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2008 J. Phys.: Condens. Matter 20 114112

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Liquid carbon density and resistivity

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Received 26 September 2007

Published 20 February 2008

Online at stacks.iop.org/JPhysCM/20/114112

Abstract

As was shown in Gathers *et al* (1974 *Report UCRL-51644* (Lawrence Livermore Laboratory, September 14)), graphite specimens of low initial densities (heated at gas pressure 2–4 kbar) contract to higher density still in the solid state and then continue further expanding up to the melting line. This effect was included in the analysis of our experimental results on the fast heating of graphite specimens in thick-walled capillary tubes. At low pressures (up to 4 kbar) the liquid carbon density $\gamma \sim 1.2 \text{ g cm}^{-3}$. In that case the resistivity of liquid carbon $\rho \sim 2200 \mu\Omega \text{ cm}$. Liquid carbon under high pressures ($P \geq 50 \text{ kbar}$) has a high density ($\gamma \geq 1.8 \text{ g cm}^{-3}$), and the resistivity equals $\sim 600\text{--}730 \mu\Omega \text{ cm}$.

1. Introduction

The authors of [2] have demonstrated that, in the case of electrical heating of low density (less than 2 g cm^{-3}) graphite specimens (as well as those annealed far below $3000 \text{ }^\circ\text{C}$), the electrical resistance of the specimen in the initial stage of heating exhibits a decreasing behavior. This results (figure 1) in increasing nonuniform electric heating of graphite, because a high power starts releasing in microdomains with decreasing electrical resistance. Therefore, uniform electric heating requires a high density of initial graphite specimens and their annealing at high temperature. The initial electrical resistivity of dense graphite specimens after this preparation is $\sim 100 \mu\Omega \text{ cm}$. The restricted volume used in the experiments (V —the inner volume of the tube; V_0 —the initial volume of the graphite specimen) leads to diminishing of the inhomogeneous heating of low density graphite (figure 1).

2. Key data on graphite expanding under pulse heating

It was revealed with microsecond pulse heating [1] that graphite specimens with low initial density (1.83 g cm^{-3}) converted to higher density (2.2 g cm^{-3}) at the input energy $\sim 5\text{--}7.5 \text{ kJ g}^{-1}$ (for our data this corresponds to $3200\text{--}4100 \text{ K}$). Only after that does the compressing graphite specimen continue to expand monotonically up to input energy $E \geq 20.5 \text{ kJ g}^{-1}$, that is in the liquid state (figure 2). This important information was applied to the results of different fast experiments with graphite specimens placed in capillary tubes.

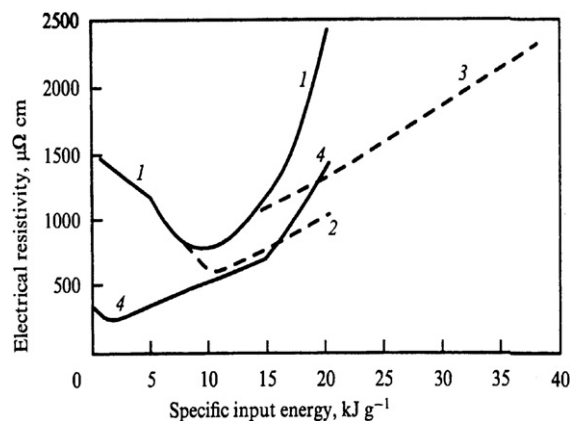


Figure 1. Resistivity ρ^0 (referred to initial dimensions) of pyrolytic graphite specimens of different initial density versus specific imparted energy. 1—pyrolytic cylindrical unannealed graphite (density 1.9 g cm^{-3}); pulse heating in the water. 2—the identical specimen is in a glass capillary tube ($V/V_0 = 1.19$). The start of the heating is along curve 1, and later, heating is along curve 2 (dashed line) after the filling of the capillary cavity with the expanded graphite. 3—the identical specimen is in a quartz capillary tube ($V/V_0 = 1.84$). The start of the heating is along curve 1, and later, the heating is along curve 3 (dashed line). 4—pyrolytic planar graphite (density 2.15 g cm^{-3}) is heated in solid colophony. The slight decrease at the start of heating is connected with the insufficient annealing of the specimen.

The moment of filling the inner volume of capillary tube V with the expanded carbon (initial volume V_0) was determined in most of the experiments by sharp changing in the dependence resistivity versus imparted energy (just as in figure 1).

