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# Capillary pressure and electrical superconductivity of nano-sized graphite particles

***Yu. I. Boyko[1], V.V. Bogdanov[1], R. V. Vovk[1], B. V. Grynyov[2]***

[1] V.N. Karazin Kharkiv National University, Svobody square, 4, Kharkiv 61022, Ukraine
[2] Institute of Scintillation Materials of the STC "Institute of Single Crystals" of the National Academy of Sciences of Ukraine, 60 Nauky Ave., Kharkiv 61072, Ukraine

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The paper considers the possibility of achieving superconductivity in nanosized graphite particles due to the capillary pressure effect. Graphite has unique electronic properties due to its specific crystalline structure, but the low density of charge carriers limits its use as a superconductor. Hypothetically, the increase in pressure inside a graphite nanoparticle caused by surface tension can lead to a significant increase in the electron density and, as a consequence, to the occurrence of superconductivity at higher temperatures. This paper theoretically substantiates this hypothesis and estimate possible values of the critical temperature of the transition to the superconducting state.
**Keywords**: Superconductivity, graphite particles, electronic properties.

**Капілярний тиск та електрична надпровідність нанорозмірних частинок графіту**. *Ю. І. Бойко, В. В. Богданов, Р. В. Вовк, Б. В. Гриньов*

У роботі розглядається можливість досягнення надпровідності у нанорозмірних частинках графіту внаслідок ефекту капілярного тиску. Відомо, що графіт має унікальні електронні властивості, обумовлені його специфічною кристалічною структурою. Однак, низька густина носіїв заряду обмежує його застосування як надпровідник. Ми припускаємо, що збільшення тиску всередині наночастинки графіту, викликане поверхневим натягом, може призвести до істотного підвищення густини електронів і, як наслідок, виникнення надпровідності при більш високих температурах. Метою даної роботи є теоретичне обґрунтування цієї гіпотези та оцінка можливих значень критичної температури переходу до надпровідного стану.

## *1. Introduction*

Graphite consists of carbon atoms and has several modifications with different electron energy spectra and crystal lattice structures [1]. The most well-known and widely used modification of graphite has a hexagonal crystal lattice and an electron configuration $sp^2$ of carbon atoms. The specified crystallographic and electronic structure of graphite determines its physical properties; in particular, graphite has a specific temperature dependence of the electrical conductivity σ(T). At low temperatures, graphite has a fairly high electrical conductivity, similar to classical metals.

However, at elevated temperatures, the electrical conductivity of graphite increases with increasing temperature, similar to semiconductors. In addition, the density of free electrons in graphite $n \approx 10^{23}$ m$^{-3}$ ($n = N/V$, $N$ is the number of electrons, $V$ is the volume of the sample), that is $\approx 10^5$ times less than in metals. Based on its electrical properties, graphite is classified as a "non-degenerate" semiconductor [2]. The temperature dependence of the electrical conductivity of graphite is due to the structure of the electron energy spectrum. The energy spectrum contains regions of overlapping valence and conduction bands [3]. In addition, the low density of free electrons in the conduction band determines the low value of the Fermi energy: $E_F \approx 10^{-2}$ eV. For comparison, in metals, the average value of $E_F \approx 1$ eV.

The structural features of the electron energy spectrum of graphite and the low value of the Fermi energy make it possible to increase the number of free electrons under the influence of external factors such as pressure, external electric field, photon irradiation etc. A significant increase in the number of free electrons causes the so-called "metallization" of the substance. This means that the valence electrons in the "metallized" substance become "degenerate," i.e. their energy spectrum is described by Fermi-Dirac quantum statistics. In this case, the density of energy states in the vicinity of the Fermi level increases, i.e. a very important parameter $n^* = (dN/dE)$, which characterizes the quantum state of electrons, increases at energy values $E \approx E_F$. The increase in this parameter causes an increase in the electron pairing constant λ, i.e. the process of formation of so-called "Cooper" pairs of electrons – quantum particles capable of carrying an electric charge without resistance – becomes possible and is activated. Thus, "metallized" graphite can be an "electrical superconductor". The numerical value of the pairing constant determines the value of the critical temperature $T_c$ of the substance transition into a superconducting state [4].

