liquid carbon is also a semimetal with metal-like characteristics. A rise in pressure (transition from curve *I* to curve *3* in Fig. 11) is accompanied by a reduction in resistivity in both solid ( $E \le 10$  kJ g<sup>-1</sup>) and liquid ( $E \ge 20$  kJ g<sup>-1</sup>) phases.

In contrast to this analysis, the authors of [64] maintain that graphite resistivity increases with pressure at the beginning of melting (a statement not confirmed by Fig. 11) and decreases in the liquid phase. However, it follows from Fig. 11 that a rise in pressure (transition from curve 1 to curve 2) is accompanied by a reduction in carbon resistivity in both solid and liquid phases. We think that liquid carbon retains its metal character under high pressure and can be regarded as a semimetal with metal-like properties.

In fact, the electrical resistivity of graphite behaves during melting like that of a metal. This standpoint of ours agrees with Togaya's opinion that "liquid carbon is a weakly conducting metal" [46].

In contrast to M Togaya, the authors of [64] argue that the metal–nonmetal transition takes place at the graphite melting point. This inference is based on the following line of reasoning: the isochoric resistivity temperature coefficient at the melting point is positive for the solid phase but negative for the liquid one. These coefficients were not determined directly in [64], because the authors did not measure temperature.

It should be borne in mind that the isochoric derivative of electrical resistivity  $(d\rho/dT)_V < 0$  is not a reliable indicator of the metal–nonmetal transition. For example, relative electrical resistivity at the mercury isochore in Senchenkov's publication [68] is negative in a 1273–1473 K temperature range at metallic mercury density  $\gamma = 11 \text{ g cm}^{-3}$  (peculiarities of mercury's properties are manifested only at the density  $\gamma \approx 9 \text{ g cm}^{-3}$ ). Based on the data from Ref. [68], the author of book [69, p. 196] shows that the TCR for liquid mercury with density  $\gamma = 11 \text{ g cm}^{-3}$  in the temperature range from 1773 to 2073 K is  $1/\rho(d\rho/dT) = -5 \times 10^{-4} \text{ K}^{-1} < 0$ , i.e., is negative, even though liquid mercury is a convincing example of a conducting liquid substance.

Let us turn to the classic literature to search for an answer to the question of how substances are classified according to electrical conductivity. Metals demonstrate enhanced electrical resistivity with increasing temperature (a main feature of metallicity). Semiconductors, unlike metals, undergo a reduction in electrical resistivity under the same conditions. A R Regel' and V M Glazov [70], reputed researchers of liquid metals and semiconductors, recommend the following resistivity-based classification of various materials in their book [70, p. 243]:

• metals—resistivity  $\rho \leq 200 \ \mu\Omega \ cm$ ,

• semimetals— $\rho = 200 - 1000 \ \mu\Omega$  cm (weakly conducting metals),

• liquid semiconductors —  $\rho > 1000 \ \mu\Omega \ cm$ ,

• ionic conductors —  $\rho = 10^6 \ \mu\Omega \ cm$ .

According to this classification, liquid carbon behaves after melting like a liquid semimetal ( $\rho \leq 1000 \ \mu\Omega$  cm; see Fig. 10b).

### 6. Pulsed current heating of graphite in plates and sapphire capillaries. The first experiments on determining graphite and liquid carbon specific heat

A large set of experiments on fast (microsecond) electrical heating of graphite was carried out with the measurement design shown in Fig. 12.

The force diagram of the experimental setup (left part of the figure) includes a low-inductance capacitor C having a capacity of 10–15  $\mu$ F and an inductance of 12–15 nH. To recall, modern low-inductance capacitors are small in size but sensitive to negative loads in excess of 10%. This does not restrict their application in pulse heating, because high-energy



Figure 12. Schematic of experimental setup. The main electrical circuit and the optical layout of the pyrometer. C—capacitor bank, R—resistor determining unipolar current, A—vacuum arrester, M—5046 current monitor (Pearson Electronics, USA), U—specimen voltage sensor, S—specimen, PD—PDA-10A silicon photodetector (Thorlabs), 1—pyrometer lens, 2—optical fiber, 3—lens, 4—interference filter (856 nm).

power resistors like that depicted in Fig. 12 (R, 0.2–0.5  $\Omega$ ) determine the current waveform of positive polarity, which permits thermal characteristics to be calculated by digital techniques in which negative signal values are forbidden. Also, the use of a low-inductance busbar assembly is desirable for recording 1-5-µs and shorter signals. The entire electrical system is earthed at a single point (see the diagram). Pulse heating processes do not require separate grounding of the oscilloscope, which can be earthed through measuring cable shields to prevent signal distortion. After the capacitor is charged to 10-20 kV, the current is started by feeding a rectangular pulse from a standard generator to the highvoltage thyratron designed for a voltage up to 30 kV and 50-100-kA currents. The latest models of such thyratrons are highly efficient and protected against high voltage effects on starting circuits.

The optical temperature measurement system is designed to register radiation normally to the plane of the plate (foil) being heated, allowing the temperature to be calculated using the Planck formula and literature data about normal spectral emissivity of the material of interest. If this characteristic is unavailable, it is recommended to use the specimen in the form of a blackbody model. The simplest variant is the angular model (half-open book model that forms a slit between two planes). The receiving lens of the pyrometer receives a signal from the inside of the slit. Importantly, the lens needs to be focused not through the full depth of the slit but only on the top of the angular model, because the efficiency of a blackbody model depends only on the number of reflections that tend to accumulate in its upper part. Paradoxically, the smoother the inner side planes, the higher the efficacy of the model. A detailed discussion of this issue can be found in [3, 4]. In experimental studies, the efficiency can be as high as 0.95% of the blackbody efficacy, which is quite enough for the pulsed measurement of a temperature on the order of 4000 K with  $\pm 100$  K uncertainty.

Figure 13 presents the result of one of the experiments on the pulsed heating of a UPV-1T graphite plate clamped between glass plates. The figure demonstrates the possibility of measuring very high temperatures and calculating pulsed pressure in the investigation of flat graphite specimens (with the use of the data from Fig. 7).