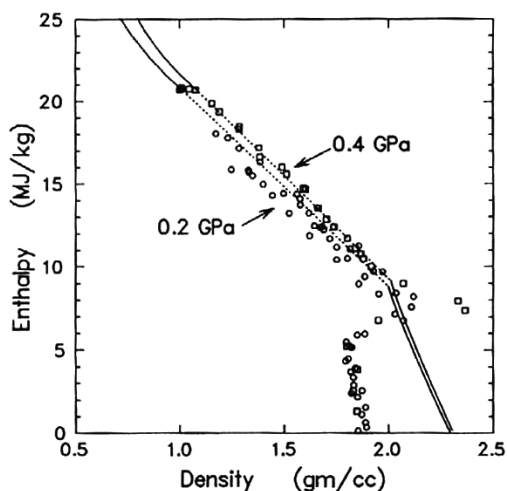


Figure 2. Density versus imparted energy (enthalpy) of the graphite (initial density 1.83 g cm^{-3}) under pulse (microseconds) current heating. Experimental data [1]: circles—at 2 kbar pressure; squares—at 4 kbar. Solid lines—calculations [3] according to model; dotted line—possible melting region under input energy from 9 up to 21 kJ g^{-1} .

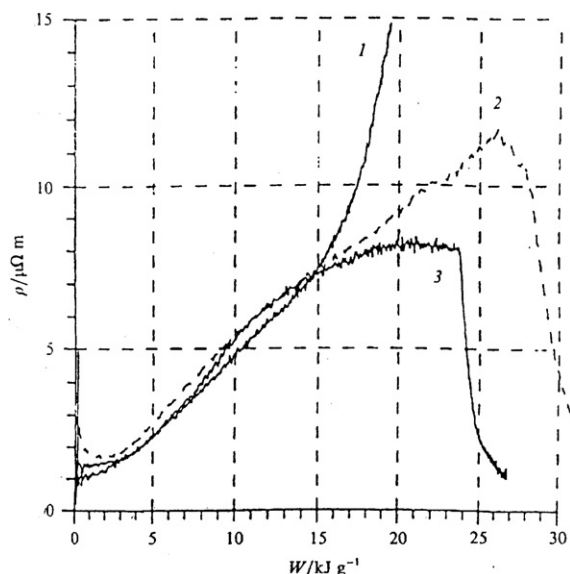


Figure 3. Resistivity of pyrolytic graphite specimens annealed (in needle form) versus specific imparted energy. The start of the melting is at $W = 10.5 \text{ kJ g}^{-1}$, the finish at $W = 20.5 \text{ kJ g}^{-1}$. 1—heating in the water; 2—in the sapphire tube, $V/V_0 = 1.7$; 3—in the sapphire tube, $V/V_0 = 1.4$. Sharp diminishing in the curves 2 and 3—the destruction of the tubes due to high pulse pressure.

One can see in figure 3 [4], that the smaller the value of the parameter V/V_0 is (pressure rises), the lower the resistance reached (up to $8 \mu\Omega \text{ m}$). This is just the same as for Bundy's experiments [5]: the higher the pressure, the lower the resistivity. We draw attention to the fact that at input energy $W = 20.5 \text{ kJ g}^{-1}$ (finish of melting) the resistivity of the liquid carbon at high pressure diminishes with rising pressure (curve 3).

It should be mentioned that temperature measurement is difficult for a pyrolytic graphite specimen grown as a round stick (figure 4) as the outer surface (plane *a*) restricted the

