Graphite melting line

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Abstract. The study was performed to establish a graphite melting line. Bundy’s phase diagrams are presented, in which the melting point of graphite (Tm) does not exceed 5500 K for all the considered pressures, up to (at least) 1 Mbar. The results of several studies on pulsed current heating related to measuring the melting temperature of graphite and obtaining the liquid phase of carbon are discussed. It is indicated that the Tm ≈ 6300 K was obtained at a pulse pressure of 38-50 kbar (estimates) in 1999 year. The results of pulsed heating of graphite with current pulse for 1µs duration and obtaining Tm ≈ 6400 K with calculation of pressure ≈ 3-18 kbar in 2019 are considered. Possible errors of this last experiment are noted.

1. Introduction
Currently, the carbon triple point (pressure 120 bar [1], temperature ~ 4800-4900 K (see reviews [2,3]) is fairly well established. The specified melting point (at a pressure of 1-4 kbar) was repeatedly measured, both with the help of a laser and with pulsed current heating. Graphite at high pressures (up to 100 kbar) was thoroughly studied in detail, first by Francis Bundy [4,5], and then by Motohiro Togaya [6]. In the review [2] and in the book [3], the results of measuring the melting temperature of graphite at the corresponding pressures and different heating times are given (see Table 1).

| Time of heating | Heating rate (K c⁻¹) | Melting temperature Tm, K and method | Pressure P (bar) |
|-----------------|----------------------|-------------------------------------|-----------------|
| 1 10 seconds    | 5.10²                | 5000 laser                          | 100             |
| 2 20-30 milliseconds | 1.6-10⁵            | 4800±150 laser                      | "110 bar up to 2500 bar with no detectable effect of P on T" |
| 3 15 ms         | 3-10⁵                | 4530±150 current                    | 140-200         |
| 4 2 ms          | 2.3-10⁶              | > 4700 current                      | 1000            |
| 5 1.7 ms        | 3.10⁶                | 5080±70 current                     | 1000-2000       |
| 6 0.7 ms        | 6.8-10⁶              | 4750±150 laser                      | 150             |
| 7 ~ 20 microseconds | 2.4-10⁶          | 4900±200 current                    | 3000            |
| 8 1 microsecond | 4.8-10⁹              | 4800±200 current                    | ≥ 1000          |
| 9 8 ns × 1000 (averaged over 1000 pulses) | ≥ 4.8-10⁹ | (4765-5000)±200 laser |

The Table shows that the value of Tm - does not depend on the heating rate or the pressure P, in the range of 0.1-3 kbar.

2. Carbon phase diagram, published by F. Bundy
Bundy gives two main versions of the carbon phase diagram, Figure1 [4] and Figure2 [5].
Figure 1 [4]. Carbon phase diagram (Bundy, 1989). The dotted lines indicate the calculated P, T heating trajectories of the graphite sample, which undergoes various expansions. "0 ΔV" means constant volume heating.

Figure 2 [5]. Carbon phase diagram (Bundy et al, 1996). Graphite melting temperature $T_m = 5000 \text{K}$ is shown according to [7] where the pressure reached 2 kbar.

$T_m \sim 6000 \text{K}$ is not even reached in the liquid phase region in pressure range (Figures 1 and 2).

3. Experimental data for carbon obtained by fast (5 microseconds) heating.

In 1999 [8] the melting point of graphite was obtained at 6300 K under heating HOPG-type graphite inside a sapphire capillary tube (Fig.3). Estimation of pressure for this moment by Goxen [1] ($\frac{dP}{dT} = 27 \text{ bar/K}$) gives $\approx 38 \text{ kbar}$; by Vereshchagin [9] ($\frac{dP}{dT} = 50 \text{ bar/K}$) $\approx 50 \text{ kbar}$. Thus, the melting point of graphite 6300 K is achieved only at high pressure, about 38-50 kbar. That is, the bulge on the melting line (from low pressures up to 100 kbar in Fig.2) should be much more extended to the right - to match the experimental data associated with an increase in the melting temperature when the pressure increases to 37-50 kbar.