**Figure 13.** (a) Schematic representation of a highly-oriented UPV-1T graphite specimen (in the form of a plate) enclosed in a hard shell [45]. I — graphite specimen, 2—glass plates, 3—Canadian balsam. Temperature was measured from the deposition plane surface *a* (upper plane). (b) Input energy *E* dependences of voltage on the specimen (*U*), temperature (*T*), and resistivity ( $\rho$ ) during pulse heating of the graphite plate shown in Fig. 13a. *I*—start of melting, 2—end of melting [45].

Two vertical lines in Fig. 13b mark the melting region; melting of six measured samples started at  $E = 12 \pm 1$  kJ g<sup>-1</sup> and ended at  $E = 23 \pm 1$  kJ g<sup>-1</sup>. Melting began at 5500 K under elevated (unmeasured) pressure and ended at  $\approx 6000$  K and slightly higher pressure. Electrical resistivity  $\rho$  refers to the initial sample size. Digits *1* and *2* near the voltage curve *U* (Fig. 13b) indicate the beginning and end of melting, respectively.

An essential conclusion follows from the analysis of displacement of the melting temperature plateau (vertical bar) relative to the melting marks on the voltage curve U(1-2). The displacement results from the cooling of the anisotropic graphite surface layer (the deposition plane *a*) when it is in close contact with the glass. Compensation of thermal losses at the cost of middle graphite layers is delayed due to low heat conductivity between graphite layers.

An experiment in the cell depicted in Fig. 13a showed that specific heat  $C_{\rm P}$  of solid graphite before melting was 3.2 J g<sup>-1</sup> K<sup>-1</sup>, i.e., close to the published equilibrium values. The specific heat of liquid carbon was evaluated in [11, 45] as the derivative dE/dT. It was  $C_{\rm P} \approx 4.2$  J g<sup>-1</sup> K<sup>-1</sup> for



**Figure 14.** (a) Schematic representation of the shape and position of deposition planes *a* of an anisotropic UPV-1T graphite specimen roughly 1 mm in diameter after manual drawing of the square-section specimen through diamond dies of diminishing size. The horizontal arrow indicates the direction of temperature measurement (from plane *c*). The vertical arrow shows the direction from the deposition plane *a*.  $V_c/V_0 = 1.24$ ,  $V_c$  — capillary cavity volume,  $V_0$  — initial graphite volume. (b) Melting of UPV-1T graphite shaped like a rod in a thick-walled sapphire capillary tube. Temperature was measured by a Korobenko high-speed pyrometer. The inclined plateau formed in the course of graphite heating under high pulsed pressure is indicated by vertical bars; melting started at 5000 K and ended at 6200 K. (From Ref. [11].)

temperatures from 6000 to 12,000 K (the specimen in the form of a blackbody model was not used to obtain these results). Temperature in the 6000–12,000 K range was measured on the assumption that emissivity equaling 0.6 at temperatures from 4500 to 12,000 K remained unaltered. It should be emphasized that no attempts were specially made in these pulse experiments a few microseconds in duration to tightly clamp the graphite specimens, i.e., from the sides.

An experiment designed to determine specific heat  $C_V$  for UPV-T1 graphite under high pulsed pressure is presented in Fig. 14 [11].

Temperature shown in Fig. 14b was measured from the 'black' side, i.e., from the side of plane *c* (without a 'delay', as in Fig. 13b). High heat conductivity over graphite layers *a* during its expansion upon contact with the sapphire tube compensates thermal losses. Therefore, the beginning of melting is fixed in Fig. 14b at a usual input energy value of  $\approx 10.5$  kJ g<sup>-1</sup>. Temperature was measured through the wall

of the sapphire tube and the glass plate stuck a top the tube with optical glue. The temperature was calibrated based on data from Ref. [32] ( $E = 9.14 \text{ kJ g}^{-1}$  corresponds to 4500 K, Fig. 1a). The ratio of the sapphire tube internal volume ( $V_c$ ) to the graphite specimen volume ( $V_0$ ) was  $V_c/V_0 = 1.24$ . It allowed the graphite to expand freely before melting; according to the literature data, solid graphite expansion prior to melting is  $\approx 20\%$ . As soon as melting begins, graphite fills practically the entire tube cavity; its density at this moment ( $V_c/V_0 = 1.24$ ) is 1.82 g cm<sup>-3</sup>.

The pressure is not very high at the beginning of melting (a few kilobar) and the temperature  $\approx 5000$  K (Fig. 14b). Pressure enhancement at the end of melting causes the temperature to increase to  $\approx 6200$  K. Figure 7 shows that this temperature corresponds to a pressure of  $\approx 15$  kbar [57], but calculations taking into account dP/dT = 50 bar K<sup>-1</sup> (right part of Fig. 7) give a much higher value by the completion of melting in a thick-walled sapphire capillary tube (of the order of 50 kbar).

It follows from Fig. 14b that pressure is already slightly elevated soon after the start of melting (at 5000 K). Because liquid carbon was heated under nearly isochoric conditions, it was possible to evaluate its isochoric specific heat  $(C_V \sim 3 \text{ J g}^{-1} \text{ K}^{-1})$  [11]. Note that our subsequent measurements yielded  $C_V \sim 2 \text{ J g}^{-1} \text{ K}^{-1}$  under conditions close to isochoric heating [71] (see Section 7 below). The energy at the onset of melting (10.5 kJ g<sup>-1</sup>, according to measurements under microsecond heating [11]) was similar to that measured under millisecond electrical current heating (10.45 kJ g<sup>-1</sup> [41]).

The influence of high pressure on a sapphire tube (during heating of Japanese-made dense isotropic MF-307 graphite) is illustrated in Fig. 15. At the beginning of heating by a  $5-8-\mu$ s current pulse, the butts of the tube were closed by massive electrodes with aluminum foil seals.

