QUASI-METAL PROPERTIES OF LIQUID CARBON AT HIGH TEMPERATURES AND PRESSURES

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Introduction

- The four planets in our own solar system (Mercury, Venus, Earth and Mars) are rocky and made out of silicates. However, it has been proposed by the astronomer *Marc Kuchner* (University of Princeton, USA), that planets made mostly out of *carbon compounds* could exist.

- Some of the Neptune-sized planets could also be carbon planets. Carbon planets are believed to be frequent near the center of the galaxy, since the concentration of carbon is higher there.
  NASA is planning on launching a mission, called TPF - Terrestrial Planet Finder in the year 2015. This observatory which will be much larger than the Hubble Space Telescope will be able to detect such planets.

- It's quite possible that there are many carbon planets orbiting stars close to the ancient galactic center, possibly even in globular clusters orbiting the Milky Way galaxy. As times passes and more and more generations of stars end their existence as stars, the carbon which was fused in the core will get more abundant. Thus, the concentration of carbon planets will increase. Maybe at a point, all planets formed will be carbon planets.

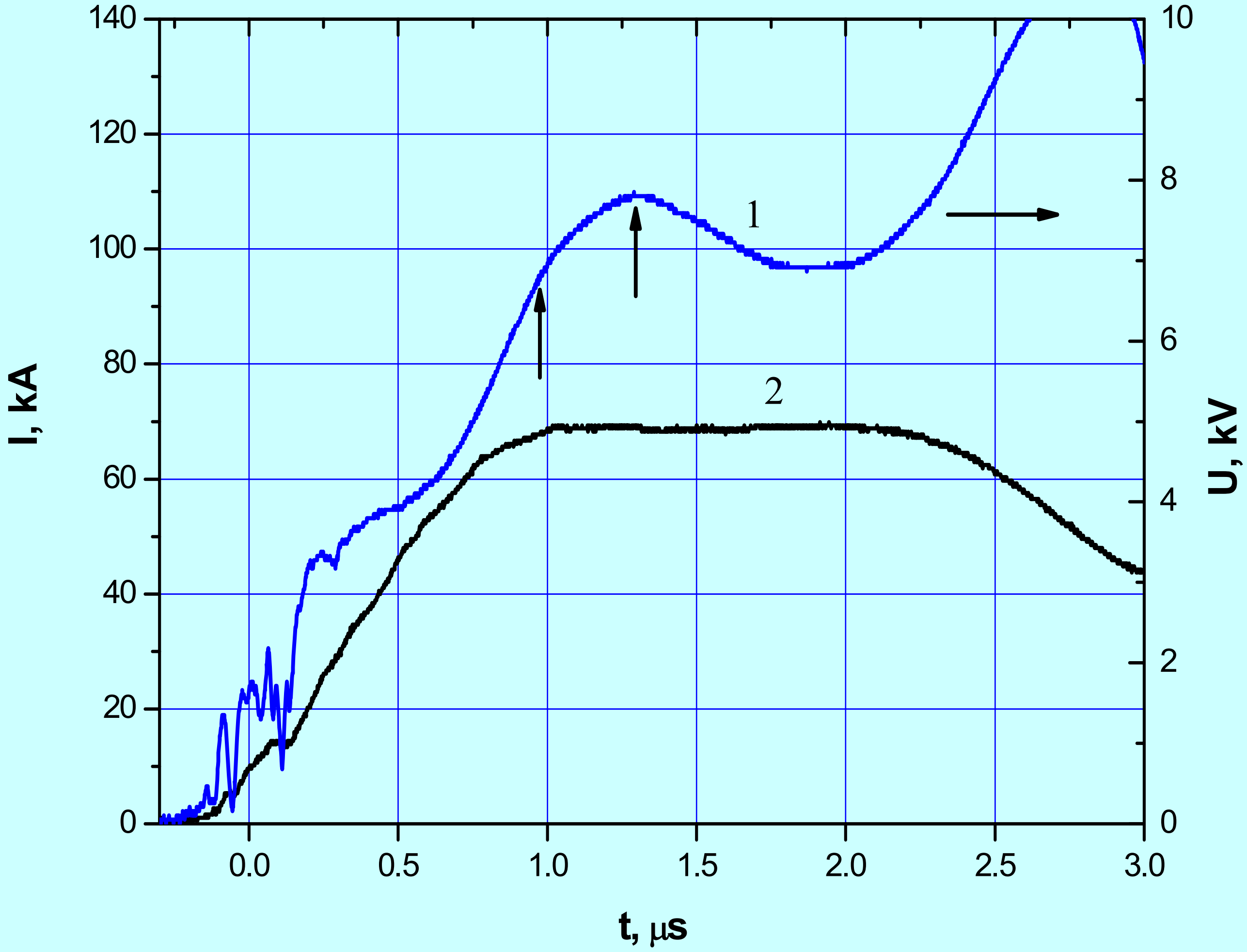
- Предлагаемая методика позволяет получать экспериментальные данные по свойствам углерода до весьма высоких температур: для углерода достигнута температура 35000 К. Эта же методика способна обеспечить создание и измерение высоких импульсных давлениях (до сотни кбар).

LIQUID CARBON at the PULSE HIGH PRESSURE EXPERIMENT

The current is equal constant (**68 kA**) during melting of **anisotropic** graphite (time between two arrows) and further for liquid state (sapphire tube was used). The specimen begins melting in one microsecond after start of heating. The average pressure inside the specimen equals **4.5** kbar**,** or **9** kbar in the center (due to pinch-effect).

1 - Voltage (arrows show the melting region).

2 – Current.



The diminishing of the liquid carbon resistivity after the melting

Arrows show the finish of melting and the start of fast heating of liquid carbon under isochoric heating.

1 – density γ = 1.10 g/cm3 = const; (V/Vo = 2);

2 - density γ = 1.76 g/cm3 = const; (V/Vo = 1.25);

3 - density γ = 1.88 g/cm3 = const; V/Vo = 1.17).

At the melting point liquid carbon resistivity is diminishing with rising pressure, just as in M.Togaya experiment

(790 – 690 – 640 mcOhm·cm. - The diminishing with the pressure rising)

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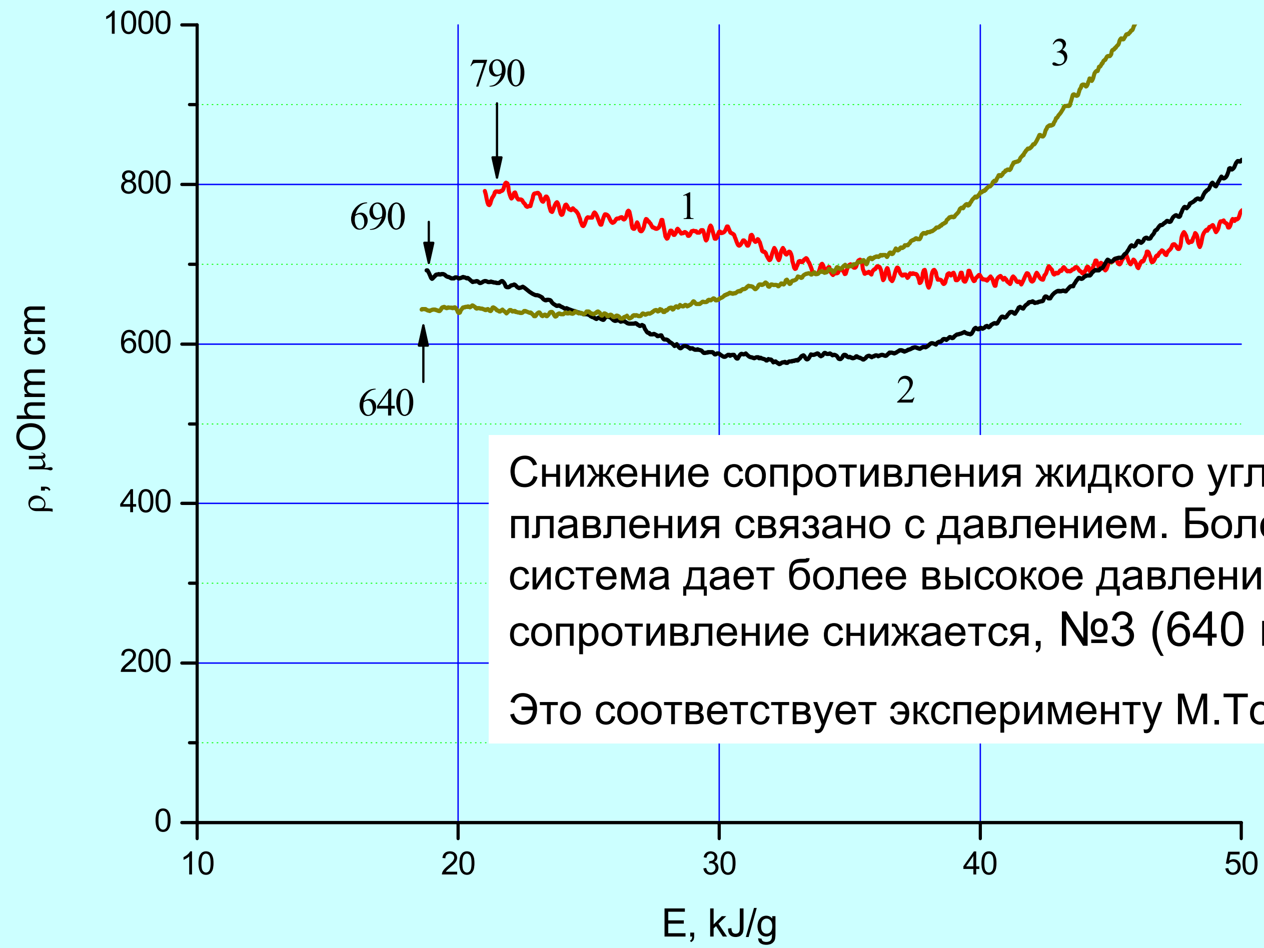