This paper discusses the possibility of electrical superconductivity in nano-sized graphite particles. Moreover, superconductivity of these particles can be realized at higher temperatures than is observed in metals. We explain the effect by the fact that with a decrease in the particle size, the magnitude of the capillary pressure increases; as a result, the density of energy states of electrons near the Fermi level increases and, accordingly, the electron pairing constant λ increases, which ultimately leads to electrical superconductivity of graphite.

## 2. Physical parameters determining the critical temperature $T_c$ of the transition of graphite to the superconducting state

The pressure of all-round compression of a crystalline particle caused by the particle's tendency to minimize free surface energy (capillary pressure), is described by the formula:

$$p = 2\gamma / r. \tag{1}$$

Here γ is the specific free surface energy; $r$ is the characteristic particle size. Since for most substances $\gamma \approx 1$ J/m$^2$, then at $r \approx 10^{-9}$ m $= 1$ nm for a spherical particle we have: $p \approx 10^9$ N/m$^2 = 1$ GPa. A pressure of this magnitude is sufficient to "metallize" graphite particles of the specified size, i.e. to significantly increase the density of free electrons compared to the density of electrons in graphite particles of normal size ($\geq 100$ nm).

Indeed, in classical metals the pressure of "free electron gas" reaches a value $\approx 10^2$ GPa, which is associated with the high density of valence electrons $n \approx 10^{28}$ m$^{-3}$ [5]. From the above estimate it follows that the capillary pressure compressing a graphite particle of size $\approx 1$ nm can cause an increase in the density of free electrons to a value of $\approx 10^{26}$ m$^{-3}$. This value is $\approx 10^2$ times less than that of metals, but three orders of magnitude greater than that of graphite particles of normal size. This increase in the density of free electrons should be accompanied by a significant increase in the electron pairing constant λ, which determines the critical temperature $T_c$ of the transition of a substance to a superconducting state (BCS theory [4]).

Indeed, according to the theory, $\lambda = \mu \cdot n^*$. Here $\mu$ is the potential of the electron-phonon interaction, which determines the formation of "Cooper" pairs of electrons (electron pairing); $n^*$ is the density of electron energy states in the vicinity of the Fermi level. At $\lambda \leq 1$ (weak electron-phonon interaction, characteristic of classical metals) the transition temperature $T_c$ is described by the formula:

$$T_c \approx \theta \cdot exp\ (-1/\lambda). \tag{2}$$

Here $\theta$ is the Debye temperature. For most metals and metal alloys $\theta \approx 100$K, and the pairing constant $\lambda \approx (0.1 - 0.3)$ and, accordingly, for particles of these substances, the transition temperature to the superconducting state is in the range of values $(1 - 40)$ K, which is in good agreement with experimental data. For nano-sized crystalline graphite particles, due to their "metallization" as a result of capillary pressure, the pairing constant can reach values $\lambda \geq 1$. As already indicated, the parameter determining the numerical value of the pairing constant is the density of energy states in the vicinity of the Fermi energy level $n^*$. This parameter is estimated as:

$$n^* \approx N/E_F. \quad (3)$$

Since $E_F \sim N^{2/3}$, $n^* \sim N^{1/3}$ and, consequently, an increase in the number of electrons in nano-sized graphite particles by $\approx 10^3$ times should cause an increase in the pairing constant by $\approx 10$ times compared to metals. Thus, the electron pairing constant $\lambda$ of nano-sized crystalline graphite particles can reach the value $\lambda \geq 1$. For such values of the pairing constant, the temperature of the transition to the superconducting state is described by the formula [4], which is different from formula (2):

$$T_c \approx 0.2 \cdot \theta \cdot \lambda^{1/2}. \quad (4)$$

Substituting reasonable values of $\theta$ and $\lambda$ into formula (4), it is easy to verify that in nano-sized graphite particles, electrical superconductivity can manifest itself at a transition temperature $\approx 100$ K.

Of course, the indicated temperature $T_c$ is an estimate and may differ for graphite particles of a specific size and shape. In addition, it should be noted that the superconductivity of graphite particles, caused by the action of capillary pressure, differs in nature from the superconductivity realized in other modifications of graphite, for example, in "two-layer 2D graphite" (graphene) [6].

## 3. Conclusions

Based on the analysis and assessments made, the following conclusion can be drawn. Nano-sized crystalline graphite particles (with a size of $r \approx 1$ nm) can go into a superconducting state as a result of capillary pressure at a transition temperature $T_c \approx 100$ K, which is an order of magnitude greater than in classical metals.

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