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MAGNETIC SUSCEPTIBILITY OF EVAPORATED CARBON

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The results of measurements of the magnetic susceptibility of evaporated carbon are presented. The samples were prepared from high purity carbon by electric arc evaporation in vacuum and in Ar atmosphere. Measurements were performed between 77 and 1400 K using a Faraday–Curie balance. Changes in both the paramagnetic and diamagnetic parts of susceptibility due to the presence of Ar during the evaporation process as well as heat treatment were investigated.

1. Introduction

Magnetic susceptibility of carbon depends heavily on its crystalline structure. It may vary considerably, reflecting a variety of crystalline structures in which carbon occurs.

For the object of the present investigations evaporated carbon was chosen. It combines high purity with a high disorder of crystalline structure, which allows the investigation of early steps of graphitization without chemical complications, appearing for instance during the carbonization of organic compounds.

During the last decade ESR of evaporated carbon has been investigated [1–3]. The main results of those investigations are that the concentration of unpaired electrons may reach up to 10^{20} per gram, and it decreases considerably when carbon is annealed at a relatively low temperature.

ESR is a powerfull and commonly used method of investigating carbons. The main advantage of ESR is its high sensitivity. However, when one has to deal with low intensity broad lines or samples with high electrical conductivity, ESR results are charged with considerable errors. It has been shown [1] that in such a case the static magnetic sucseptibility measurements may supply more accurate results than ESR does, provided that concentration of unpaired electrons is high. Moreover, the static measurements supply information concerning the diamagnetic part of magnetic susceptibility which are not available by ESR. In fact, the static method gives the net result of paramagnetism and diamagnetism of the sample. Fortunately, the total susceptibility may be decomposed on the basis of the temperature dependences.

Paramagnetism of localized unpaired electrons located in crystalline defects of carbon

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obeys the Curie law expressed by the equation

$$\chi^{\text{para}} = \frac{N\mu_B^2}{kT}, \tag{1}$$

where N is the number of unpaired electrons per gram, μ_B is the Bohr mageton, k is the Boltzman constatnt and T is the temperature in degrees Kelvin. Diamagnetism of carbon is in general anisotropic. For policrystalline samples it may be expressed by its mean value [4]

$$\bar{\chi}^{\text{dia}} = \bar{\chi}_0 + \frac{K_0}{3}(1-e^{-\frac{\theta}{T}}). \tag{2}$$

The first term $\bar{\chi}_0$ represents a temperature independent component. It originates from all the electrons present in the crystalline lattice, e.g., σ and π electrons. The second, temperature dependent term, represents the Landau diamagnetism of free electric charge cariers. K_0 and θ are the parameters depending on the concentration and effective mass of free charge carriers. Eqs (1) and (2) enable one to separate the magnetic susceptibility into three components: pararamagnetism of localized unpaired electrons, diamagnetism of crystalline lattice, and that of free charge carriers[1].

2. Experimental

The samples of evaporated carbon were prepared by arc evaporation using a technique similar to that applied by Antonowicz et al. [1]. As a starting material, spectroscopically pure pyrolytic carbon electrodes were used. 500 A a.c. arc discharge was ignited in the centre of a 25 cm diam. glass vessel connected to the high vacuum and Ar pressure control systems. The carbon deposit condensed on the walls of the vessel. Intense arc radiation heats the deposit, therefore, to avoid undesirable structural changes, evaporation was carried out in about 1 second intervals with about 1 minute breaks. 50 ignitions produced about 100 mg of deposit — the amount necessary for preparing one sample. The carbon deposit was scraped from the vessel after the admission of air. The deposit prepared in Ar was very easy to scrape. On the contrary, the one prepared in vacuum adhered to the glass so tightly that it was almost impossible to scrape it. To avoid this difficulty, evaporation in vacuum was followed by a short evaporation in $1.6 \cdot 10^{-1}$ Tr of Ar, producing a thin, easy to scrape film on which the main deposit was condensed.