Fig. 4 shows a view of the destroyed thick-walled sapphire capillary tube after pulse heating (5µs) of the MF-307 isotropic graphite rod (initial density 2.0 g/cm$^3$).

Figure 3 [8]: ([3] page 171). Pulse heating of graphite in a sapphire tube. Melting is marked with strokes. The end of melting is fixed at $T \approx 6300 \text{K}$.

Figure 4. The result of the same pulse heating of isotropic graphite MF-307 (density 2.0 g/cm$^3$) in a sapphire tube (Ø10×18 mm). The diameter of the inner hole in the sapphire is 1 mm (almost unchanged after the experiment). The pressure reached is so high that the tubes were destroyed.
4. Pulse heating by fast (1 microsecond) heating with calculation data

In 2019, there was an experimental and calculation study [10], in which a graphite plates tightly clamped in insulating plates were heated by current pulse for 1 microsecond (that is, even faster than in [8]). A plate of anisotropic graphite was clamped between quartz or sapphire plates – a sample has a “sandwich” type. The expansion of graphite was measured by interferometric method in the direction perpendicular to the plates. The expansion was measured at one (central) point of the sample, and the authors [10], were considered it to be the same for the entire graphite plane. Further, it was assumed in [10] that the entire graphite plate expanded perpendicular to its plane (one-dimensional expansion) - also as under central measured point. Then the general expansion was used in the equation of state of sapphire (or silica-glass) – to obtain the calculated pressure. The result of determination of the melting curve is shown in Fig. 5.

Figure 5 [10]. Graphite melting line. The figure from [10] is given to demonstrate the deviation of the results [10] from the known data (mainly experimental) on the graphite melting line. 1-silica-glass cells; 2-sapphire cells.

The temperature, measured up to 8000 K, was calibrated only at one point for the solid phase (4000 K). The graphite melting curve is obtained (Fig.5) at pressures of 3-18 kbar, (corresponding temperatures of 6300-6700 K), which is far from all known experimental results.

We point out possible errors in the expansion measurement in [10], which led to disagreement of the graphite melting curve of [10] with other literature experimental data.

5. Discussion on the graphite melting curve

In [10] does not specify: how tightly the sample of the "sandwich" type was packed, in which the graphite plate was clamped, - (on the two sides or on the 4 sides). It should be noted here that the level of pressure reached and its distribution over the entire graphite plate depends on the method of "packing" the graphite plate in the glass cell. To illustrate the importance of this, consider an example. Suppose that the edges of the plates are rigidly clamped and do not move, then when the sample is pulse heated, its central part will shift due to thermal expansion. The registration of this displacement will allow in [10] to determine the pressure in the central part of the sample, but this pressure will be lower than the pressure at the edge of the sample where there is no expansion. This consideration in the case of graphite is confirmed by the dependences presented in Figure 1 by dashed lines: the smaller the expansion, the higher the pressure.
However, the authors [10] do not provide specific data about this package. One-dimensional expansion of the entire graphite plate (across the glasses) was assumed. However, the expansion of graphite obtained by interferometer was measured only at one point — in the center of the plate. Just in the center is the "weakest" place for the expansion of the melting graphite at high pressure, provided that additional glasses were also glued along the sides of the cell. (Note that these side glasses work - to break, and under pulse loading, the strength limit of materials increases by an order of magnitude).

As a result, a high expansion in the center (unreasonably extended to the entire graphite plate) was inserted into the equation of the sapphire state, from which the calculated pressure was extracted. As a result, curve 7 is obtained (Fig. 5), which differs significantly in pressure from other known experimental data. The pressure in [10] is underestimated by at least an order of magnitude. An independent calculation of the pressure from the derivative at the melting point of graphite dP/dT = 27 bar / K (Gokcen [1]) for a temperature of 6400 K, gives a pressure of \( \approx 38 \) kbar (instead of the three kbar shown in Fig.5 for the lower part of the curve 7). The calculation for the same point, according to dP/dT \( \approx 50 \) bar/K (Vereshchagin [9]), gives \( \approx 50 \) kbar.