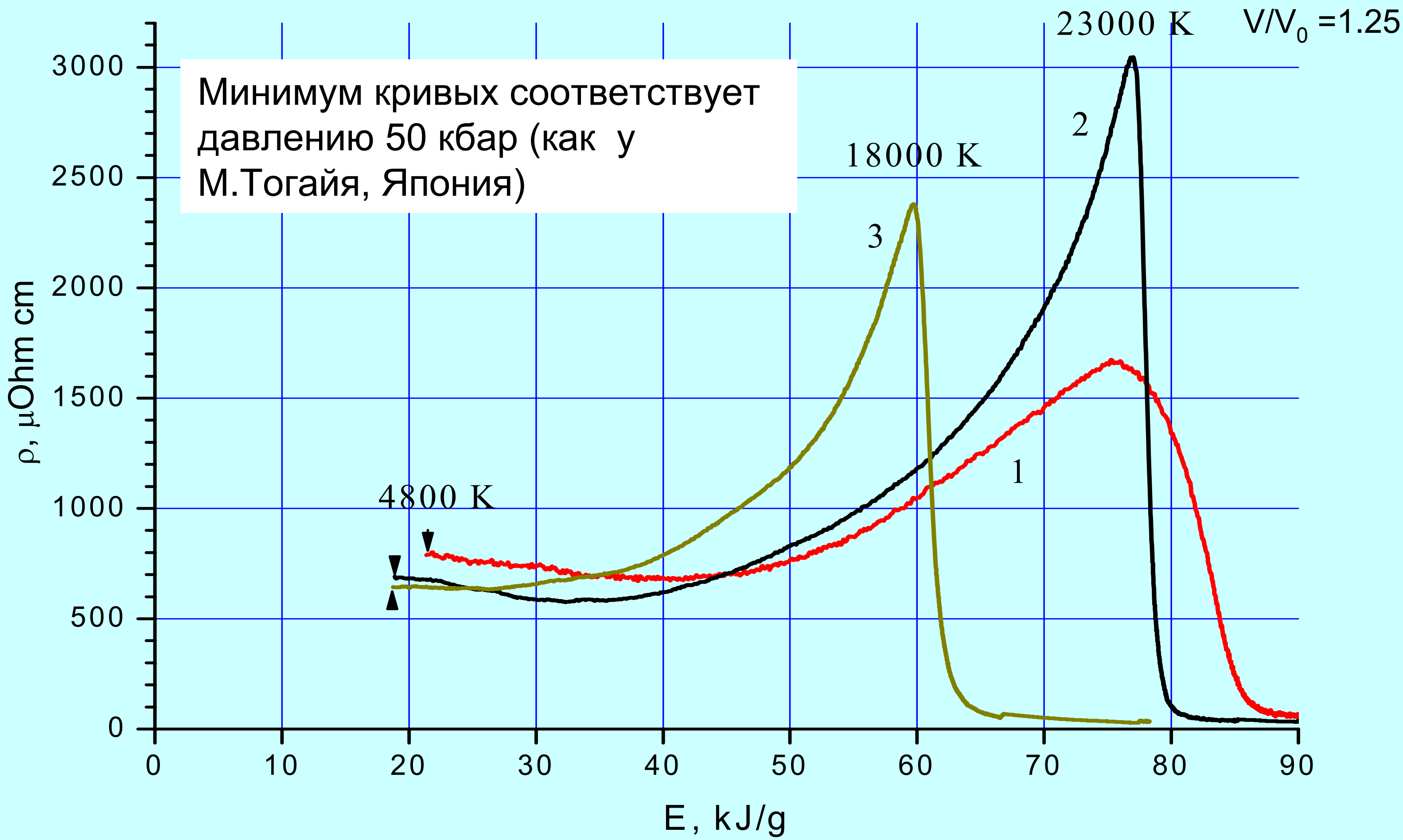
Снижение сопротивления жидкого углерода в точке плавления связано с давлением. Более плотная система дает более высокое давление и сопротивление снижается, №3 (640 мкОм*см).

Это соответствует эксперименту М.Тогайя (Япония)

Specific resistivity (mcOhm*cm) of liquid carbon at high temperatures and pressures (the diminishing is changed to rising at P> 50 kbar pressure)

Isochoric heating: 1 -density γ = **1.1** g/cm3; 2 - γ = **1.76** g/cm3; 3 –γ = **1.88** g/cm3

Heating in sapphire tubes. Arrows – the start of liquid state.



Carbon transition from semiconducting properties to metal-like properties.
The highest density has the highest resistivity.

Pulse heating of the dense anisotropic graphite in sapphire capillary tube (at rising pressure up to 50 kbar after the melting)

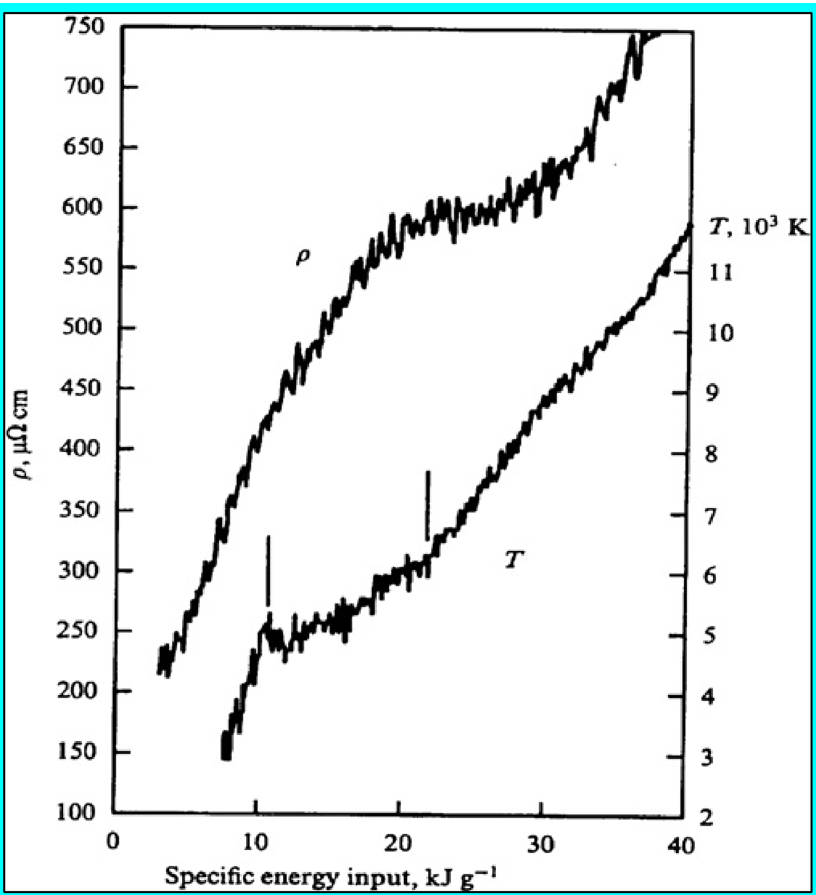
Оценка температуры

$\Delta E = C_V \Delta T$

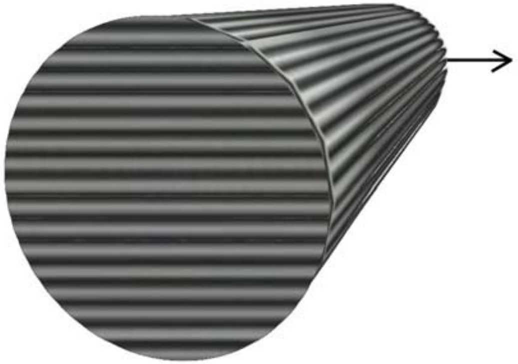
75 кДж/г – 21 кДж/г = 3 Дж/гК(Т – 4800 К)

C_V определялось из эксперимента

В итоге Т ~ 23000 К для 75 кДж/г



- Resistivity (ρ) and Temperature (**T**) near melting region for unisotropic graphite HOPG.
- Graphite specimen is in the needle form with the diameter 0.87 mm.
- Sapphire thick tube (d/D = 0.97mm /12 mm), therefore Vtube/Vgraphite is lower 1.24.
- Inclined temperature plateau is marked with the vertical lines.
- Temperature (at the start of melting) is lower than 5000 K, because pressure is high. Pressure is equal 54 kbar at the finish of melting.
- The start of melting is at 10.5 kJ/g.
- Arrow shows the direction of temperature measurement.