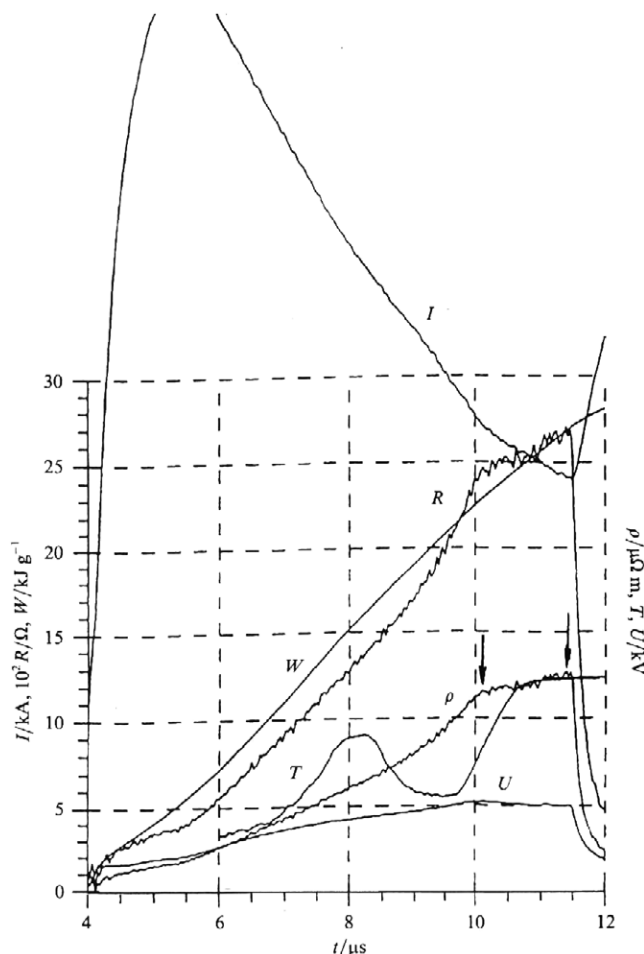


Figure 4. Pulse heating of annealed pyrolytic needle in a sapphire capillary tube. Sapphire capillary tube (inner diameter 1.4 mm; outer 6.2 mm, length 19.5 mm); $V/V_0 = 1.5$. *U*—voltage; *I*—current; *R*—resistance; ρ —resistivity (with expansion included); *W*—specific imparted energy. Left-hand arrow—the moment (at 23 kJ g^{-1}) of filling the inner volume of the tube with expanded graphite in the liquid state. Right-hand arrow—the moment (at 27 kJ g^{-1}) of destruction of the tube and the shunting discharge appeared (a current rise at the moment). One can see that $d\rho/dE > 0$ in isochoric heating under rising pressure for liquid carbon.

radial expansion with the larger expansion coefficient (plane *c*). This leads to destruction of the specimen before melting.

Active graphite expansion at the melting point under low pressures is evident (judging from the rising resistance higher $\sim 15 \text{ kJ g}^{-1}$) in the figure 3 (curve 1) [6]. It leads to a strong rise of resistivity, that looks like a metal–nonmetal transition.

The authors [7] obtained results on the graphite temperature of high initial density (2.25 g cm^{-3}) at the melting point using solid-state light guides ($4800 \pm 200 \text{ K}$), on the enthalpy at the beginning of melting (10.5 kJ g^{-1}), on the melting heat (10 kJ g^{-1}), and on the heat capacity ($4.2 \text{ J g}^{-1} \text{ K}^{-1}$) of liquid carbon. The thermal expansion of graphite during melting at low pressures was estimated as 70% [7]; 50% [3]. The electrical resistivity of liquid carbon was measured [7, 8]: $734 \mu\Omega \text{ cm}$ ($\pm 7\%$) for the density of 1.8 g cm^{-3} at a pressure $\sim 54 \text{ kbar}$.

The resistivity values obtained are in a good relation to the experimental data of Togaya [9]. The result of the experiment

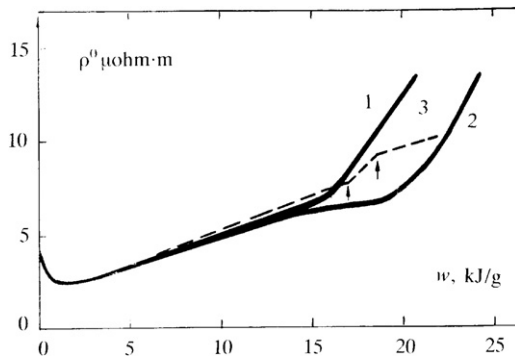


Figure 5. Pulse heating of planar pyrolytic graphite (initial density 2.2 g cm^{-3}) in boiled water (1), colophony (2), and a glass capillary tube (3). Ordinate axis: resistivity ρ^0 ($\mu\Omega \text{ m}$) referred to the initial dimensions. Curve 3: planar graphite specimen with the cross-section $0.22 \text{ mm} \times 0.26 \text{ mm}$ in a glass capillary with internal diameter 0.349 mm , external diameter 5.2 mm . The right-hand arrow shows the moment at which the rate of change of the resistivity with input energy changes abruptly. This moment is attributed to the filling of the inner tube volume with the thermally expanded graphite. The relative volume at that moment $V/V_0 = 1.67$ for the imparted energy $\sim 18.5 \text{ kJ g}^{-1}$, which is just before the completion of melting (20.5 kJ g^{-1}).

with the pulse high pressure value is shown in figures 6(a) and (b) [8, 10].