Magnetic susceptibility measurements were performed using the Faraday–Curie method. The method is based on measuring the force F_x exerted on a sample of mass m by an inhomogeneous magnetic field H, according to the equation $F_x = \frac{1}{2}\chi m \frac{\partial}{\partial x} H^2$. The apparatus was modelled on that described by Pacault et al. [5]. F_x and m were measured using a sensitive antimagnetic silica spring balance. Optical reading of the balance enabled measurements within an accuracy of 0.02 mg. The sample was placed in a tiny fused silica

[1] Paramagnetism of free charge carriers depends on the temperature in the same manner as diamagnetism does [4], therefore it is not possible to separate it on the basis of static magnetic susceptibility measurements. Fortunately, it is much smaller than diamagnetism, therefore it may be neglected.

container of temperature independent magnetic susceptibility. In order to eliminate the electrostatic forces, the container and inner walls of a fused silica tube in which the sample was hung were coated with an optically semitransparent but electrically conductive carbon film, produced by pyrolysis of benzene vapor. The poles of the electromagnet were specially shaped [6] in order to have the factor $\frac{\partial}{\partial x} H^2$ constant over the whole volume of the sample. In this way, loss of accuracy due to inhomogenity of the powder samples was avoided. The apparatus was calibrated doubly using distilled water and sugar as the standards. For a typical sample with magnetic susceptibility $1 \cdot 10^{-6}$ e.m.u. g^{-1}, the absolute and relative accuracies of about 5% and 1% respectively were achieved. The apparatus was equipped with a cryostat and a furnace covering the temperature range between 77 and 1400 K. The samples were heat treated in vacuum already placed at the balance and then measured in 1 Tr He atmosphere. Presence of He improved heat transfer and damped balance oscillations. The heat treatment to higher temperatures was performed in a separate vacuum furnace, where the samples were placed in a carbon crucible.

3. Results

The results of magnetic susceptibility measurements are presented in Fig. 1 — 5. Fig. 1a shows the magnetic susceptibility of carbon evaporated in vacuum versus the reciprocal of temperature. The sample was outgased and heat treated at 200°C for 20 minutes

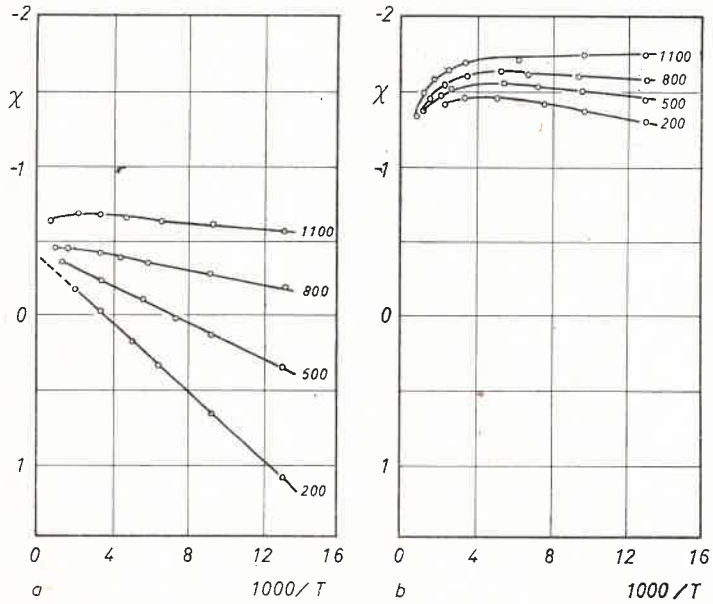

Fig. 1. Magnetic susceptibility of evaporated carbon heat treated at the indicated temperatures, versus the reciprocal of temperature: a) carbon evaporated in vacuum, b) carbon evaporated in 1.1 Tr of Ar

[2] Further in the text and figures the magnetic susceptibility is quoted in 10^{-6} e.m.u.g^{-1} and the units are omitted.

then cooled down in steps, magnetic susceptibility measured each time. As a result, the curve indicated by number 200 was plotted. In a similar way, the next heat treatments at 500, 800 and 1100 °C and successive magnetic suceptibility measurements were performed. The same procedure was applied to the sample evaporated in 1.1 Tr of Ar and the results are shown in Fig. 1b.