It is possible to predict the thickness of the sapphire layer that melts in the course of experiment. The penetration depth of the heat wave  $\delta$  in sapphire can be found from the expression

$$\delta = \left(a\Delta t\right)^{1/2},$$

where *a* is the temperature conductivity coefficient  $a = \lambda/(C_P\gamma)$ ,  $\lambda$  is heat conductivity,  $C_P$  is the thermal capacity,  $\gamma$  is the density, and  $\Delta t$  is the time interval. For  $\Delta t = 3 \ \mu s$ , calculations give  $\delta \sim 2 \ \mu m$  (such is the thickness of



**Figure 15.** Fragments of a destroyed thick-walled sapphire capillary tube after pulse heating of an MF-307 isotropic graphite rod (starting density 2.0 g cm<sup>-3</sup>). The initial outer diameter of the tube is 10 mm, its length is 18 mm. Diameter of the inner opening in sapphire is 1 mm [4].

the sapphire layer that can be melted for 3  $\mu$ s). The initial orifice diameter being 1 mm (1000  $\mu$ m), it is unlikely to change significantly for 3  $\mu$ s (no more than  $\sim$  4  $\mu$ m). Indeed, it follows from Fig. 15 that the diameter of the inner tube opening remained virtually unaltered compared with its initial size, suggesting that the short duration of heating and the small change in the geometric size of the tube opening taken together make it possible to determine specific properties of a substance under nearly isochoric heating conditions.

# 7. Direct measurement of specific heat at a constant liquid carbon volume

Reference [71] reports an experiment conducted by the authors of the present review, including temperature measurements for obtaining data on specific heat  $C_V$ . To ensure conditions for the stability of the initial volume during heating of a HOPG graphite specimen, a method for limiting the initial volume was used. Two 34-µm-thick graphite strips were glued close side by side into a cell consisting of two thick-walled glass plates ( $10 \times 15 \times 15$ -mm TF-5 dense flint, Fig. 16a). The cell was fixed with a 'Supermoment-gel' glue and glass-textolite side plates and fastened between current-carrying copper end electrodes. In addition, the TF-5 plates were placed vertically in a glass-textolite clamp.

The specimen was heated for  $\sim 3-5 \,\mu s$  to obtain the liquid phase. The material of the plates, their thickness, and their transverse size were chosen to keep the cell intact while studying its properties. Heating the graphite caused evapora-



**Figure 16.** (a) Cell providing conditions for preserving the initial specific volume of HOPG graphite. Two graphite strips are glued close to each other between two thick-walled pieces of TF-5 glass, each 10 mm thick (dense flint). The glued textolite side plates ensure volume retention at the onset of heating. (b) Temperature dependence of HOPG sample resistivity (Fig. 16a). After melting (the vertical arrow), resistivity slightly increased with temperature up to 8500 K. The temperature was measured from the center of one of the plates (from Ref. [71]).



**Figure 17.** (a) HOPG melting region (two strips, Fig. 16a). 1—start of melting ( $E_1 \approx 11.5$  kJ g<sup>-1</sup> at  $T \approx 4800-4900$  K). 2—end of melting ( $E_2 \approx 21.5$  kJ g<sup>-1</sup> at  $T \approx 5000$  K). The measurement error  $E \approx 6\%$ . 3—curve showing mean specific heat at a constant volume  $C_V \approx 2$  J g<sup>-1</sup> K<sup>-1</sup> in a 5500–7000 K range for liquid carbon. (b) The temperature coefficient of resistivity of the HOPG specimen shown in Fig. 16a in solid and liquid states. The peak on the curve corresponds to melting. TCR under quasi-isochoric heating conditions is a positive quantity ( $\rho_0 = 50 \ \mu\Omega$  cm).

tion of the glue and melting and evaporation of the plate material. It resulted in the formation of a cavity around the specimen filled with vapors under pressure through which heat exchange with the cell walls occurred. It was found that the layer of the melted material was as thick as 1  $\mu$ m by the time the graphite melting temperature (5000 K) was reached; it continued to gradually increase after the sample transition into the liquid phase. After melting (the arrow in Fig. 16b), resistance of liquid carbon began to slightly increase as soon as the liquid phase was achieved. The temperature dependence of the inserted specific energy for the cell depicted in Fig. 16a is presented in Fig. 17a.

The true values of  $E_1$  and  $E_2$  in Fig. 17a must be  $\approx 7\%$ lower due to the heat losses resulting from close contact of the graphite surface with the upper cell glass for approximately 3 µs. In this experiment, such a small value of specific heat  $(C_V = 2 \text{ J g}^{-1} \text{ K}^{-1})$  for liquid carbon was obtained for the first time; the previously reported value was  $C_V \approx 3 \text{ J g}^{-1} \text{ K}^{-1}$ [11, 67]. The measured temperature coefficient of resistivity (Fig. 17b) was not negative.

An additional control experiment was carried out using the same graphite with a single strip glued as in Fig. 16a between two TF-5 glass pieces (Fig. 18a). All the free surfaces of the glass were glued on both sides. The size of the cell and the mode of its fixation were as described above. However, a reduction in the strip width by half provided better conditions for the



**Figure 18.** (a) Cell providing conditions for preserving the initial specific volume of HOPG graphite. One graphite strip is glued between two 10-mm-thick pieces of TF-5 glass (dense flint). Gluing a single plate provides better conditions for the preservation of the sample volume. The glass is glued together over the entire contact plane. (b) Resistivity  $\rho$  for a single HOPG strip. *1*—start of melting, *2*—end of melting, *3*—onset of slight resistivity growth. After melting, graphite resistivity remained unaltered up to  $\approx$  7000 K.

preservation of the sample volume. Clearly, stronger gluing better preserves the starting volume.

Results of this experiment (Fig. 18b) confirm the supposed preservation of the volume: electrical resistivity remained at the same level during the long-term rise in temperature (from 5000 to 7000 K); weak growth started only at 7000 K. In this temperature range, the temperature derivative of resistivity is zero but not negative.

The conditions of the experiment presented in Fig. 18 better contribute to the maintenance of constant graphite volume during heating, with the TCR in the beginning of the carbon liquid phase being positive.