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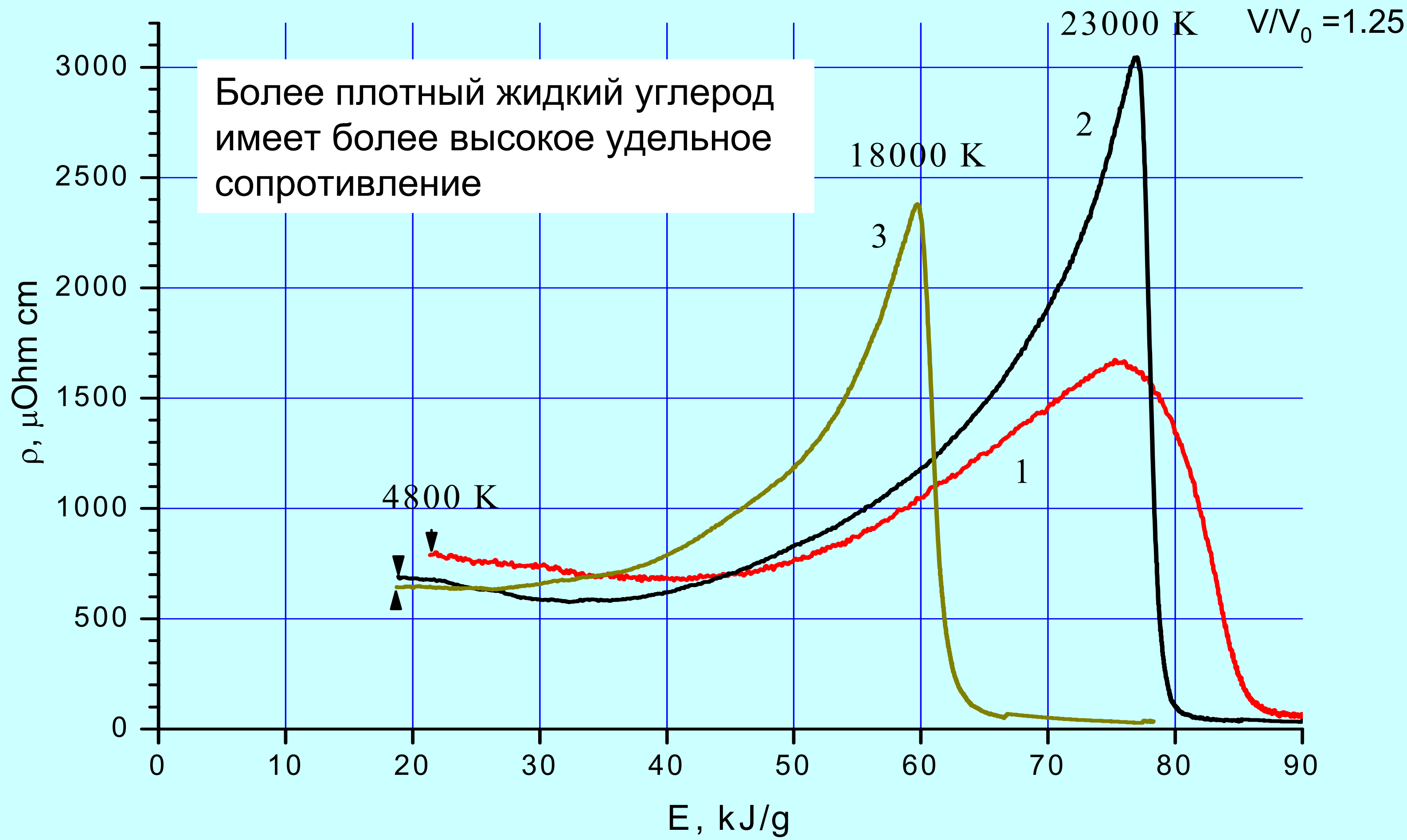
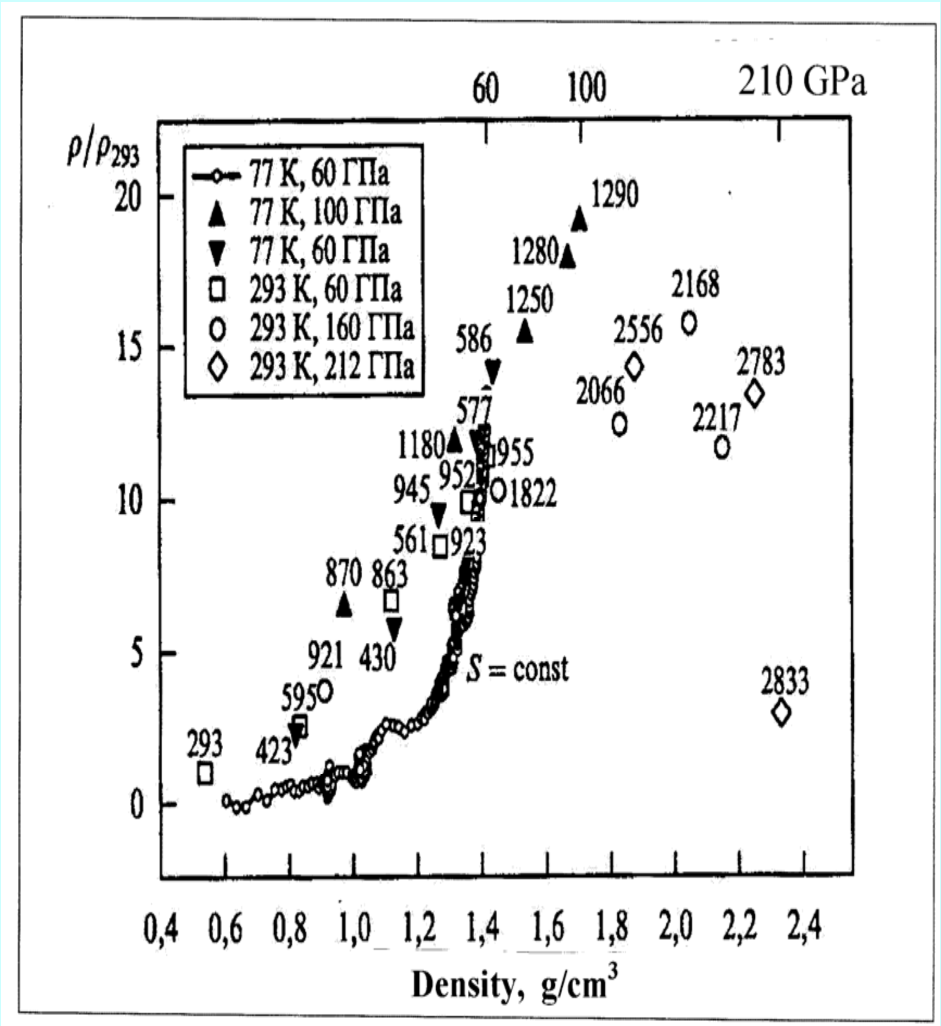


Carbon transition from semiconducting properties to metal-like properties.
The highest density has the highest resistivity.

Resistivity rises for liquid Lithium (60-100GPa) with rising density
Resistivity rises for liquid Carbon (5-10 GPa) with rising pressure
(Maksimov,Magnitskaya,Fortov - Physics-Uspekhi, **2005**,v.175,№8)



- В диапазоне 300-1500 кбар электросопротивление ρ лития возрастает примерно в 20 раз от типичных для металла значений. Электронный спектр лития становится близким к спектру полуметаллов, чем к спектру простых металлов.
- Возрастание сопротивления связано со сложной поверхностью Ферми, которая не сфера, а несколько малых поверхностей, содержащих очень малое число носителей.
- Maksimov,Magnitskaya,Fortov
  2005

Возможные объяснения эффекта смены знака $d\rho/dE$

СНИЖЕНИЕ СОПР. ПОСЛЕ ПЛАВЛЕНИЯ

$d\rho/dT < 0$ Это может быть связано не с дополнительной ионизацией при нагреве, а с ролью **структурного фактора** L_Z/g^2, где

L_Z – длина свободного пробега электрона в теории Займана;

g – фактор Мотта; $\mathbf{g = n(E_F)/n(E_F)_{своб.}}$

$\mathbf{E_F}$ - энергия Ферми, **n** – плотность состояний.

Электросопротивление $\rho = \mathbf{12\pi^3\hbar/g^2Se^2L}$,

где **S** – площадь поверхности Ферми в приближении свободных электронов,

L – длина свободного пробега электрона.

The transition of carbon with covalent bonds under melting to the state with negative temperature coefficient (diminishing of the resistivity) may be accompanied by the **compression of structure due to the rising of coordination number,**
giving the additional free electrons.

- Классификация А.Р.РЕГЕЛЯ по величине удельного электросопротивления

МЕТАЛЛЫ ρ **< 200** $\mu\Omega\cdot$cm

ПОЛУМЕТАЛЛЫ ρ = **200-1000** $\mu\Omega\cdot$cm

ЖИДКИЕ ПОЛУПРОВОДНИКИ ρ **> 1000** $\mu\Omega\cdot$cm

ИОННЫЕ ПРОВОДНИКИ ρ = $\mathbf{10^6}$ $\mu\Omega\cdot$cm

По этой классификации жидкий углерод:

При невысоких давлениях, сразу после плавления – это жидкий полупроводник, (ρ ~ **2000** $\mu\Omega\cdot$cm).

При высоких давлениях (P=40-50 кбар) жидкий углерод – полуметалл ρ ~ **700-800** $\mu\Omega\cdot$cm.