Comparing both figures, one may see that heat treatment as well as the presence of Ar during evaporation strongly influence magnetic susceptibility of evaporated carbon. Closer inspection of Fig. 1a shows that carbon evaporated in vacuum and then heat treated at 200°C is weakly diamagnetic at room temperature, and strongly paramagnetic at lower

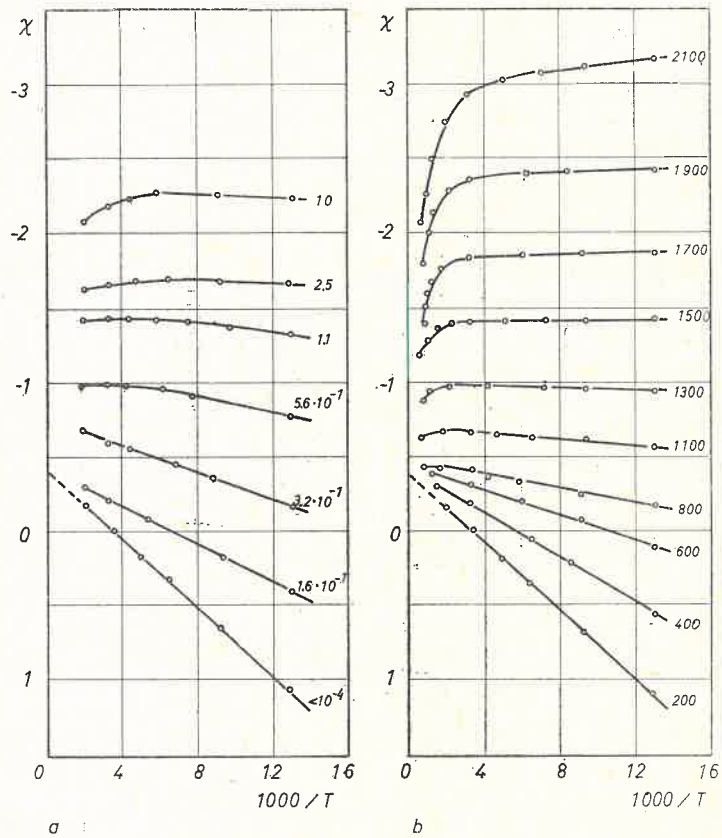

Fig. 2. Magnetic susceptibility of evaporated carbon versus the reciprocal of temperature: a) carbons evaporated in indicated pressures of Ar and outgased at 200°C, b) carbon evaporated in vacuum and heat treated at the indicated temperatures

temperatures. Experimental points lay on a straight line which means that paramagnetism obeys the Curie law. Application of Eq. (1) gives the concentration of unpaired electrons $N = 1.9 \cdot 10^{20}\ g^{-1}$. Extension of the straight line up to infinite temperature (dotted line) gives the temperature independent diamagnetism $\bar{\chi}_0 = -0.4 \pm 0.05$. For higher heat treatment temperatures, the experimental points lie on straight lines with decreasing slope

which means decreasing concentration of unpaired electrons. In fact, the straight lines are really straight in the low temperature range only. In the high temperature range they are slightly curved which according to Eq. (2) may be interpreted as the trace of Landau diamagnetism.

As may be seen in Fig. 1b, carbon evaporated in Ar atmosphere behaves quite differently. Its paramagnetism evaluated from measurements in the low temperature range is about one order of magnitude smaller. The curvature in the high temperature range is much more prominent than previously, indicating that the Landau diamagnetism is now dominant. Heat treatment to 1100 °C destroys paramagnetism practically completely,

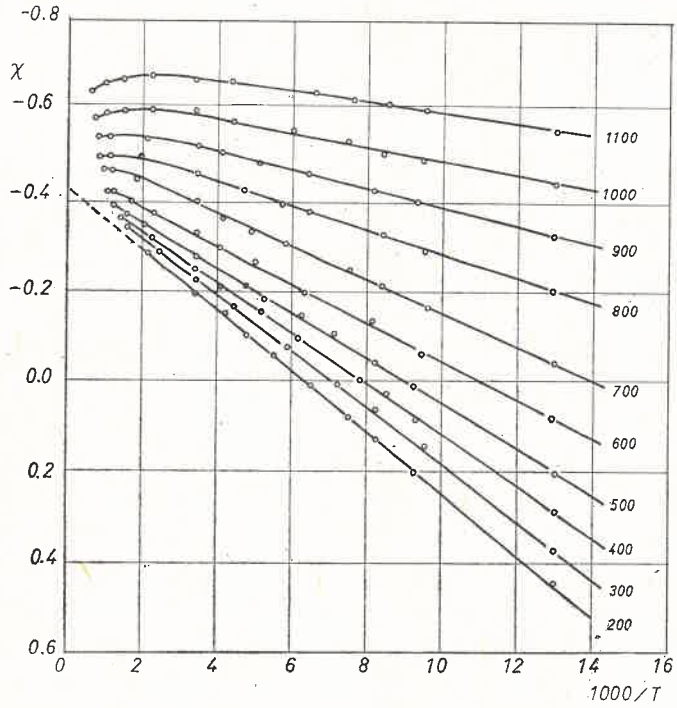

Fig. 3. Magnetic susceptibility versus the reciprocal of temperature for carbon evaporated in 1.6 10^{-1} Tr of Ar and heat treated at the indicated temperatures

while diamagnetism seems to be almost uninfluenced. Formally, the parameters $\bar{\chi}_0$, K_0 and θ of Eq. (2) may be chosen to fit the experimental curve. However, in the case under consideration this cannot be done within reasonable error, so nothing can be said about temperature independent diamagnetism $\bar{\chi}_0$.