# 8. Measuring temperature and specific heat in pulse heating processes

### 8.1 Measurement of temperature

The measurement of conductor temperature in experiments with pulsed current heating (heating rate  $\sim 10^8 - 10^9$  K s<sup>-1</sup>) is a challenging task. Its solution permits us to obtain the temperature dependences of the thermophysical and electrophysical properties of conductors in both solid and liquid phases, as well as in melting. Temperature measurement is

necessary to derive equations of state for a substance of interest, its specific heat, and the thermal coefficients.

It is known that at temperatures above 2000 K the most reliable method for their measurement is the noncontact technique making use of luminous object radiation. Measurements of substance temperature in the condensed phase are based on thermal emission laws (radiation pyrometry). As a rule, the brightness method is used. The temperature scale is constructed on the basis of the registered melting area obtained during pulse heating. In most cases, the melting temperature of a substance  $T_{\rm m}$  known from the literature (steady-state measurements) is ascribed to this area. The main disadvantage of this method is it does not allow detecting the so-called 'overheating' of the solid phase above the melting point (or its absence) that occurs when the heating rate influences melting temperature and thereby causes, for one reason or another, an upward shift of  $T_{\rm m}$ . This situation gave rise to a number of publications aimed at substantiating the probability of massive (hundreds of degrees) overheating of metals at heating rates of  $\sim 10^8 - 10^9$  K s<sup>-1</sup> [72, 73]. We undertook an experiment (with the tantalum blackbody model) [22] that demonstrated the absence of such overheating.

A different (technically more adequate) method is used in pulse heating of conductors to construct the temperature scale by calibration of the optical path using a temperature lamp. This method is designed to measure temperature under stationary conditions and is successfully applied for temperature measurement in pulsed processes, such as the detonation of explosives, shock waves, and burning powders.

In the brightness method employed in the study, sample temperature was calculated using the Planck formula

$$T = \frac{C_2}{\lambda \ln\left[ (U_{0\lambda} \varepsilon_{n\lambda} \tau_{\lambda} / U_{\lambda} \varepsilon_{n\lambda}^0 \tau_{\lambda}^0) \left( \exp\left(C_2 / \lambda T_0\right) - 1 \right) + 1 \right]}, \quad (1)$$

where  $C_2$  is constant,  $U_{0\lambda}$ ,  $U_{\lambda}$  are signals from the pyrometer during calibration and the specimen, respectively,  $\varepsilon_{n\lambda}$ ,  $\varepsilon_{n\lambda}^0$  are normal spectral emissivities of the specimen surface and the SI-10-300 tungsten band lamp respectively,  $\tau_{\lambda}$  is the transmission coefficient of the protective glass (removed to calibrate the pyrometer),  $\tau_{\lambda}^0 \approx 0.92$  is the transmission coefficient of the tungsten lamp window, and  $T_0 = 2515$  K is the temperature of the SI-10-300 lamp used to calibrate the pyrometer.

Calculations with the use of formula (1) require knowledge of normal emissivity at a definite wavelength  $\lambda$  (the pyrometer wavelength), i.e.,  $\varepsilon_{n\lambda}$ . Usually, this parameter is borrowed from published experimental data because it can hardly be calculated with acceptable accuracy. For example, the authors of the experimental study [10] found that the emissivity of liquid carbon equals 0.6 for  $\lambda = 650$  nm. This value is close to the result obtained for liquid metals, which gives reason to regard liquid carbon as a liquid conductor.

Using formula (1) and assuming  $\varepsilon_{n\lambda} = 1$  make it possible to determine the surface brightness temperature of a specimen. The knowledge of brightness and true temperatures of the specimen allows determining  $\varepsilon_{n\lambda}$ . The problem of temperature measurement in pulse heating experiments is considered in detail in [74]. The literature data on the emissivity of structurally complex refractory composites are unavailable. An optimal option in this case is to use the specimen of interest in the form of a blackbody model (BBM).



**Figure 19.** (a) Wedge-shaped blackbody model made of two glass plates with inner surfaces covered with a sprayed (or glued) conducting material (metal, graphite, carbide, nitride). (b) The dependence of effective emissivity of the wedge BBM for a wedge angle of  $14^{\circ}$  (solid lines) and  $20^{\circ}$  (dashed lines) on emittance of the wedge cavity surface: *I*—mirror reflection from the surface, *2*—diffuse reflection, *3*—average between the values given by curves *I* and *2* (estimated for the case of mirror diffuse reflection).

To determine the true temperature of a sample subjected to pulse heating, the authors used a wedge-shaped BBM. Usually, different variants of radiation reflection from wedge cavity walls and formulas for calculating effective blackness of such model are considered [75]. Figure 19a demonstrates the blackbody model composed of two planes, and Fig. 19b presents the dependences of  $\varepsilon_{\text{eff},\lambda}$  on the degree of cavity wall blackness  $\varepsilon_{n\lambda}$  for a wedge with apex angles of 14° and 20°.

It would be appropriate to note that BBM design must ensure mirror reflection from the inner walls of the model to make it efficient, because its efficiency depends only on the number of reflections. (A more detailed historical description of the BBM theory can be found in [3, 4, 76].)

Transmission coefficient of the protective glass  $\tau_{\lambda}$  between the specimen and the pyrometer was determined using a Shimadzu UV-240 spectrophotometer at a wavelength of 856 nm. To reduce the radiation flow from the specimen at temperatures above 4000 K in graphite studies and preserve the linear dependence of the pyrometer signal on the radiation flow, an HC-7 type neutral absorption filter was introduced into the pyrometer circuit before measurement; its transmission was also measured by the spectrophotometer. Temperature in the melting region was measured in several studies, e.g., for tantalum [22], the solidus and liquidus in a Zr–C binary system [24], zirconium nitride [77], and quasi-monocrystalline HAPG graphite under pulse heating [78]. The measurement error was 50 K and 150 K at 3000 and 5000 K, respectively.