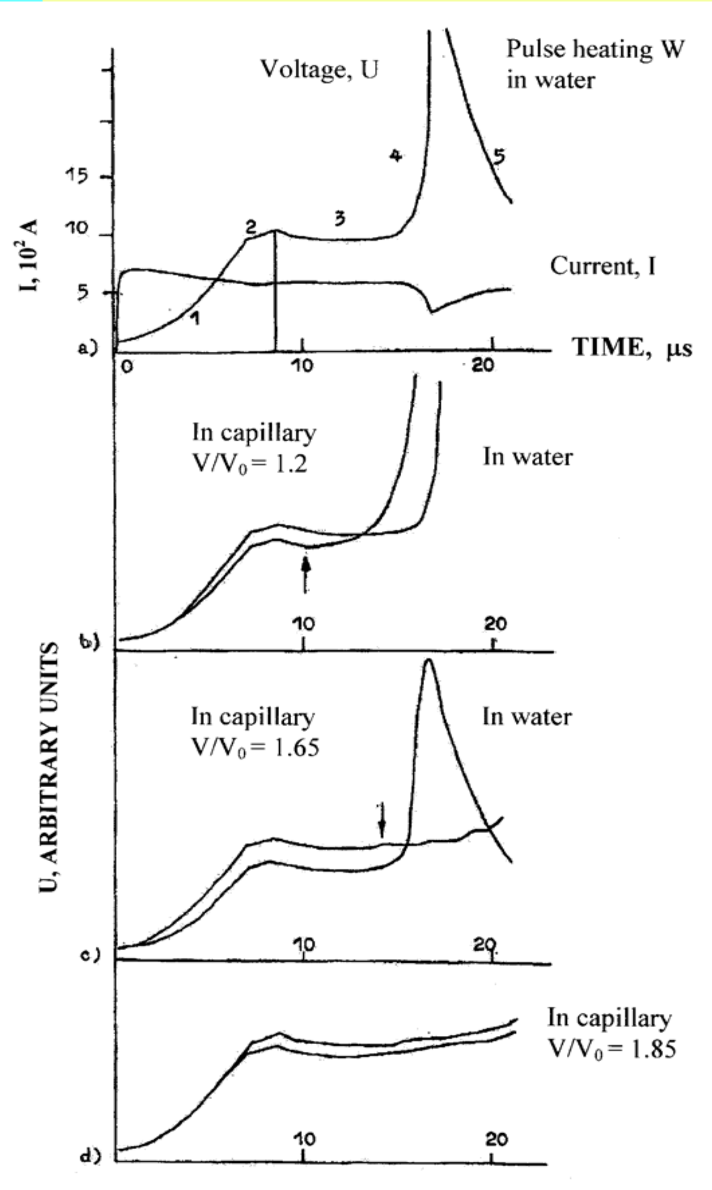
При высоких введенных энергиях (E > 50 кДж/г) и высоких (более 50 кбар) давлениях, жидкий углерод – это снова полупроводник (ρ > 1**000** $\mu\Omega\cdot$cm) с металлоподобными свойствами: электросопротивление ρ растет с ростом Т.

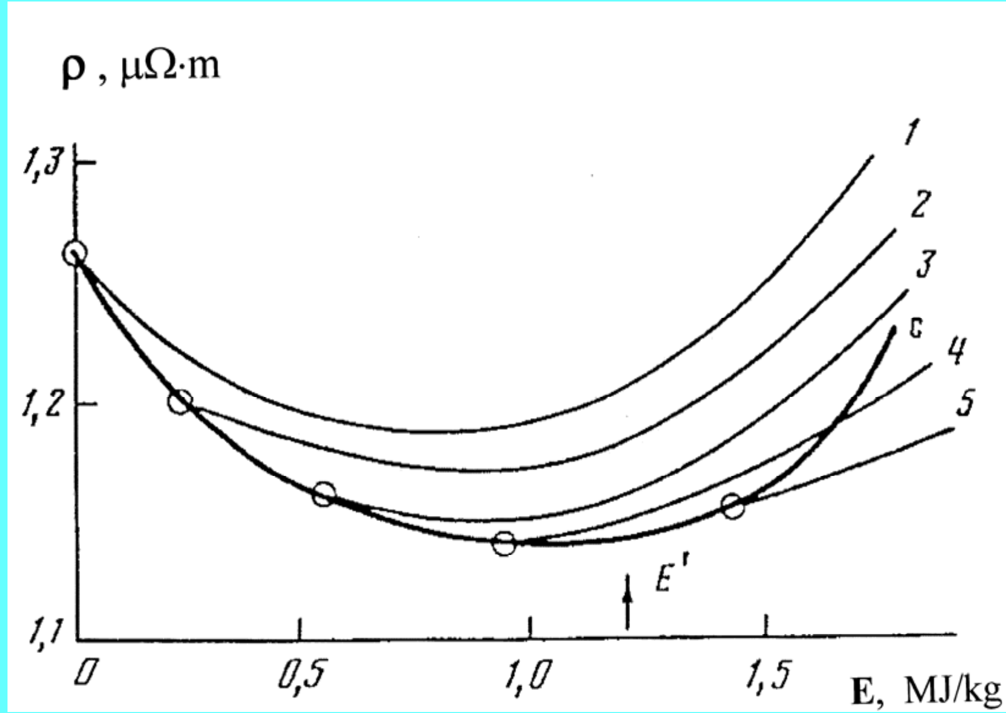
РОСТ СОПР. ПРИ ВЫСОКИХ ЭНЕРГИЯХ

Стандартное поведение металлоподобного вещества с ростом температуры

The rising of the liquid tungsten resistivity at higher density

Ivanov V.V., Lebedev S.V., Savvatimskiy A.I. Teplofizika Vysokikh Temperatur, **1982**, V.20, #6,1093-1097 (in Russian)

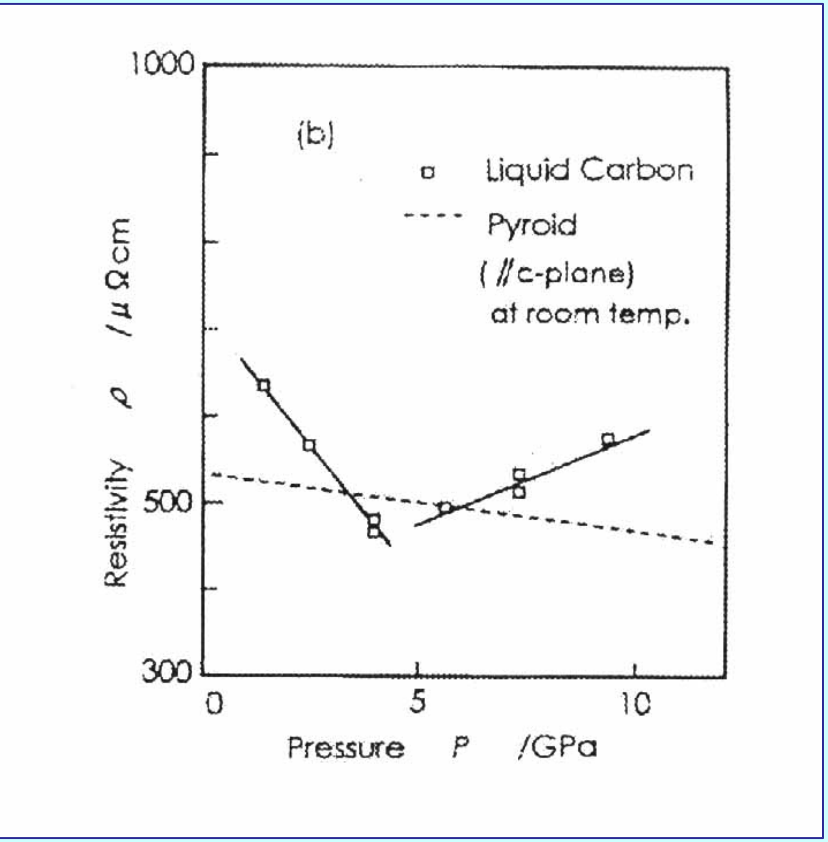




Resistivity ρ of liquid tungsten in capillary tubes

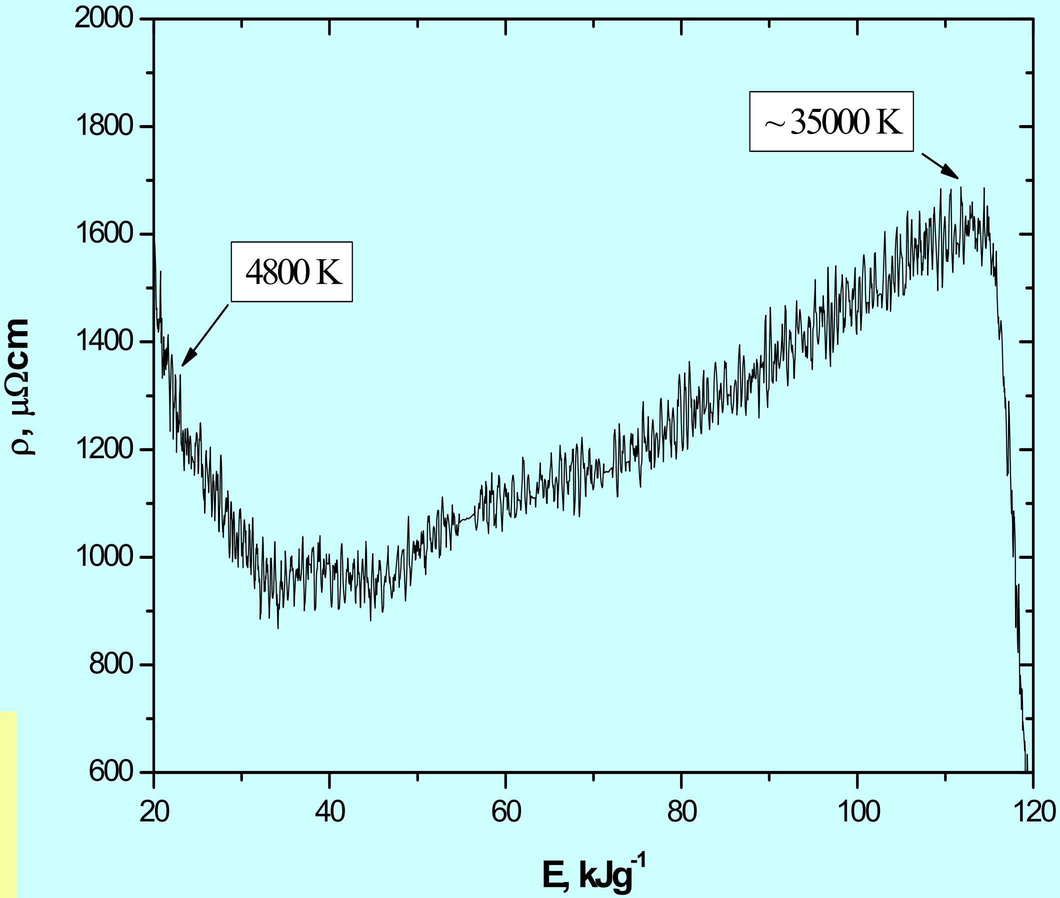
1- V/Vo=**1.07**; 2 -**1.13**; 3-**1.20**; 4-**1.31**; 5-**1.54**
C – free expansion (in the water)
E = 0 (finish of melting)
dρ/dE >0 before E' =1.20 MJ/kg