It seems that the main reason for the shift of the melting line of graphite in [10] is the error in the measurement of pressure associated with the assumption that the expansion of the graphite sample is one-dimensional.

Another fact that confirms the error in [10]. Recall that Bundy (at 48 kbar!) obtained the input energy \( E = 13.2 \) kJ/g for the start of graphite melting [11] (see [3], page 51). This is close to the input energy obtained in [10] \( E \sim 13 \) kJ/g. However, at \( E \sim 13 \) kJ/g, the calculated pressure in [10] is indicated as \( \sim 3 \) kbar (for the lower part of curve 7). While Bundy indicates (for about the same energy input) the measured pressure as 48 kbar. This comparison confirms the error of the pressure calculation in [10], based on the assumption of one-dimensional expansion of the graphite plate.

In another study of the same group [12], it is stated that at the melting of graphite there is a metal-nonmetal transition, which is not consistent with the results of all known experiments. In [12] based on the analysis of temperature derivatives (T was not measured!) the presence of a metal - nonmetal transition at the melting point of graphite is stated, and the basis is given: the isochoric derivative of electrical resistance \( (d\rho/dT)_V < 0 \) for liquid carbon. This conclusion is not confirmed by other experimental studies. First, the electrical resistance of liquid carbon has relatively low values (Figs. 3 and 6 [13, 14]). Second, the temperature coefficient of resistance of liquid carbon under close to isochoric conditions \( (d\rho/dT) \geq 0 \), as shown by our experiment (Fig.7 [13, 14]). Third, mercury (for a density of \( \sim 11 \) g/cm\(^3\)) has a weak negative value of the isochoric derivative \( (d\rho/dT)_V < 0 \) [15], which does not prevent it from being a metal.

6. Conclusion
V.N.Korobenko in 2001 [16] stated: "For the first time it was established that the specific electrical resistance of liquid carbon weakly increases with the temperature near the melting point, that is, it has a metallic character." Motohiro Togaya also noted (starting with 1994 year [6]), on the metal-like of liquid carbon.

Thus, the use of unverified by the experiments assumptions in pulse experiments [10, 12] led to incorrect conclusions about the parameters of the graphite melting line and the metal-nonmetal transition for carbon.
Figure 6 [13, 14]. Electrical resistance $R$ of HOPG graphite sandwiched between thin silica-glasses. 1 – start of melting; 2 - end of melting.

Figure 7 [13,14]. Electrical resistance $R$ of HOPG graphite sandwiched between thick glasses of TF-5 (heavy flint) to create isochoric heating. 1 – start of melting; 2 - end of melting.

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References
[1] Gokcen N A, et al. 1976 High Temp. Sci. 8 81
[2] Savvatimskiy A I, 2005 Carbon 43 1115-42
[3] Savvatimskiy A I 2015 Carbon at High Temperatures. Springer Ser. in Mater. Sci., 134 246 p.
[4] Bundy F P 1989 Physica A 156 169-78
[5] Bundy FP, et al. 1996 Carbon 34(2) 141-53
[6] Togaya M, et al. 1994 AIP Conf. Proc. 309 255-58
[7] Baitin AV, et al. 1990 High Temp.-High Press. 21 157-70.
[8] Korobenko V N, et al.1999 Int. J. Thermophy. 20(4) 1247–56
[9] Fateeva N S, et al. 1963 Doklady Academy of SSSR 152 317 (in Russian)
[10] Kondratyev A M and Rakhel A D 2019 Physical review letters 122 175702
[11] Bundy F P 1963 J. Chemical Physics 38 618-30
[12] Kondratyev A M, et al. 2016 J. Phys.: Condens. Matter 28 265501
[13] Savvatimskiy A I and Onufriev S V 2018 Carbon 135 260-62
[14] Savvatimskiy A I and Onufriev S V 2020 Phys. Usp, to be published DOI:10.3367/UFNe.2019.10.038665
[15] Vukalovich M P, et al. 1971 Thermophysical Properties of Mercury. Moscow: Izd. Standartov, 312 pages (in Russian)
[16] Korobenko V N 2001 PhD Thesis Moscow, JIHT (in Russian)