#### 8.2 Measurement of specific heat

Under conditions of isobaric heating, e.g., in water, air, or a gaseous medium, the heat generated by Joule heating E(t) is equal to enthalpy H(t). Heating samples in a thick-walled capillary or a flat glass cell is accompanied by a pressure increase in the specimen, because its expansion is limited. It can be shown that the difference between specific heat measured under such conditions (10 kbar) and that measured under atmospheric pressure amounts to 10% [79].

The authors of the present article measured mean graphite specific heat

$$C_{\rm P} = \frac{H(T_2) - H(T_1)}{T_2 - T_1} \tag{2}$$

over the  $\Delta T = T_2 - T_1$  interval where  $T_2 > T_1$ . Mean specific heat (2) tends to true specific heat  $C_P = (\partial H/\partial T)_P$  as  $\Delta T$  decreases.

 $C_{\rm P}$  is measured as follows [79]. A constant time interval  $\Delta t = n \delta t$  is set up (where *n* is a given number of points on the time scale) and moved successively along the time axis with step  $\delta t$ . This interval corresponds to the  $\Delta T$  interval determined from the measured T(t) dependence, namely  $\Delta T_i = T(t_i + n) - T(t_i)$ , and the energy interval  $\Delta E_i = E(t_i+n)-E(t_i)$ . Specific heat is calculated as  $C_{{\rm P},i} = \Delta E_i / \Delta T_i$  and refers to the mean temperature of the interval,  $T_{{\rm ref},i} = 0.5[T(t_i + n) + T(t_i)]$ . In graphite experiments described below, the sweep duration was usually chosen to be 10–20 µs with the discretization period  $\delta t = 1-2$  ns (the number of points at the time scale 10<sup>4</sup>) and n = 150,  $\Delta t = 0.15$ –0.3 µs, meaning that specific heat is calculated with step  $\delta t$ .

This method of  $C_P$  calculation may give an additional increase in specific heat for entry into the melting region and its reduction at the exit as a result of alteration of the curve slope T(t) in the melting region and the finiteness of the  $\Delta t$ interval. To exclude this effect, the specific heat of the solid phase must be calculated under the  $t_i + n \leq t_{m,1}$  condition, where  $t_{m,1}$  is the moment melting is initiated (the melting shelf) and  $C_P$  of the liquid phase starting from moment  $t_i \geq t_{m,2}$ , where  $t_{m,2}$  is the moment melting is terminated. The values of specific heat thus calculated (taking into consideration the above comments) are close to the true ones.

The described method of  $C_P$  measurement during pulse heating was used to study metals [9], zirconium carbide [24, 80], zirconium nitride [77], and graphite.

Let us consider by way of example the measurement of specific heat of HAPG graphite, a quasi-monocrystal of carbon superior to HOPG graphite in terms of certain properties.

HAPG is an important source of graphene produced by micromechanical cleavage. The use of HAPG allows thinner specimens of several graphene layers containing fewer defects to be obtained. It is not unlikely that the weak bondage between graphite layers is responsible for the reduced melting heat of HAPG graphite ( $\approx 7 \text{ kJ g}^{-1}$  instead of the expected 10 kJ g<sup>-1</sup> for all other varieties of graphite) [78].

HAPG emissivity was assumed to be 0.6 over the entire temperature range based on the data from [10, 81]. In Ref. [10], mean emissivity  $\varepsilon_{n\lambda}$  of the deposition plane of highly annealed pyrolytic graphite (orthogonal to the *c* axis) was found to be  $\approx 0.6$  at 2000–4500 K. The value of  $\varepsilon_{n\lambda} = 0.6$  was accepted on the assumption of a weak dependence of  $\varepsilon_{n\lambda}$  on temperature and wavelength (650–860 nm) for solid and fluid phases of carbon.

The specimen temperature was measured by the highspeed pyrometer described in [22] (see Section 8.1).

As a rule, melting starts after the specimen is saturated with a certain number of defects. This leads to a loss of the long-range order which triggers melting. It is desirable to record the actual instance of melting not only from temperature but also based on other bulk properties of a heated substance, such as changes in density and resistivity.

At the site of HAPG contact with the quartz cell, the quartz could soften, transit to the liquid state, and evaporate with decomposition into silicon monoxide and oxygen  $SiO_2 \rightarrow SiO + O_2$  [82]. A layer of liquid SiO<sub>2</sub> had no effect on quartz plate transmission, because the absorption coefficient remained unaltered during quartz melting [83, 84]. The layer of vapor did not appreciably affect quartz cell transmissivity either, judging by similar HAPG melting temperatures obtained in a number of experiments with different heating rates (hence, different thicknesses of the vapor layer ranging from one micrometer to fractions of a micrometer). In experiments with a sapphire cell, the temperature at the graphite melting point was  $\approx 400 \text{ K}$ lower, the cause being the formation of a liquid sapphire layer with a higher absorption coefficient [83, 84]. The introduction of computational correction for absorption gave a melting temperature of HAPG graphite of 4900 K [78] and  $C_{\rm P}(T)$  dependence coincident with measurements in quartz plates.

# 9. Enhanced pre-melting specific heat of rapidly heated graphite

Pulsed (microsecond) current heating of conducting materials (metals, alloys, carbides, graphite) is associated with enhanced specific heat (exceeding the equilibrium one) just before melting [85], as exemplified by HAPG specific heat (under pulsed heating) in comparison with that of highly purified UPV-1T graphite having an initial density of 2.25 g cm<sup>-3</sup> (under steady heating). The studied HAPG was initially 99.99% pure; therefore, admixtures could not be the main cause of its enhanced pre-melting specific heat.

Such a sharp increase in specific heat can not be accounted for by inaccuracies in its calculation as a temperature derivative of input energy (dE/dT). The specific heat of HAPG was computed using the algorithm presented in Section 8.2. Almost 150 specific heat values were obtained in the enhancement region that fall into the curve showing its abrupt rise.