Measurements performed in wider ranges of heat treatment temperatures and pressures of Ar are presented in Fig. 2a and 2b respectively. It is clearly evident from here that the increase of Ar pressure leads to results quite similar to those arising from increase of heat treatment temperature. For instance, evaporation in 10 Tr of Ar produces carbon magnetically equivalent to that evaporated in vacuum and then heat treated at 1900 °C, at least as far as diamagnetism is concerned.

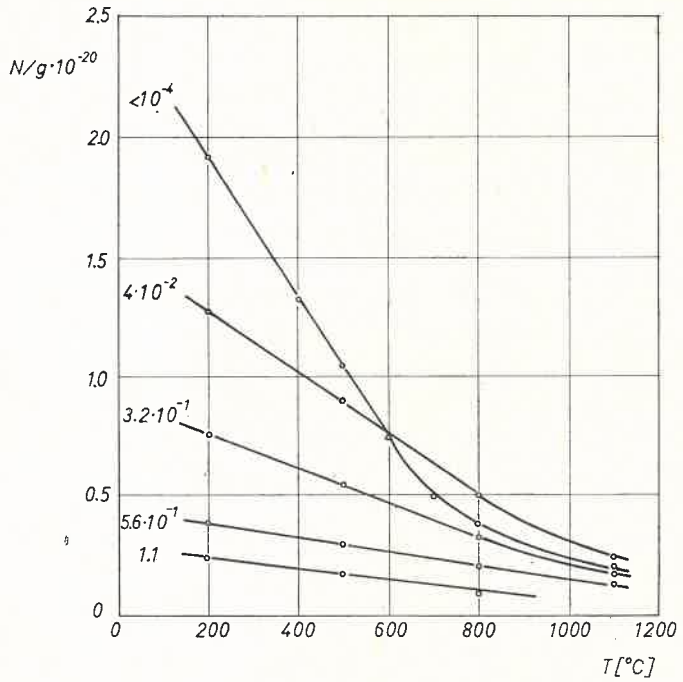

Fig. 4. Concentration of unpaired spins versus heat treatment temperature for carbons evaporated in indicated pressures of Ar

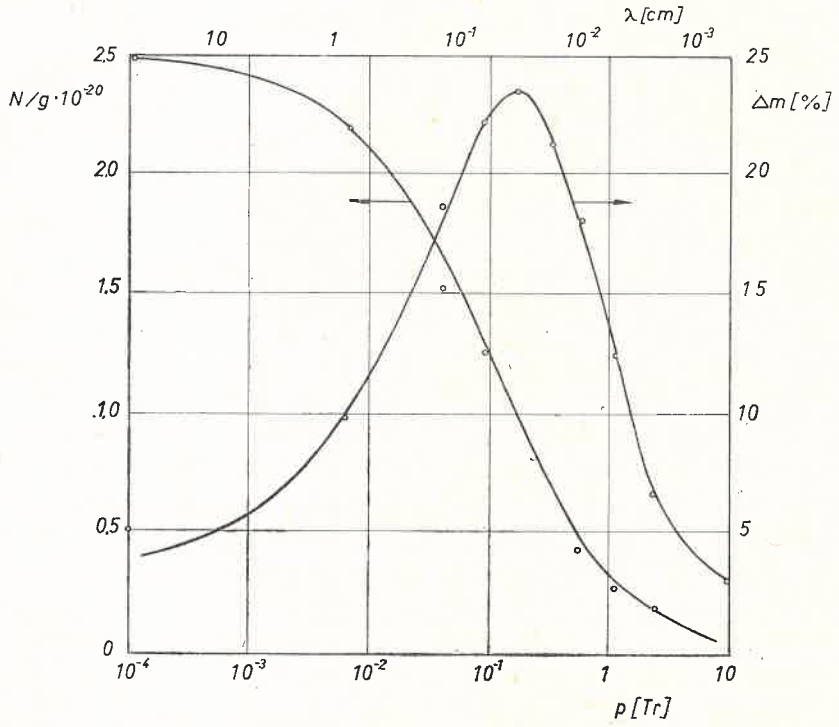

Fig. 5. Initial concentration of unpaired spins and amount of desorbed gases versus the pressure of Ar (or mean free path)