Fast pulse heating of **isotropic** graphite MF-307 (ρ_0 = 1250 $\mu\Omega$cm)



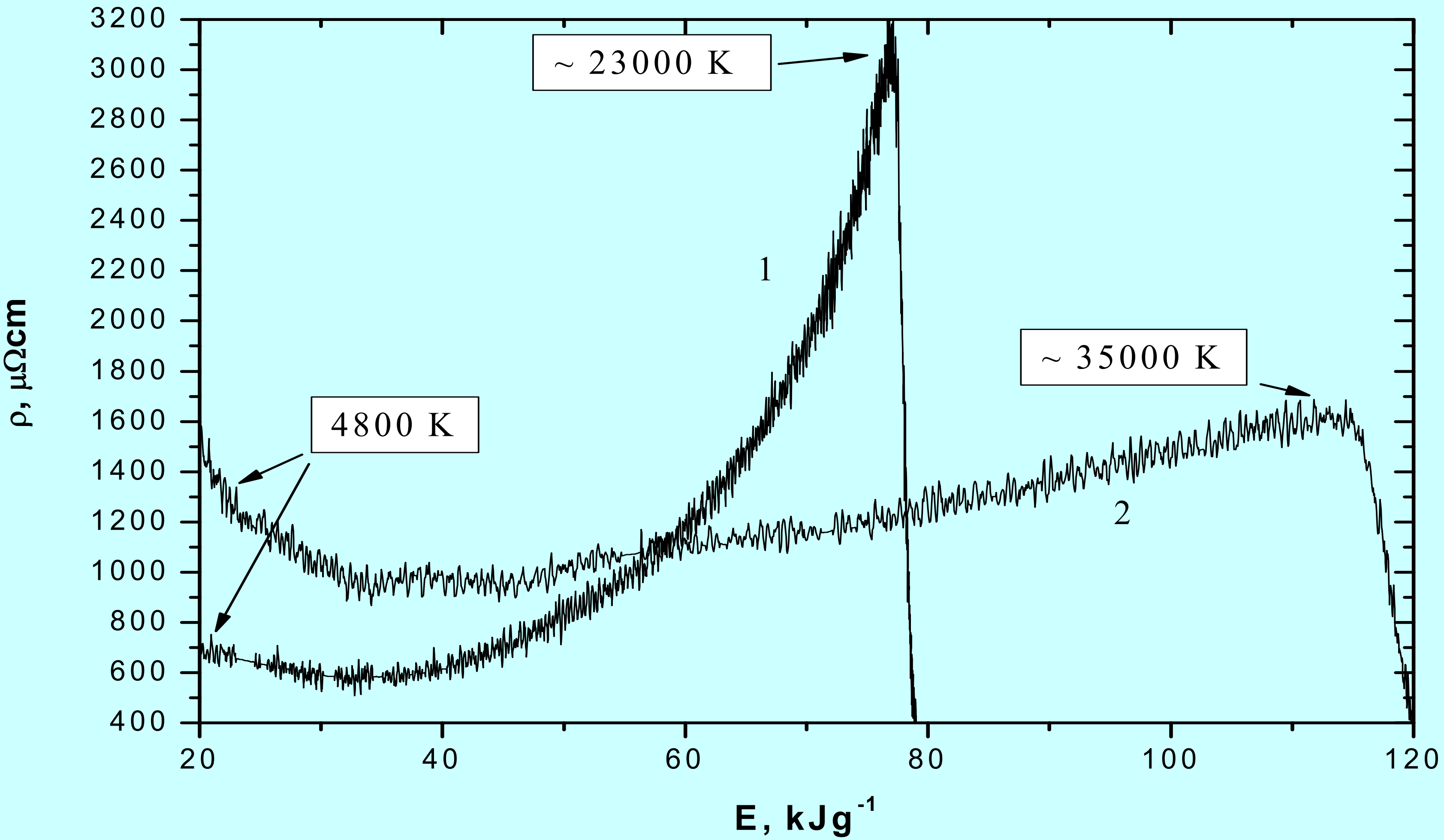
Static pressure: M.Togaya, Behaviors of liquid carbon at high pressure. Published in: VV. Brazhkin et al. (eds.), New Kinds of Phase Transitions: Transformations in Disordered Substances, **2002**; 255-66., Kluver Academic Publishers

Ось ординат – начало жидкого состояния (4800 К);
V/V_0 = 1.45 Диаметр 0.797мм, длина 15.2 мм (равна сапфиру),∅=0.96мм, D=10.8 мм;



Введенная энергия E

Fast heating of anisotropic ($V/V_0 = 1.25$) and isotropic graphite ($V/V_0 = 1.45$)



ЗАКЛЮЧЕНИЕ

- 1. Показано, что более высокая плотность жидкого углерода (как и жидкого вольфрама и лития) имеет более высокое удельное электросопротивление. Таким образом, - это не исключение, а общее свойство веществ при высоких давлениях, которое проявляется при различном уровне приложенных давлений. Для вольфрама – низкий, для углерода – 50 кбар, для лития $\sim$ 600 кбар.

- 2. Методика быстрого импульсного нагрева электрическим током позволяет получать экспериментальные данные по свойствам проводящих веществ (металлы и углерод) до весьма высоких температур: для углерода достигнута температура 35000 К - оценка по теплоемкости и введенной энергии (для плотности углерода 1.4 г/см^3).

- 3. Эта же методика способна обеспечить создание высоких импульсных давлениях (до сотни кбар). Давление может быть измерено по сдвигу линии люминесценции рубина в спектре как показано в работах: (Коробенко, Рахель, Фортов).

CONCLUSION

- Liquid carbon (volume) density at the melting line under low pressures is rather small ~ **1.0-1.2 g/cm³**). It is much higher (**1.8 g/cm³**) at higher pressures ($P > 50$ kbar).

- In experiments far above melting point during the isochoric process of heating (up to **E =** 110 **kJ/g, T ≈ 35,000 K**), the derivative $d\rho/dE$ varies from negative to positive in a wide range of high energy input (E = 25 - 45 kJ/g) for different densities.

- It should be mentioned that the transition to metal-like properties at the input energy E (75 kJ/g) leads to higher values of resistivity ρ (**3000 μΩ·cm**), which are higher than those for liquid semi-metal carbon near melting (**~ 700-800** μΩ·cm, but for lower pressures and at lower temperatures).

  The main achievement of our experiment at a high input energy is the dependency of the specific resistivity on the density: the higher the density, the higher the resistivity of the liquid carbon.
  Apparently, the increase of the resistivity under a high pressure (or/and for a higher density) is a common behavior for metals, semi-metals, and semi conductors in liquid state.

THANK YOU

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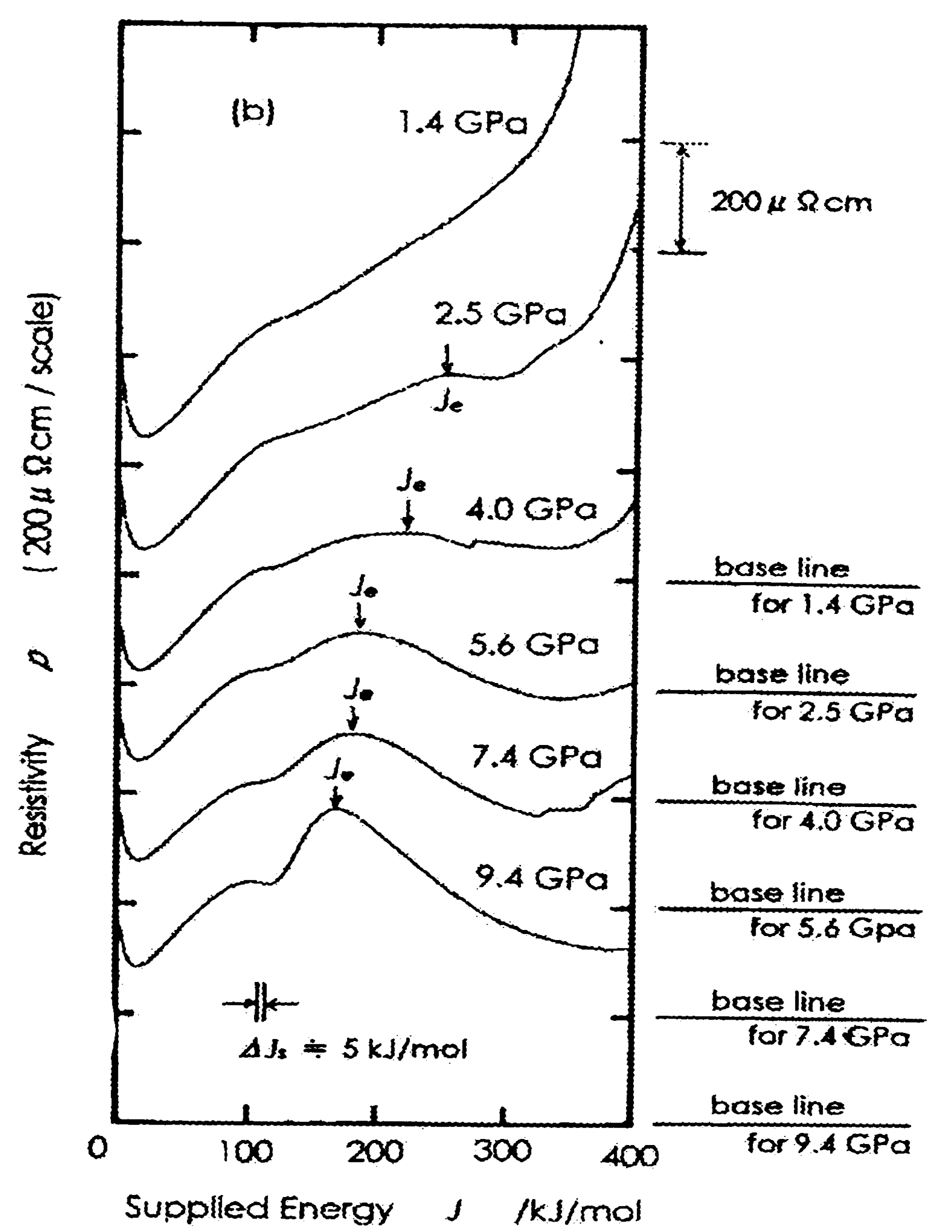
Электросопротивление углерода при плавлении (M.Togaya)