Rising pressure during melting may explain the inclined plateau recorded by the pyrometer. Pressure of 54 kbar was calculated for the finish of melting with the data [12] ($dP/dT = 54 \text{ bar K}^{-1}$) included. At low pressures the experiments (pulse laser and current heating) give 4800 K as a correct established melting temperature for graphite. Temperature calibrations were fulfilled in [7, 8] using well-known data of [11] (input energy $E = 9.1 \text{ kJ g}^{-1}$ corresponds to the true temperature of 4500 K).

All the experiments like those discussed above sum up in providing the resistivity of liquid carbon at the melting line for different density γ (table 1). For the graphite of low initial density ($\gamma_0 = 1.9 \text{ g cm}^{-3}$) the resistivity ρ^0 (referred to the initial dimensions) and resistivity ρ (with the expansion included) are shown in table 1 for the different values of imparted energy E . The start of the melting takes place at the imparted energy 10.5 kJ g^{-1} ; the finish, at 20.5 kJ g^{-1} . Density γ was calculated with the experimental fact used of contracting the specimen (in microsecond timescale heating) from 1.9 g cm^{-3} up to density $\gamma = 2.2 \text{ g cm}^{-3}$ (at $\sim 3200\text{--}4100 \text{ K}$) and further expanding at higher temperatures [1, 3]. For practical purposes this fact is used in calculating V/V_0 : if the initial density $\gamma_0 = 1.9 \text{ g cm}^{-3}$, and the value $V/V_0 = \gamma_0/\gamma$; we used 2.2 g cm^{-3} instead of $\gamma_0 = 1.9 \text{ g cm}^{-3}$. Data calculated in such a way are shown in table 1. If we do not use this rule, the liquid carbon density (at one and the same imparted energy values, i.e. at the same temperatures) will be different for graphite specimens of different initial densities. The last result looks abnormal; that is why we will use experimental data [1, 3] on compressed loose graphite specimens even for the solid state at high temperatures.

The expansion (i.e. on diminishing of the density) of one and the same graphite grade gives the monotonic rise of

resistivity ρ . The rise of ρ from No. 6 to No. 7 (table 1) for one and the same density may be accounted for simultaneously by rising of temperature and pressure in the isochoric process of heating.

The results of the experiments with the resistivity ρ for liquid carbon at the melting line, that is for specific imparted energy $E = 20.5 \text{ kJ g}^{-1}$, are shown in table 2. The enumeration in the table is disposed (roughly) within the rising of the pressure. In the last case (position No. 4) the highest pressure is reached ($\sim 54 \text{ kbar}$).

The results of microsecond heating [13] for the graphite of initial density $\gamma_0 \sim 1.83 \text{ g cm}^{-3}$ at 4 kbar gas pressure give an approximately constant liquid carbon resistivity $\sim 1000 \mu\Omega \text{ cm}$, up to the temperature 6000 K . This resistivity value is in accordance with the result of the third line in table 2.

It was shown in table 2 that the liquid carbon resistivity ρ diminishes (from 2200 to $730 \mu\Omega \text{ cm}$) at the melting line with simultaneous rising of the density γ (from 1.2 to 1.8 g cm^{-3}). The same behavior is observed for the solid graphite also. For the spectroscopic graphite with the low initial density ($\gamma_0 = 1.6 \text{ g cm}^{-3}$) the resistivity ρ^0 at room temperature is diminished from 1400 to $\sim 1000 \mu\Omega \text{ cm}$ under rising of pressure from 0 to 130 kbar [9]. That is, the contracting of the density is not shown in the solid state as opposed to the case at high temperature (figure 2).