Figure 20 illustrates the difference between equilibrium specific heat (points) and specific heat recorded during fast (microsecond) electrical heating (solid curve). The melting temperature of 4900 K in the pulsed heating experiment (indicated by the arrow) is identical to that calculated in the steady-state study (points). In the stationary experiment of



**Figure 20.** Results of our experiment (solid curve) with HAPG placed in a silica glass [86]. Squares — the stationary experiment (up to 3800 K) and calculated values up to the melting temperature for quasi-monocrystalline UPV-1T graphite [35]. The arrow indicates the melting point (4900 K) obtained in two studies [86] and [35].

Buchnev [35], the maximum attainable temperature was 3818 K; calculations for higher temperatures were made taking account of all possible effects, including the formation of equilibrium vacancies and anharmonicity.

The specific heat of fast-heated graphite begins to rapidly increase (for microseconds) at temperatures above 4600 K up to the melting temperature (4900 K). This effect can be accounted for by the emergence of nonequilibrium Frenkel pair defects, i.e., the simultaneous appearance of the introduced atom and a vacancy substituting it, which requires additional energy. What is behind the emergence of these nonequilibrium defects? Melting occurs provided that the lattice is saturated with equilibrium vacancies—this is a condition for the loss of the long-range order. Certain authors (see [87]) believe that the main condition for metal melting is saturation with defects.

Under fast heating conditions, equilibrium diffusion can not ensure the intake of the necessary number of equilibrium vacancies in the bulk of a substance from grain boundaries or the sample surface. The emergence of nonequilibrium defects (possibly Frenkel defects) is a least-evil scenario providing the loss of long-range order in a solid compound needed for its melting.

The exceedance of input energy by the onset of melting by pulse heating goes to increase specific heat, i.e., the lattice energy, rather than temperature. The lattice becomes nonequilibrium for a short time. Moreover, specific heat anomalies are recorded immediately before melting, regardless of the degree of substance refractoriness. In other words, this effect is related to melting of the substance itself but not to the presence of an admixture boiling at high temperatures.

At the same time, the authors of [88] observed a slightly accelerated pre-melting growth of specific heat of highly purified tantalum heated for 200  $\mu$ s. They attributed this effect to the formation of nonequilibrium vacancies, notwith-standing rather slow heating.

An analysis of several studies dealing with similar anomalous effects confirms the validity of the assumption of the appearance of nonequilibrium defects during fast (microsecond and nanosecond) heating. In our microsecond experiments, their manifestation (the post-melting lifetime) lasted 2  $\mu$ s, which means that they may play the key role in all nanosecond heating processes, including explosive electron emission.

### **10. Electronic processes on graphite electrodes**

## **10.1** Possibility of detecting drop-like carbon particles during graphite heating under low external pressure

In Ref. [89], dated 2018, as in an earlier study [90], the authors examined surfaces of graphite electrodes after electric arc exposure in an argon atmosphere at 0.5 bar. An arc discharge of less than 1 s in duration left 0.1–0.3-mm drop-like particles on the electrode surface, which suggests local formation of the carbon liquid phase.

Here is our view of this issue.

The liquid phase is highly likely to form on the surface of graphite electrodes (e.g., under atmospheric pressure and even in a vacuum) under the effect of a local arc or electron beam impact. This effect can be attributed to the fact that a pressure of at least 100 bar at the graphite triple point is reached in the surface layer of solid graphite as a result of its local thermal expansion and generation of thermoelastic stresses at a high energy concentration near cathode spots or in the electron or ion beam absorption region. The liquid phase is formed at separate points of the near-surface layer, is pushed onto the surface above which the pressure is low, and solidifies. The discovery of such droplets after the termination of the experiment is sometimes interpreted as a sign of melting of the graphite specimen. As a rule, the low temperature of the solid graphite surface rather than the temperature of a smalldiameter (fractions of a millimeter) droplet is measured in this case.

It seems appropriate to turn to Ref. [91], in which a graphite rod was rotated at 40,000 rev min<sup>-1</sup> and simultaneously heated by laser radiation from one side. The pressure inside the chamber ranged from  $10^{-5}$  to 11 bar (i.e., was much lower than the graphite triple point pressure). Heating caused particles to leave the graphite surface; on hitting an obstacle, they revealed the destruction of a solder droplet that fell on the floor. This example confirms the soundness of the above line of reasoning.

The pressure in the graphite surface layer due to its expansion is supplemented by recoil pressure created by active graphite sublimation. It is not very high, but laser pulse heating under conditions of growing laser heating power for the time duration of the pulse was found to be accompanied by graphite surface melting in a vacuum [66]. In all probability, the recoil pressure in this case was very high by virtue of increasing radiation power.

#### 10.2 Explosive electron emission of graphite cathodes

To recall, experimental data obtained largely in studies of microsecond metal heating processes [85] are equally applicable to graphite heating. According to [85] and earlier studies [92, 93], the following representation of substance behavior in cathode spots of an electric arc or discharge is observed. In the case of discharge between the electrodes, the rapid (nanoseconds) formation of micrometer and submicrometer cathode spots on the cathode surface takes place followed by their disappearance, in all probability due to the loss of conductivity in each spot by analogy with the wire explosion in [85].

Electrical explosion of cathode spots results in an inevitable, even if insignificant, loss of material caused by explosive ejection of the metal from the conductivity loss region. Current density in a spot amounts to  $10^{6}-10^{8}$  A cm<sup>-2</sup>. It reaches a maximum in the current spot and decreases in deeper metal layers [85, 94]. At a certain moment, the spot loses electrical conductivity, which leads to the formation of a new spot in a neighboring part of the electrode. "The loss of conductivity is related to the disappearance of bond strengths, i.e., metal transformation into a finely dispersed medium (an explosion). This medium expands at a rate of  $\sim 10^{4}-10^{5}$  cm/s" [92, p. 989].

The finely dispersed layer that is formed at the site of the blasted spot expands and forms a torch moving with a certain high speed. Metal layers that melted over the time of current spot action splash as bigger drops at a lower speed. Experiments published abroad in 1956–1959 (see [92] for references) demonstrated the displacement of the current spot with  $10^{-7}-10^{-9}$  s intervals, which suggests the formation of 10 to  $10^4$  current spots for the short pulse time of  $10^{-5}-10^{-6}$  s. The described picture provides indirect evidence of the feasibility of interpreting the nature of the cathode spot as an explosive loss of conductivity under the effect of heating the conductor by a dense current pulse.