Je – окончание плавления



Падение сопротивления после значка

J_e – признак завершения плавления.

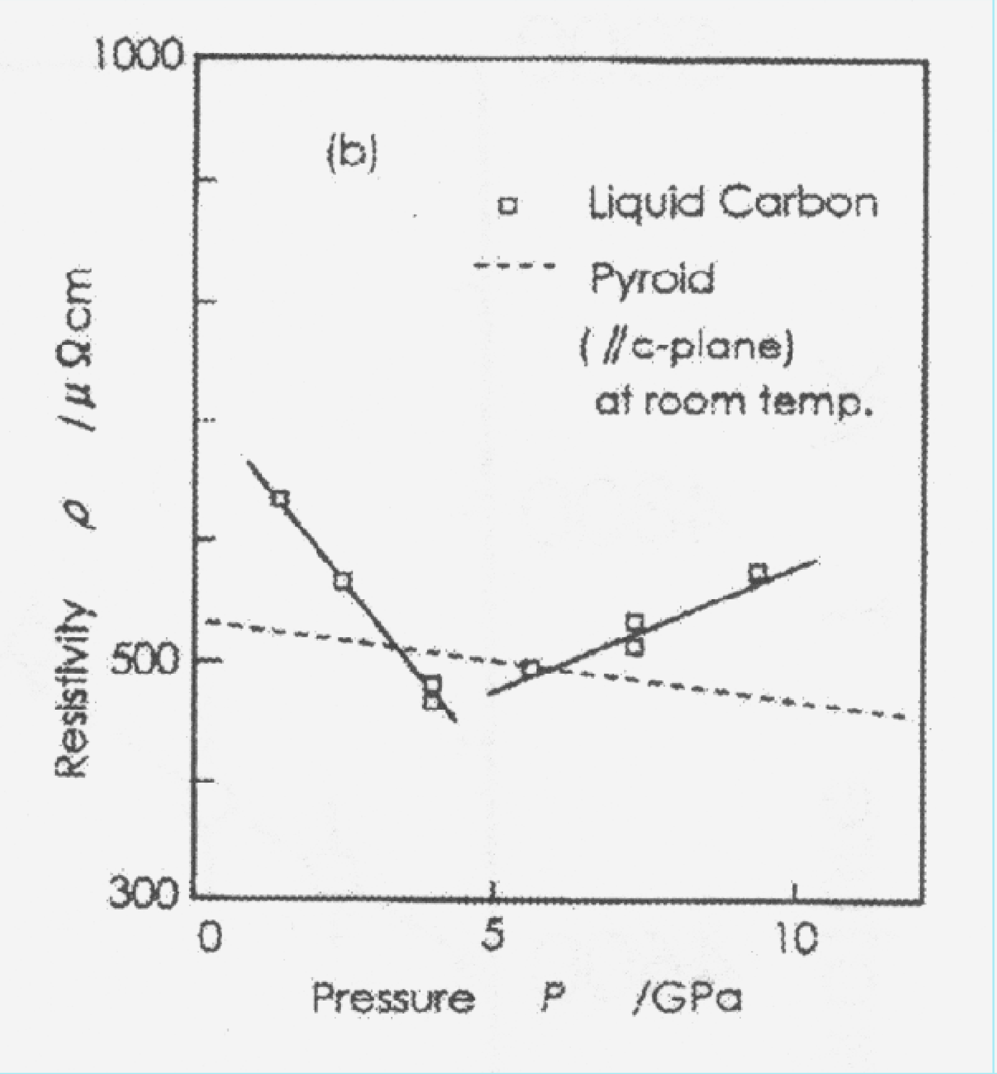
При P менее 25 кбар сопротивление жидкости растет.

Данные М.Тогайя для J_e при окончании плавления

25 кбар	**20.8 кДж/г**
40 кбар	**18.3**
56 кбар	**15.8**
74 кбар	**14.6**
94 кбар	**14.2**

Таким образом, с ростом давления плавление завершается раньше

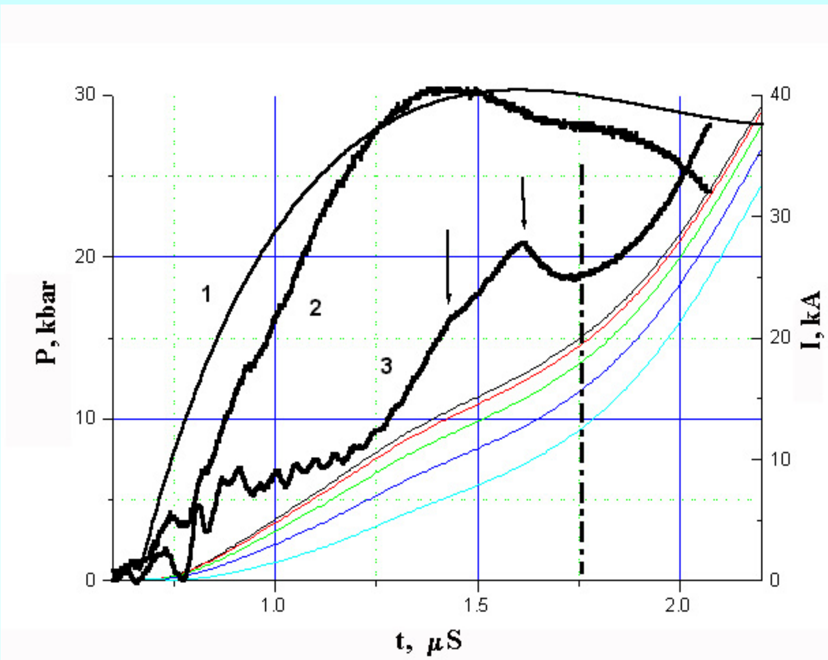
The data of M.Togaya (Japan): the liquid carbon resistivity at the melting point versus pressure

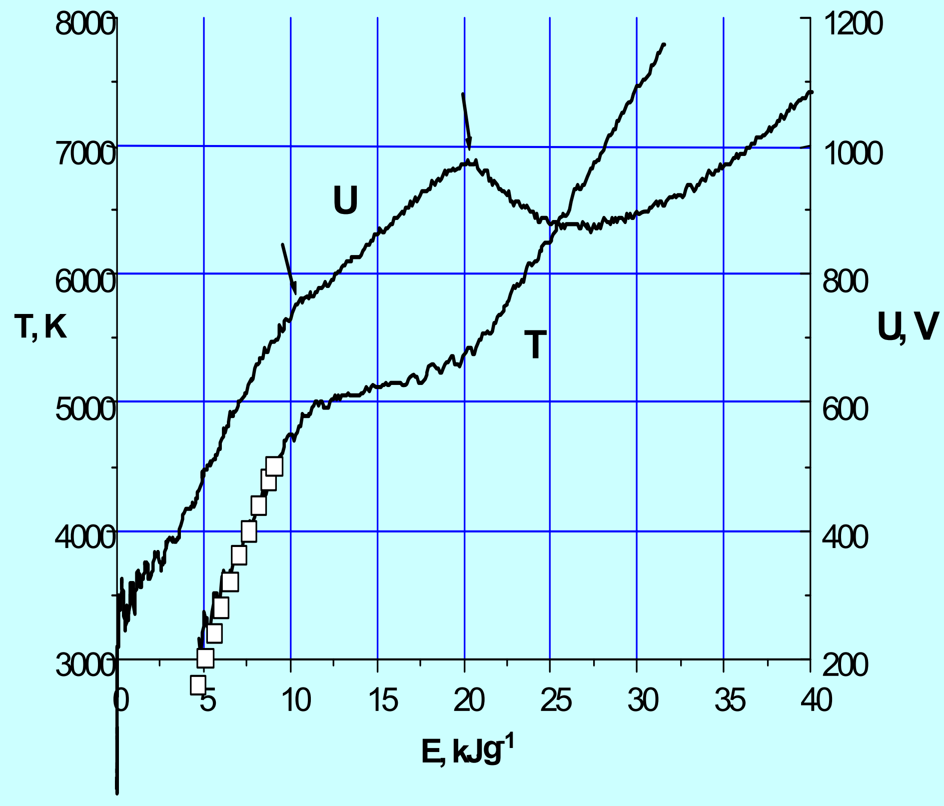


- Initial pyrolytical graphite with the density 2.2 g/cm3.
- The specimens were heated in the wall material MgO.
- Solid lines – experiments with the graphite melting under pressure;
- Dashed line - experiments under pressure but without heating.
- M. Togaya show the parameters of the points (in the Figure) of the dependence resistivity ρ against imparted energy E **for melting point.**

Melting of the annealled pyrolytic graphite (thin strip) placed between thick glass plates

Left side. 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 (10-15 kbar at melting), the lower line – for the surface graphite layer.
Right side. Melting of the graphite (thickness of the strip 0.4 mm) during 2 μs heating. U – voltage; T –temperature. Squares –exp. data of M.Sheindlin and V.Senchenko.