There is a conclusion which follows from table 2. The liquid carbon density rises with the rising pressure as if this is a compressed gas (this was noted also in [14]), and accordingly the resistivity is diminishing. Under the completion of melting (for the low pressures) some parts of carbon-carbon bonds has lost and the carbon ‘sublimes’ in the whole volume. The impression appeared that the sublimation (that appeared in the solid state from the surface at temperature $\geq 3000 \text{ K}$) has changed in the liquid state to the carbon ‘sublimation’ over the entire volume (at $T > 4800 \text{ K}$ and at $P > 100\text{--}200 \text{ bar}$), and only the pressure keeps liquid carbon from further expanding. This ‘volume sublimation’ does not lead to the breaking of all carbon-carbon bonds. There is a good chance for experimental scenarios to form different structures (from isolated atoms to their complexes and up to the extensive fragments) if there will be created conditions for further liquid carbon expansion along the melting line. Apparently the structures of these formations will be depending on outer pressure and the further cooling of the carbon.

It should be mentioned that for highly annealed graphite specimens of high initial density ($\gamma_0 = 2.25 \text{ g cm}^{-3}$) the moments of the start and finish of melting are clearly seen in the voltage oscillogram traces (figure 7). In the case of unannealed graphite specimens with much lower initial density ($\gamma_0 = 1.6 \text{ g cm}^{-3}$), it is difficult to determine the start and the finish of melting, but in Togaya experiments [9, 15] this has been achieved.

The path of pulse (microseconds) heating may be shown qualitatively in $T\text{--}\gamma$ phase diagrams (figure 8). Experimental data of figure 1 are included in figure 8. Graphite expansion during melting has a maximum value $\sim 70\%$ at low pressures. The temperature 10600 K at the input energy $\sim 38 \text{ kJ g}^{-1}$ (figure 1) was calculated using $C_V = 3 \text{ J g}^{-1} \text{ K}^{-1}$ [8].

Table 1. Graphite specimens of low initial density ($\gamma_0 = 1.9 \text{ g cm}^{-3}$) at the different energies imparted.

No	ρ^0 ($\mu\Omega \text{ cm}$)	$\rho = \rho^0(V/V_0)$ ($\mu\Omega \text{ cm}$)	γ (g cm^{-3})	V/V_0 Relative increase of the volume	E (kJ g^{-1})	Reference to figs	Pressure P rise from E_1 to E_2 (kJ g^{-1})
1	750	890	1.85	1.19	7.9	figure 1, curve 2	—
2	800	1100	1.57	1.4	20.5	figure 3, curve 3	$E_1 = 15$ $E_2 = 20.5$
3	—	1200	1.4	1.5	23 in liquid state	figure 4	$E_1 = 23$ $E_2 = 27$
4	880	1500	1.29	1.7	20.5	figure 3, curve 2	—
5	900	1650	1.2	1.84	14	figure 1, curve 3	—
6	1200	2200	1.2	1.84	20.5	figure 1, curve 3	$E_1 = 14$ $E_2 = 20.5$
7	2170	4000	1.2	1.84	38 in liquid state	figure 1, curve 3	$E_1 = 14$ $E_2 = 38$

Table 2. Liquid carbon at the melting line under $E = 20.5 \text{ kJ g}^{-1}$.

No.	ρ^0 ($\mu\Omega \text{ cm}$)	$\rho = \rho^0(V/V_0)$ ($\mu\Omega \text{ cm}$)	γ (g cm^{-3})	γ_0 (g cm^{-3})	V/V_0 Relative expansion	Reference to figs
1	1200	2200	1.2	1.9	1.84	figure 1, curve 3
2	880	1500	1.29	1.9	1.7	figure 3, curve 2
3	800	1100	1.57	1.9	1.4	figure 3, curve 3
4	590	734	1.81	2.25	<1.24	figure 6