An effect of abnormally high specific heat before fast heating of metals was reported as early as 1954 in a joint study by Lebedev and Khaikin [17]. It was confirmed in later studies [18, 95] and explained thereafter in the framework of the modern solid state theory.

In our experiments on fast (microsecond) heating of all available materials (metals, graphite, carbides), their melting was preceded by a sharp rise in specific heat at temperatures 200–300 K lower than those at which melting was clearly observed. The rise can be related to the appearance of nonequilibrium Frenkel defects (an interstitial atom plus vacancy), which are actually nature's response to the impossibility of supplying the lattice (for such a short time) with equilibrium point defects needed to ensure long-range losses (i.e., the beginning of melting) via diffusion. We showed in a tantalum study [22] that the specific energy determined by such specific heat is spent to support lattice absorption rather than a rise in melting temperature.

This energy is numerically small: no more than 6-8% of the energy input before melting, which is comparable to the measurement error of this energy. Therefore, fast heating does not strongly affect the thermal properties of a substance, but its influence on the electronic subsystem is much more pronounced: a rapidly heated metal exhibits enhanced electron emission in the anomalous specific heat region (tens of times the normal emission at the same temperature [85]).

The possible cause is a reduction in the Fermi energy responsible for enhanced electron emission. This conjecture may give an impetus to the further development of the theory.

Explosive electron emission (EEE) is a widely known phenomenon registered as a discovery in 1975 (priority date: 1966). G A Mesyats and other authors of the discovery consider the so-called dense plasma over a solid body to be the underlying cause of EEE. The effect is described in [23, pp. 210–213].

The discovery of EEE provided a basis for the development and production of various electron accelerators (an example of successful industrial implementation of basic research results).

We would like to show that EEE in the nanosecond range associated with cathode destruction is the destination path of anomalous emission preceding fast melting (see above). In other words, the true cause is the interaction between condensed matter and the passing current rather than the appearance of dense plasma over the solid body. In the case of nanosecond heating (associated with EEE), metal melting and subsequent explosive destruction from the liquid phase are close together in time and the properties of matter acquired in the melting region are totally transferred to the liquid phase destruction region. The time segment of Lebedev's anomalous emission [93, 95] with a lifetime of several microseconds in the liquid phase overlaps with all nanosecond processes. Therefore, in the case of liquid metal disintegration in the current spot into millions of small (of the order of 100 Å [85]) particles, they all show abnormally high emissivity; this occurs in the nanosecond range. Each of these small particles solidified during dispersion remains the source of enhanced emission for at least 1000 ns. Such is the hypothetical picture of matching anomalous properties of a rapidly heated solid body and explosive electron emission postulated by G A Mesvats [97–99].

EEE fundamentals were originally formulated for metals. Graphite is equally successfully used under EEE conditions. Reference [99] published in 1980 contains the following definition of EEE: "The phenomenon of explosive electron emission consists in intense emission of electron current due to the transition of the cathode material from the condensed phase into dense plasma as a result of heating local regions by intrinsic emission current.... Explosion of micro-part of the cathode results in the formation of the so called cathode torch consisting of the plasma and vapors of the cathode material... direct experiments showed that plasma expansion over the cathode surface in the presence of the external electric field leads to the appearance of new emission centers in the course of interaction between the plasma and the cathode."

According to [99], the plasma and metal vapors together serve as a source of electrons. In contrast, the concept discussed in [85] gives priority to highly emissive small particles of the condensed phase. Their enhanced emission is due to the following series of successive events:

1. Absorption of excess energy by the solid body lattice prior to melting of a rapidly heated substance, leading to the formation of nonequilibrium defects needed to initiate and maintain melting.

2. Disturbance of the zonal structure of a solid body and (allegedly) reduction in the Fermi energy, contributing to the enhancement of electron emission.

3. Explosive destruction of the emitter's cathode spot due to a conductance blockade in the spot (after equality is achieved between the free path length of electrons in the metal and the size of microregions into which the fluid is separated as a result of fluctuating microbreaks [19]).

Later on, the authors of the EEE concept slightly changed their interpretation of this phenomenon, as is natural for the treatment of a complex phenomenon. In 2011, G A Mesyats, supported by RFBR, published book [100]. The preface to the book contains the following definition of explosive electron emission: "Explosive electron emission (EEE) is the emission of electron current from the conductor surface used as the cathode as a result of an explosion of a microscopic volume at the surface... However, the commonest method for exciting EEE is *fast heating of a micro-parts of the cathode by an electric current of high density*" (italicized by the authors). In the case of pulse heating, a high specific heat of solid bodies before melting is observed simultaneously with abnormally high electron emission [85]. The emission persists across the solid-liquid phase transition during a short heating time (from nanoseconds to microseconds). The proof that Lebedev's anomalous emission [17, 18] of a rapidly heated solid body is directly related to explosive electron emission would furnish a clear physical interpretation of all the phenomena involved.

Many researchers have tried to clear up what causes EEE in graphite cathodes. Reference [95], entitled "On the Cathode Pressure by the Explosive Electron Emission," reports the estimated temperature of a graphite cathode (5500 K). The authors accepted the derivative dP/dT = 27 bar K<sup>-1</sup> (reported in experiment [6]) and obtained a pressure of 10 kbar. They argue that "Such pressure can be produced by the cathode torch plasma formed as a result of explosive evaporation and subsequent ionization of the cathode material." The authors of [95] conclude that graphite melting on the cathode under such pressures (10 kbar) is highly likely.