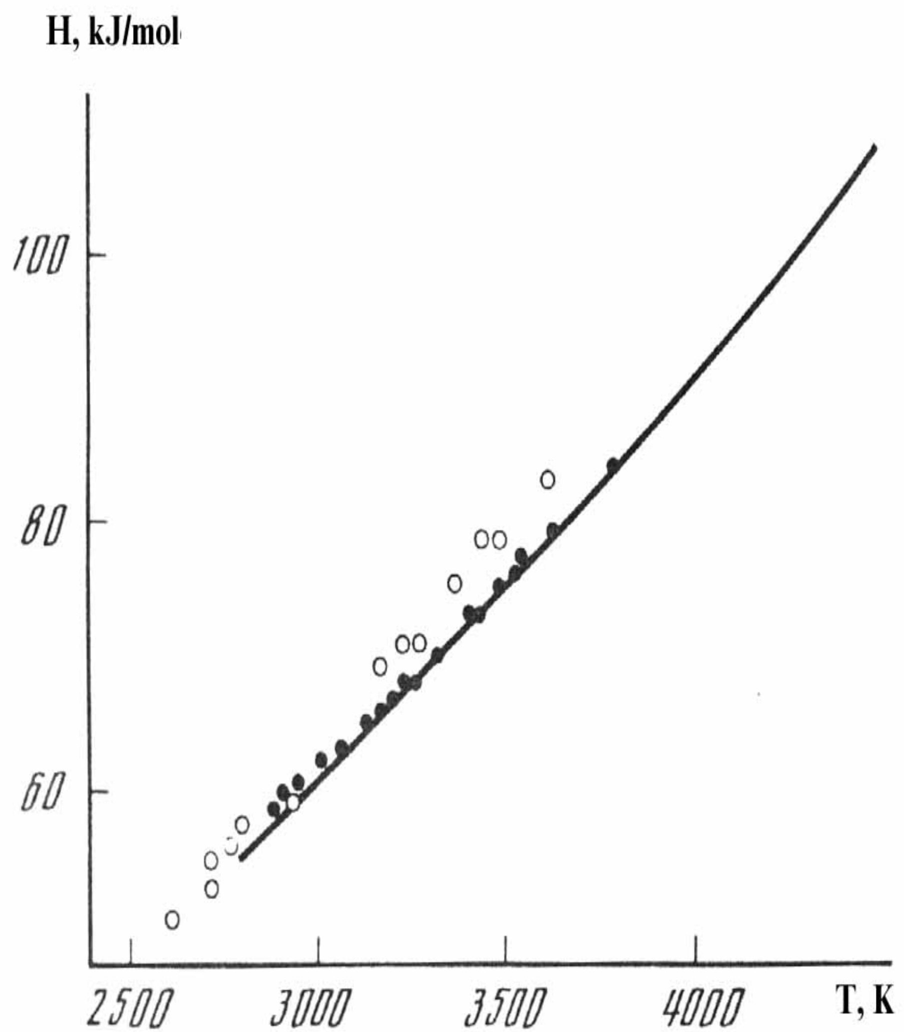




TEMPERATURE CALIBRATION

Graphite enthalpy versus temperature for grade UPV-1T

Sheindlin MA, Senchenko VN. Experimental investigation of graphite thermodynamical properties in the vicinity of melting point. Sov Phys Dokl 1988;33(6):142–5.



Solid line: measurements of M.Sheindlin and V.Senchenko.

- Solid circles: data of steady-state measurements of 1984.
- Hollow circles: steady-state measurements of 1972.
- According to Fig. the enthalpy at 4500 K is equal to 9.1 kJ/g.
- Note, that according to another calculations the enthalpy at
- 4500 K is equal to 9.2 kJ/g.
- The error in enthalpy measurements - 2.5% at the T up to 4500 K. The error in temperature measurements - 2%.

Evaluation of graphite expansion under melting (at low pressure !)

To cite the equation of Clapeyron-Klausius in the next form for graphite melting point, provided that the equation is valid for unisotropic substance (graphite):

$$\mathbf{V_{liquid} / V_{solid} = 1 + H_{melting} / V_{solid} (T_{melting} \times dP/dT),}$$

where V_{liquid} - volume of the liquid phase at melting point;

V_{solid} - volume of the solid phase at melting point (~ 1.2-1.3V_0 - literature datum);

$H_{melting}$ - heat of melting (**10 kJ·g^{-1}** - our measurement).

Heat of graphite melting: E(liquid) - E(solid) = 10 kJ·g^{-1}.

$T_{melting}$ - melting temperature (**4800 K** - our measurement);

dP/dT = **54 bar·K^{-1}** according to measurements of Vereshcagin (Russia).

Then we have: $\mathbf{V_{liquid} / V_{solid} \sim 1.7}$

As it turned out the graphite expands significantly (the expansion consists of ~ 70 %) during melting. For the expansion of the substance during melting and value of resistivity in liquid state the melted carbon retains covalent bonds, which usually characterise solid graphite.

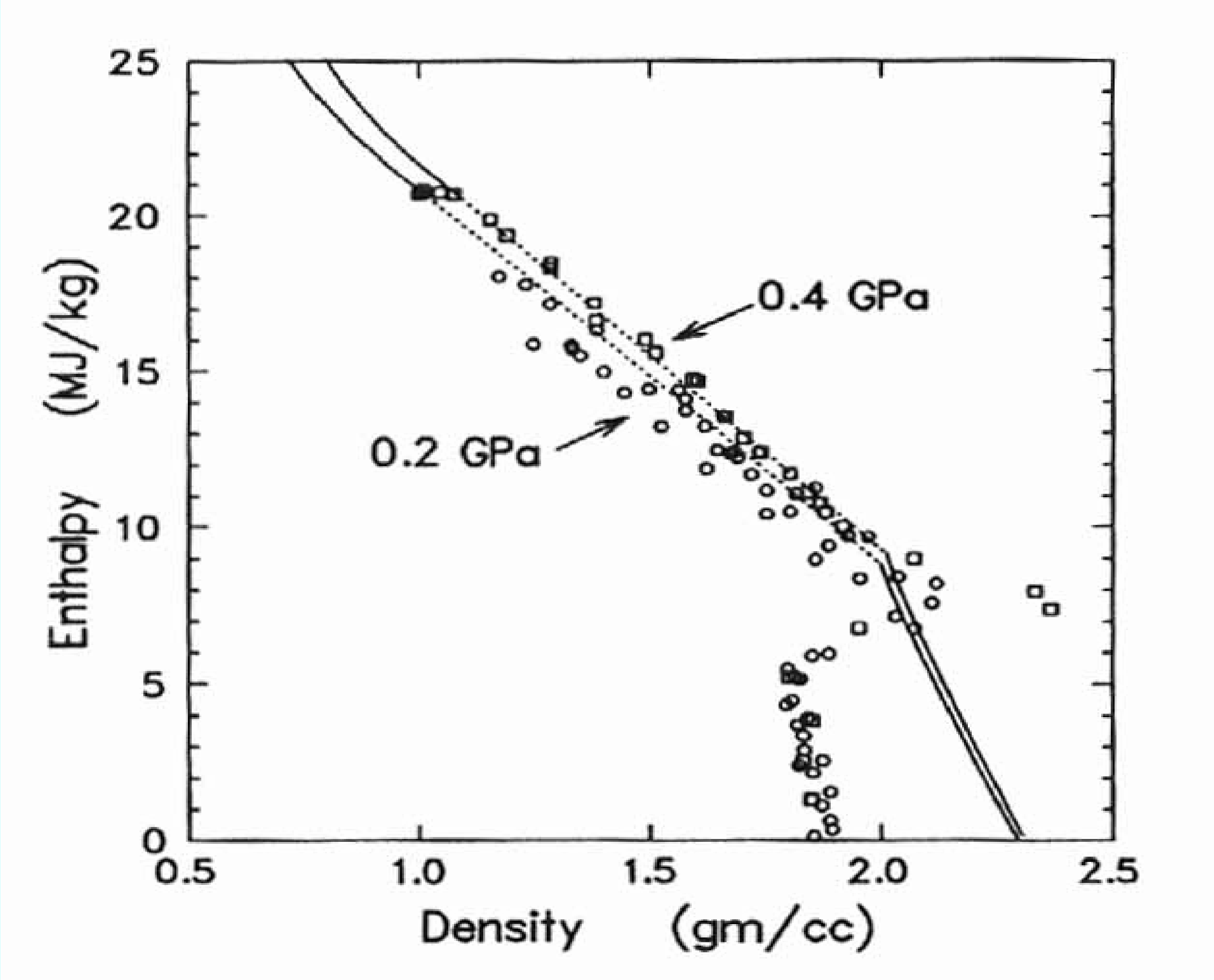
Our data, published in 1993, revealed a relative increase in the volume V/V0 = 1.67 with the specific energy input of 18.5 kJ/g, which is close to the end of melting at 20.5 kJ/g.