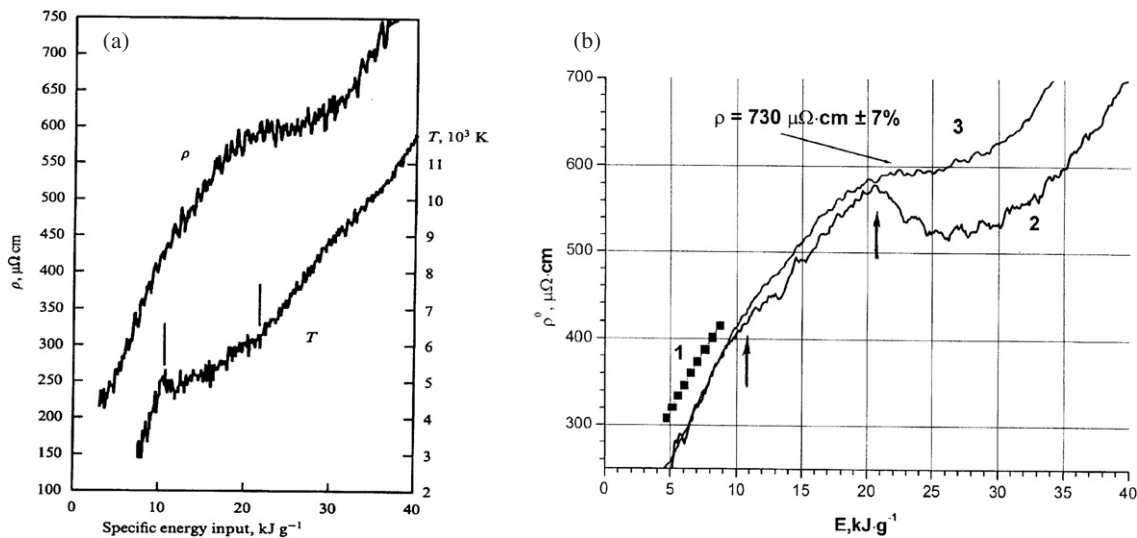


Figure 6. (a) Inclined temperature plateau (marked with vertical lines) at melting of the dense graphite UPV-1T specimen in a thick-walled sapphire capillary tube under high pulse pressure. Initial specimen diameter 0.87 mm; tube: inner ≤ 0.97 mm ($V/V_0 < 1.24$), outer diameter 11 mm. (b) Resistivity of liquid carbon at high density. Arrows show the melting region. 1—data of Sheindlin and Senchenko [11] for solid graphite before melting. 2—the plate of graphite (placed between two glass plates); liquid carbon expands during heating ($E > 20.5 \text{ kJ g}^{-1}$). 3—cylindrical (artificially fabricated) specimen with the diameter 0.87 mm of the graphite UPV-1T in a thick-walled (outer diameter 12 mm) sapphire tube: isochoric process at melting ($10.5\text{--}20.5 \text{ kJ g}^{-1}$) and at further heating under $V/V_0 < 1.24$.

Graphite resistivity ρ , for heating in water (figure 5, curve 1) or in an unfilled capillary (figure 5, curve 3), at low pressure, begins increasing rapidly at the input energy $\sim 16\text{--}17 \text{ kJ g}^{-1}$, i.e. still up to the whole melting of the specimen (20.5 kJ g^{-1}). We may suppose a rapid rise of the resistivity ρ during melting (for low pressures), is connected with the intensive expansion of the graphite at temperatures $T \geq T_{\text{melting}}$ (4800 K).

3. Conclusion

- (1) As it appeared, the measured liquid carbon density at the melting line (under low pressures) is much lower ($\leq 1.2 \text{ g cm}^{-3}$) than that calculated earlier ($\sim 1.6 \text{ g cm}^{-3}$). It is much higher (1.8 g cm^{-3}) at higher pressures ($\sim 50 \text{ kbar}$). Graphite specimens with different initial densities ($1.6\text{--}2.2 \text{ g cm}^{-3}$) have one and the same