We believe that pressure is produced by significant expansion of the heated portion of the solid graphite cathode rather than by the 'cathode torch plasma'. A substantial enlargement of the carbon volume (by  $\approx 70\%$ ) in the course of melting at a low pressure was reported in 1986 [26] and 2019 [65]. In short-term (nanosecond) cathodic processes, thermal expansion of heated graphite portions is limited by the inertia of the surrounding material, which gives rise to a significant growth of pressure. At a certain instant, it exceeds the carbon triple point pressure (120 bar) [6], and graphite melts in this part of the graphite matrix where the temperature amounts to 5000 K.

### **11.** Conclusion

Volumetric pulsed current heating and surface laser heating have been successfully applied in experimental studies. In recent years, the former method has demonstrated distinct advantages over the latter one (in investigations of thermophysical properties of such substances as carbon and carbides at high temperatures). However, laser heating provided new information about super-refractory materials, e.g., in studies of vapor composition over pyrolytic graphite at temperatures up to 4500 K [101].

The development of the aviation and space industries resulted in the creation of hypersonic air vehicles that require the use of protective high temperature-resistant coatings and ablative layers with carbon as their main component. Further progress in this field depends on designing pulse methods for the investigation of refractory substances and coatings at high temperatures. Reference [7] reports for the first time data on thermophysical properties of the most refractory ( $T_{\rm m} = 4300$  K) mixed Ta<sub>0.8</sub>Hf<sub>0.2</sub>C carbide at temperatures up to 5000 K. Simultaneously, the properties of a sprayed 1-µm-thick carbide foil were elucidated.

Evidently, investigating the post-melting liquid state of a conductor (before the loss of conductance) is possible in a broad range of input energies, i.e., in a wide temperature range (up to  $\sim 8000-10,000$  K for refractory metals, graphite, and carbides). This opens up good prospects for promoting thermophysical research in high-temperature areas inaccessible in stationary experiments.

In conclusion, here are the main experimental data on carbon properties discussed in the present review.

1. Heating of low-density  $(1.6-1.9 \text{ g cm}^{-3})$  graphites at high temperatures is accompanied by sublimation not only from the surface but also into internal pores. It may disturb the continuity of the material and therefore the uniformity of heating of the still solid graphite [1–3, 25]. Graphite is melted under a pressure of at least 107–120 bar. Heating low-density graphite at a lower pressure and an input energy of 10 kJ g<sup>-1</sup> results in 'bulk sublimation' with graphite expansion and a sharp rise in its resistivity [14, 102].

2. Pulsed current heating of loose graphite with a low initial density of  $\approx 1.8$  g cm<sup>-3</sup> even at a pressure above 120 bar results in its high-density compaction at a high temperature of  $\sim 3400$  K (i.e., in the solid phase!) [25, 26]. This effect is apparent both under very low external pressure and at a pressure caused by intrinsic current (pinch-effect) [25, 26].

3. Numerous studies allowed determining the carbon triple point (solid–liquid–vapor) with a pressure of at least 107–120 bar and melting temperature  $T_{\rm m}$  around 4800 K for pressures up to 1 kbar ( $T_{\rm m}$  can be somewhat smaller if the triple point pressure decreases, but not below  $\approx 4700$  K [30, 32, 56, 103]).

4. Graphite begins to actively sublimate from the surface at a temperature as low as 3000 K, which results in the appearance of soot. Pyrometric measurement of temperature in slow heating processes without regard for sublimation gives underestimated values. The use of optical fibers permits us to avoid temperature measurement errors [1–4, 57, 104]. Restriction of sublimation during fast (microsecond) heating by placing the graphite specimen in a silica glass cell allows the true graphite temperature to be determined both in solid and liquid states up to values of the order of 8000 K [86].

5. At low pressures (but higher than triple point pressure), the starting graphite volume almost doubles in the course of melting, showing a 70% increase [26].

6. At low pressures (around 1 kbar), graphite enthalpy at the start of melting is  $H \sim 10.5 \text{ kJ g}^{-1}$ , melting heat  $\sim 10 \text{ kJ g}^{-1}$ , liquid phase enthalpy (during melting)  $\sim 20.5 \text{ kJ g}^{-1}$ , specific heat of liquid carbon  $C_{\rm P} = 4.12 \text{ J g}^{-1} \text{ K}^{-1}$  (at 4800 to 10,000 K [67]).

Here are new facts considered in this review that are essential for further research on fast heating of liquid carbon.

1. The formation of the carbon liquid phase does not result in conductance loss. Post-melting liquid carbon remains a good conductor, having an electrical resistivity around 500–700  $\mu\Omega$  cm (lower under high pressures [54]). At low pressures (a few kbar), liquid carbon resistivity amounts to 900  $\mu\Omega$  cm at 8000 K (see Fig. 10). (The resistivity values are presented without regard for specimen thermal expansion.)

2. It was shown in experiment that graphite expansion (i.e., volume) doubles during melting under low pressures (150–200 bar) [26] while the melting temperature falls to a minimum (4765–4800 K, see Fig. 7). Pressure growth in the course of melting results in a significant reduction in expansion and a rise in temperature (6200–6400 K at 35– 50 kbar) [4, 11, 67].

3. The specific heat of liquid carbon at high pressures (tens of kbar) is  $C_V = 2.0 \text{ J g}^{-1} \text{ K}^{-1}$  at 4800–7000 K (curve 3 in Fig. 17a) [71].

4. Molten liquid carbon may contain traces of the initial solid phase structure. The difference in resistivity (with due regard for expansion) between isotropic graphite with an initial density of 2.0 g cm<sup>-3</sup> [102] and dense (2.25 g cm<sup>-3</sup>) anisotropic graphite [45] at the melting point in the liquid

phase under fast (microsecond) heating is 900 - 730 = 170  $\mu\Omega$  cm, i.e., greater than the resistivity measurement error ( $\approx 4\%$ ).

5. Fast (microsecond) heating of graphite, metals, and carbides results in a nonequilibrium state of the lattice. Graphite specific heat  $C_P$  begins to grow rapidly as the melting point is approached (at  $\approx 300$  K below the melting temperature) [86]. A presumptive cause of this rise is the formation of nonequilibrium defects (supposedly Frenkel defects) needed to maintain melting under conditions of poor saturation of the volume with equilibrium vacancies.

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