More detailed studies were performed on the sample of carbon evaporated in medium pressure of Ar, namely $1.6 \cdot 10^{-1}$ Tr. This sample was heat treated in 100 °C steps and the results of magnetic susceptibility measurements are presented in Fig. 3.

For carbons evaporated through the whole range of Ar pressures a decrease in paramagnetism due to heat treatment was evaluated. This is presented in Fig. 4 in terms of unpaired spins concentration. Linear extrapolation of the curves in Fig. 4 up to room temperature enables one to evaluate the initial concentrations expected in case the samples had not been heat treated. Those are plotted in Fig. 5 versus the pressure of Ar.

Considerable decrease in mass of the sample during heat treatment was observed due to desorption of gases. It may be treated as a measure of the surface area of carbon. The amount of desorbed gases rises with heat treatment temperature reaching at about 1000 °C a limiting value which depends on the pressure of Ar during evaporation. As it may be seen in Fig. 5, maximal decrease of mass, close to one fourth of initial mass of the sample was observed for carbon evaporated in $1.6 \cdot 10^{-1}$ Tr.

4. Discussion

Magnetic suceptibility of evaporated carbon may be discussed by comparing it with that of fine ground [7, 8] and neutron irradiated carbons [9, 10]. In both of these carbons as well as in evaporated carbon, the crystalline structure of the starting material — for instance graphite — is partially destroyed by purely physical agents. As destruction proceeds, the paramagnetism originating from broken unsaturated bonds increases [7, 9], while the Landau diamagnetism decreases with mean free path of electric charge carriers decreasing [8, 10].

Taking into consideration the very high sublimation temperature of graphite one may expect that evaporated carbon condensed at room temperature is supercooled and, therefore, [11] should display the highest frozen disorder of crystalline structure and be paramagnetic. It is so indeed, however, that because of the complicated character of sublimation of carbon some additional remarks are necessary.

Carbon vapor consists of C_1, C_2, C_3, C_4 and larger molecules, with C_3 most abundant [12, 14]. The hot surface of carbon emits also crystalline particles a few nm in size [13, 14]. Contribution of vapor and crystalline particles to the mass transport depends on the crystalline structure of carbon and the temperature of sublimation. The conditions of sublimation applied in the present work, e.g. pyrolytic carbon electrodes and high current arc favour mass transport by vapor [14].

If evaporation is carried out in vacuum a shining metallic deposit originates. Despite such appearance it is highly amorphous [11, 15, 16]. Electron diffraction reveals the crystallites about 1 nm in diameter and numerous interstitials located between turbostratic layers [16]. Interstitials and atoms located at the edges of crystallites possess unsaturated bonds. Those are considered as the localized paramagnetic centres [3]. Heat treatment provides the activation energy for diffusion of defects and creation of new bonds. As a result, the crystalline structure improves and consequently the paramagnetism and diamagnetism decreases and increases respectively.

If evaporation is carried out in the presence of Ar, it produces a carbon black like deposit. Condensation of carbon vapor is now influenced strongly by Ar, though the changes in composition of carbon vapor itself cannot be excluded. The vapor starts to condense in close vicinity of the arc where the temperature and pressure are high, producing aggregates instantly heat treated. The higher the Ar pressure, the larger the aggregates with higher equivalent heat treatment temperature. The aggregates are bound weakly to the surface of the previously condensed deposit covered with a layer of adsorbed Ar producing a porous deposit. A highly porous deposit is produced when the pressure of Ar is $1.6 \cdot 10^{-1}$ Tr (Fig. 5). If the pressure exceeds 10 Tr the carbon deposit grows mainly on the electrodes close to the arc. Such a deposit, heat treated from the very beginning at high temperature, was of no interest for the present work.

The highest concentration of unpaired spins, reaching $2.5 \cdot 10^{20}$ per gram was found in carbon evaporated in vacuum (Fig. 5). This concentration is equal to one unpaired spin per about 200 atoms. It is a rather high concentration, close to its natural limit, for 200 atoms is the order of size of graphitic planes in evaporated carbon [15] and no more than one unpaired spin per plane is expected [17].