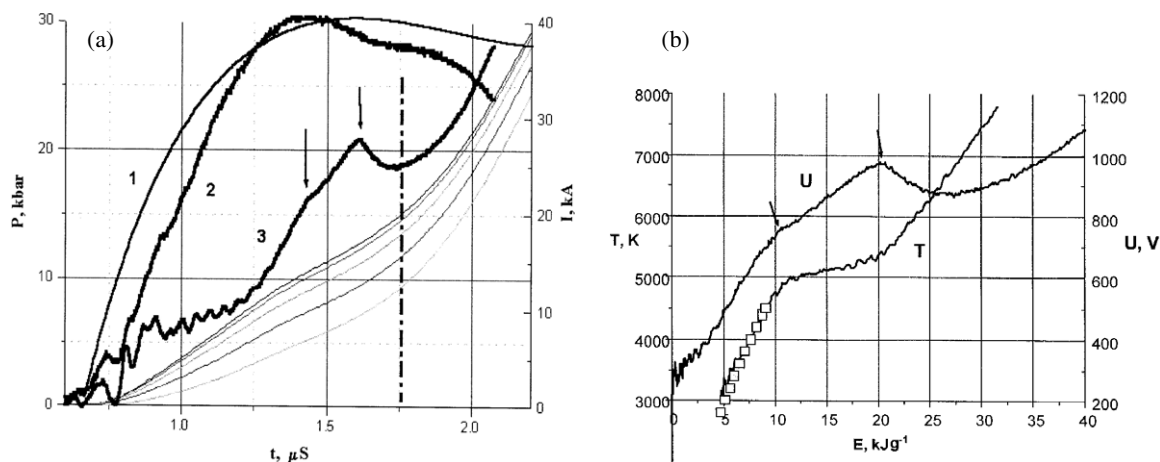


Figure 7. [14] Melting of the annealed pyrolytic graphite HOPG placed between thick glass plates. (On the left and on the right sides—one and the same experiment.) (a) 1—current (modeling by A D Rakhel); 2—current (experiment); 3—voltage U (experiment); melting region marked with arrows. Five lines lower—calculated pressure (A D Rakhel); upper line—in the center of the graphite plate (from 10 to 13 kbar during melting), the lower line—for the surface graphite layer (5–7 kbar). (b) Melting of the graphite (thickness of the plate 0.4 mm) during 2 μs heating. U —voltage; T —temperature. Squares—experimental data of Sheindlin and Senchenko [11].

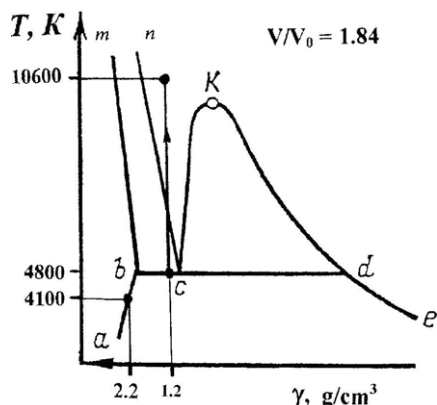


Figure 8. Carbon T - γ phase diagram near the triple point at the melting line. (a) and (b)—the start of sublimation. (d) and (e)—the finish of sublimation. (b)–(d)—triple-point line. m —the start of melting. n —the finish of melting. K —critical point. Thin line (marked with an arrow)—our experiment using a quartz tube (figure 1) specimen of initial density 1.9 g cm^{-3} reaches a density of 2.2 g cm^{-3} at 4100 K and is heated further along the line (a) and (b) up to melting ('b'); then melting occurs and heating begins in the isochoric volume $V/V_0 = 1.84$ (arrow vertical line) up to the high temperature of 10 600 K.

$\sim 1000 \text{ K}$ under pressures of $\sim 50 \text{ kbar}$. According to experiment [12], under pressures up to 30 kbar the melting temperature rises from 4500 to 6500 K. Calculated data of [9] show that the temperature rises by 200 K only under pressures up to 56 kbar. For details see the review [14]. The future efforts of scientists should be directed to the measurement of pulsed pressure with the help of the shifting of ruby luminescence r-lines in spectra. This method is widely used in steady-state conditions (diamond anvil). A method of plane loading for metal foils (convenient also for graphite investigation) placed side by side with the ruby thin plate is in progress in our laboratory [16, 17].

- (4) At low pressures (0.1–4 kbar) and at temperatures $T \geq 4800 \text{ K}$ liquid carbon 'aspires' to active expansion. The formations of different carbon structures (from isolated atoms, their complexes, up to extensive fragments) are possible under further expansion of liquid carbon. This may yield important technological applications under pulse heating of graphite.

Acknowledgment

This work was supported by the Russian Foundation for Basic Research (RFBR), scientific grant No. 07-08-00070a.

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density for the liquid state at identical pressures. For such a conclusion one may find agreement with the experimental data on contracting of loose graphite specimens (1.6 g cm^{-3}) even in the solid state (3200–4100 K) up to higher density (2.2 g cm^{-3}).

- (2) At low pressures the liquid carbon resistivity ρ equals $\sim 2200 \mu\Omega \text{ cm}$. At high pressure ($P \sim 54 \text{ kbar}$) and for high density of liquid carbon ($\gamma \sim 1.8 \text{ g cm}^{-3}$) the resistivity ρ equals $\sim 730 \mu\Omega \text{ cm}$.
- (3) The true dependence of the melting temperature versus pressure (dP/dT) was not established so far. Our direct experiment under the isochoric process of heating shows that the graphite melting temperature (4800 K) rises by

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