G.Pottlacher et al. in 1993 year have mentioned: "*by the time graphite melts it is roughly two-fold expanded*". This remark is confirmed by the opinion of M.Sheindlin and V. Senchenko (JIHT, private communication) based on their unpublished experiment.

J.W.Shaner gives two-fold expansion of carbon after the melting. Remind his result in the next slide.

Graphite expansion of low initial density

Gathers G R, Shaner J W, and Young D W Report UCRL-51644 (Lawrence Livermore Laboratory 1974) Microseconds pulse heating (Contracting solid graphite at the imparted energy 5-7 kJ/g ! It is confirmed by our experiment, see next slide)

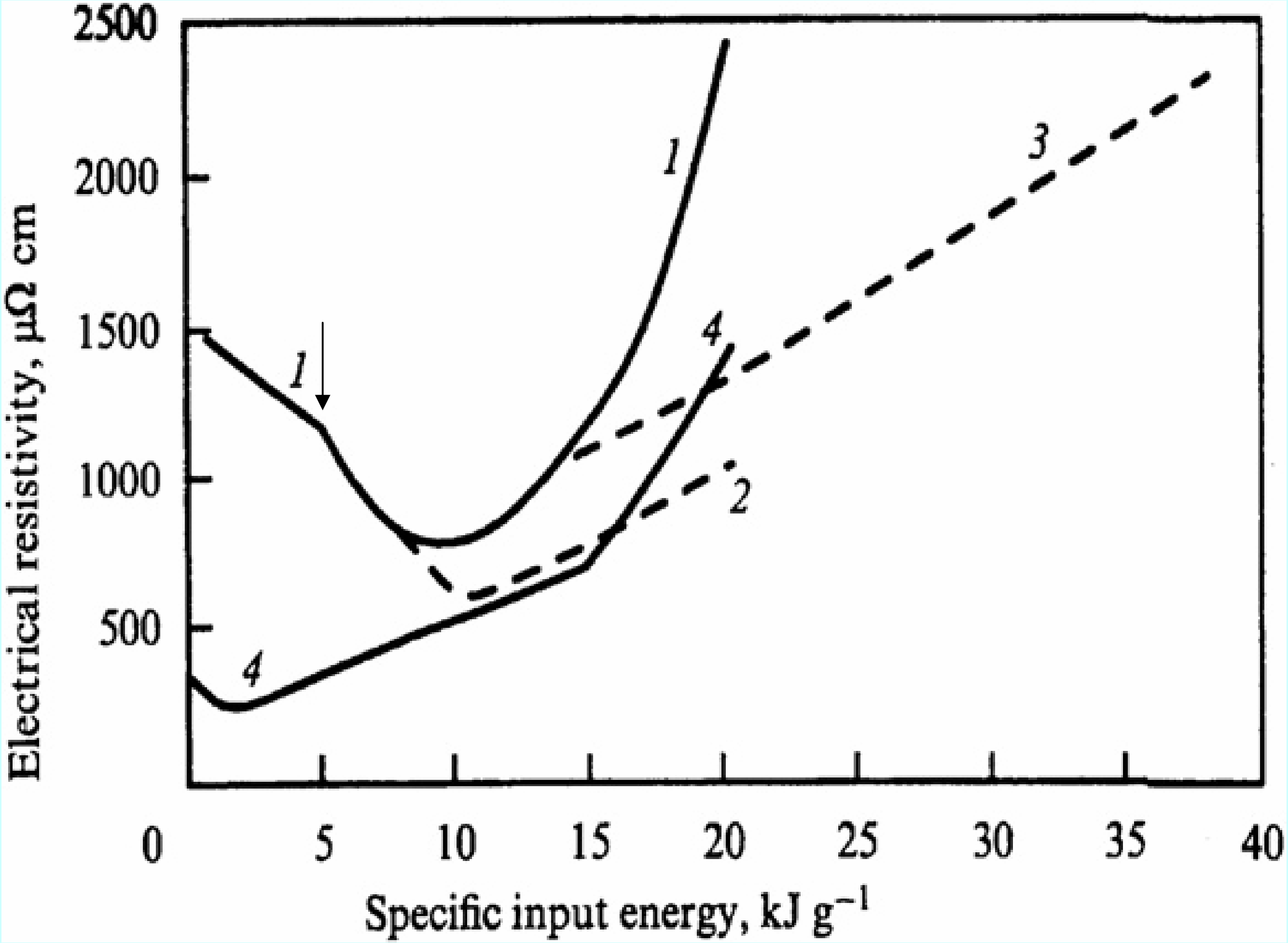


Pulse heating of graphite specimens of different initial density

Resistivity **ρ** versus imparted energy **w** for specimens heated in a water (1) and in the capillary tubes (2-3). Vcapillary/ Vgraphite = **1.84** for (3) and **1.2** for (2).

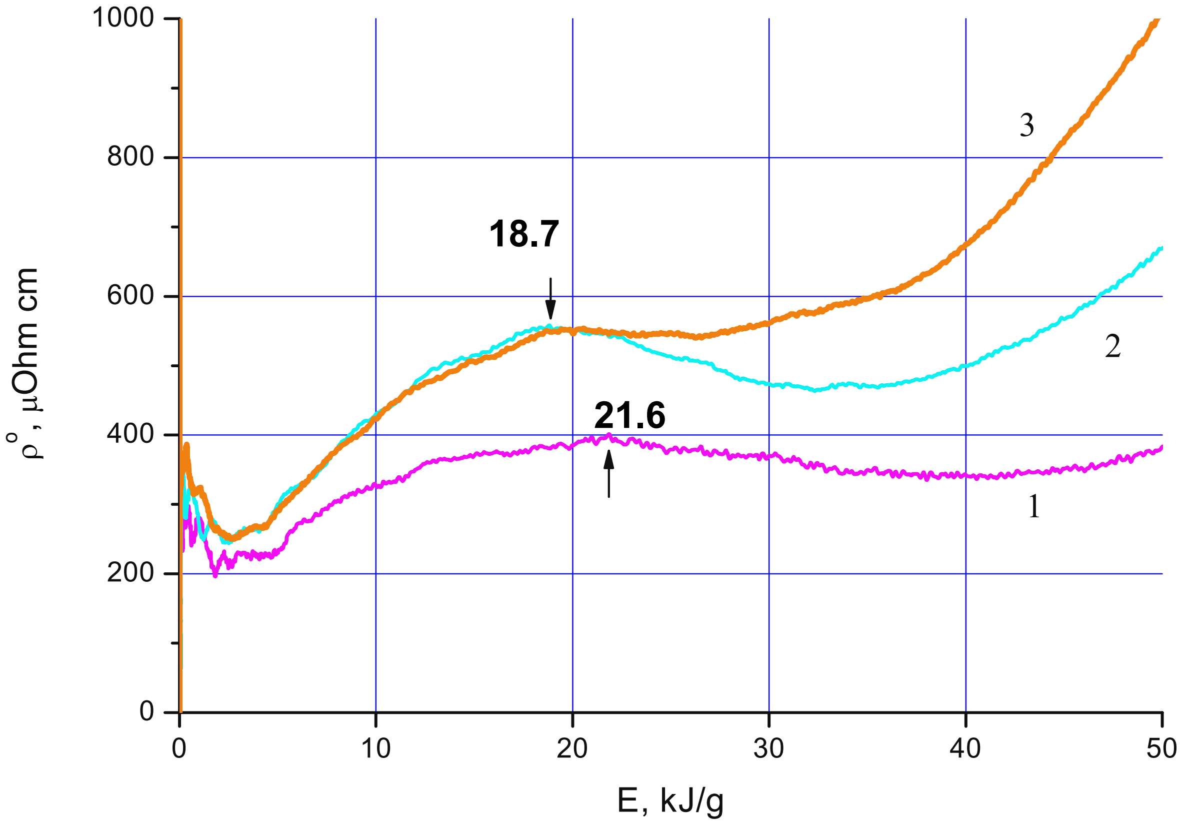
Graphite of high density (4)

Arrow shows the contracting graphite of low density in solid state at E ~ 5 kJ/g.



Resistivity ρ0 (referred to initial dimensions) for graphite UPV-1T at fast (microseconds) isochoric heating for different carbon density.

1 – Density γ = **1.1** g/cm3 (V/Vo = 2); 2 - Density γ = **1.76** g/cm3 (V/Vo = 1.25);
3 - Density γ = **1.88** g/cm3 (V/Vo = 1.17);
One can see that the finish of melting begins at higher input energy for lower density (lower pressure), - curve 1.



M.Togaya: 20.8kJ/g – 25 кбар; 18.3 kJ/g – 40 кбар

Детали последнего выстрела

- Графит MF-307 диаметр 0.787 мм (после расчета по весу p=0.0165 г дл длины 16.536 мм, получен диаметр 0.797 мм; отличие 1.3%). В сечении – круг. В расчет взят диаметр 0.797 мм. Так как он – эффективный (средний по массе). Тогда $V/V_0 = (0.96/0/797)^2 =$ **1.45.** Длина сапфира 15.124 мм.
- Данные В.Н.Коробенко. Длина графита и сапфировой трубки 15.2 мм; масса графита 15.42 мг; сечение (чего ?) 0.00507 $см^2$.