Some spin centers are annealed out at heat treatment temperature as low as 200–300 °C (Fig. 3, 4). Similar unstable spin centers in neutron irradiated graphite have been observed and identified as single interstitial atoms and small groups of few interstitials located between graphitic planes [18]. Those in evaporated carbon may be identified as interstitials too [3]. During heat treatment interstitials migrate to the edges of crystallites where they are bound. An order at the edges of crystallites grows and the spins are paired. The higher the heat treatment temperature, the larger are the groups that become mobile. At about 200 °C those are the groups of three interstitials [18]. It seems evident that these are the very groups that must be present in evaporated carbon too, for C_3 molecules are mostly abundant in vapor. Above 500 °C, in addition to the migration of interstitials, migration of vacancies occur [18], leading to further rearrangement of the crystalline structure and annealing of unpaired spins. Localized spin centers are present up to heat treatment temperatures as high as about 1500 °C (Fig. 2b). This means that for complete annealing of some localized spin centers quite a large activation energy is necessary, close to that required for rapid growth of crystallites occurring above 1800 °C [19]. Those stable spin centers are likely located at the edges of crystallites and annealing them out is not possible unless some of the crystallites grow at the expense of the disappearance of others.

It is worth adding here that the ESR signal during heat treatment of evaporated carbon increases in width by about one order of magnitude and decreases in intensity by as much as four orders of magnitude and disappears at about 900°C [1]. On the other hand, static magnetic susceptibility measurements give for the heat treatment temperature 900 °C the concentration of unpaired spins of the order of 10^{19} per gram (Fig. 4). Therefore, the disappearance of the ESR signal should be interpreted as a result of excessive signal broadening, rather than complete annealing of spin centers.

Diamagnetism of carbon evaporated in vacuum and not heat treated is -0.40 (Fig. 2a, 2b). It is smaller than diamagnetism of diamond -0.49 [20] and the temperature independent diamagnetism of graphite -0.85 [21]. The increase of diamagnetism with

heat treatment temperature is attributed to the Landau diamagnetism. The Landau diamagnetism first appears clearly at the heat treatment temperature 600 °C (Fig. 3). For this and higher heat treatment temperatures the Dysonian distartion of the ESR signal is observed. Both observations show that the heat treatment at 600 °C causes considerable increase in electrical conductivity of evaporated carbon, in agreement with direct measurements [23].

After heat treatment at 2100 °C, the magnetic susceptibility measured at room temperature is -3.0 (Fig. 2b). Using the experimentally found dependence between magnetic susceptibility and the size of crystallites [23], one may estimate that L_a for crystallites in this carbon is about 6 nm, in agreement with structural investigations of evaporated carbon [3].

The insignificant part of the increase in diamagnetism of evaporated carbon during heat treatment may be attributed to the changes of tetragonal bonds (diamond like) into trigonal ones (graphite like) occurring at 700 — 1200 °C [15].

It would be interesting to measure the magnetic susceptibility without contact of evaporated carbon with the air as has been done in a case of ESR [1]. Unfortunately, accumulation of the required amount of evaporated carbon under vacuum is a much too difficult goal. On the other hand, lack of a strong correlation between the curves in Fig. 5 may indicate that the presence of adsorbed gases does not effect considerably the magnetic properties of evaporated carbon. This is so because among the gases adsorbed on the sample, physically adsorbed molecular oxygen only is paramagnetic one. During the outgasing a t200 °C it is desorbed or loses paramagnetism when chemically bound to the surface of carbon. The other gases, e.g. nitrogen and water vapor are weakly diamagnetic. Therefore, the adsorbed gases may contribute some extent to temperature independent diamagnetism, but in present measurements such efect was not observed.

The adsorbed gases appeared in an unexpected form — in explosions of the samples. The samples of carbon evaporated in vacuum, despite their minor quantity of adsorbed gases exploded during the outgasing if the increase in temperature exceeded 3 °C per min and the temperature reached about 150 — 200 °C. This effect may be tentatively explained by the sudden desorption of gases due to the sudden rise of temperature. Such a sudden rise in temperature has been observed for neutron irradiated graphite [18] as a result of releasing the Wigner energy stored in the strains of crystalline lattice. Without a doubt, strains are present in evaporated carbon too. Some observations [15] support an assumption that those strains may be released by avalanche, however calorimetric measurements are necessary.

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