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THE CONDUCTIVITY OF THE GRAPHENE-LIKE CARBON FILMS: ANOMALY IN THE 80–120 K TEMPERATURE RANGE

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The paper presents the results of conductivity studies in natural carbon films in the temperature range from 78 to 220 K. The data of structural studies using scanning electron microscopy and Raman spectroscopy are given. It has been found that the deposition of natural carbon on substrates with a conductive coating of indium oxide allows to obtain a new type of structure, that is, thin films, represented by homogeneous carbon nets, in the nodes of which are globular nano-sized particles in the form of distorted graphene planes. The behavior of the current-voltage characteristics of carbon films containing graphene-like fragments was studied by nanosecond voltammetry. It was established that the sample resistance sharply increased and the sample diamagnetism exhibited (persisting for 50 thermal cycles) at the critical temperature.

Keywords: graphene-like carbon, thin film, conductivity, nanosecond voltammetry, diamagnetism

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АНОМАЛИЯ ПРОВОДИМОСТИ ПЛЕНОК ИЗ ГРАФЕНОПОДОБНОГО УГЛЕРОДА В ОБЛАСТИ ТЕМПЕРАТУР 80 – 120 К

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В работе представлены результаты исследования проводимости пленок из природного углерода в интервале температур 78 — 220 К. Приведены данные структурных исследований методами сканирующей электронной микроскопии и спектроскопии комбинационного рассеяния. Выявлено, что осаждение природного углерода на подложки с нанесенным токопроводящим покрытием оксида индия позволяет получать структуры нового типа — тонкие пленки, построенные из однородных углеродных сеток, в узлах которых находятся глобулярные наноразмерные частицы в виде искаженных графеновых плоскостей. Методом наносекундной вольт-амперометрии изучено поведение вольт-амперных характеристик углеродных пленок, содержащих графеноподобные фрагменты. Установлено, что при достижении критической температуры резко увеличивается сопротивление образца и проявляется диамагнетизм, сохраняющийся на протяжении 50 термоциклов.

Ключевые слова: графеноподобный углерод, тонкая пленка, проводимость, наносекундная вольт-амперометрия, диамагнетизм

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Introduction

The superconducting properties of natural carbon-containing compounds with phase transition temperatures from 10 to 110 K were first observed in 1993 [1]. It was assumed then that these properties manifested because of fullerides present in the compound.

A number of studies published at that time (see, for example, [2]) reported on an anomaly observed for high-temperature superconductivity (HTSC) of C_{60}-Cu carbon structures.

A 2005 study [3] discovered diamagnetism in natural carbonaceous matter (range 90–150 K) with pronounced structural anisotropy. It was found that diamagnetic properties are not associated with fullerenes or high copper concentrations in natural fullerene. It was hypothesized in [3] that the observed effect is due to the peculiar structure of natural carbon.

A phase transition to diamagnetic state was later detected at 77–100 K for a membrane based on a mixture of C_{60} and C_{70} fullerenes doped with copper [4]. However, this membrane had a characteristic diamagnetic "well" (i.e., the diamagnetic properties manifested in a certain temperature range), and diagmagnetism did not persist in repeated cooling and heating cycles.

A new technology for producing thin films based on natural carbon was developed in a series of papers [5]. Preliminary results indicating that carbon samples of the new type exhibit diamagnetic properties were presented in [6].

The goal of this study has been to find conductivity anomalies in the temperature range of 78–220 K in films of natural carbon containing graphene-like fragments.

Experimental samples

The experimental samples were thin films based on natural graphene-like carbon. They were obtained by sublimation of the initial carbon powder in a small-sized thermal chamber [5].

Carbon powder made from type I shungite from the Shunga deposit (Karelia, Russia) [12] used as the source was prepared by the technology described in [11].

Shungite was first ground to powder with particle sizes of 0.1–10 μm; the resulting material was dispersed in an aqueous medium for 1–2 h (grinding bodies of 1–3 mm in size were used); it was then filtered and dried under natural conditions. Particle sizes of the finished powder were 0.01–1.0 μm.

The powder obtained was placed into a thermal chamber located on a heater. A glass substrate with a conductive contact made of indium oxide, intended for depositing the carbon film on it, was located in the upper part of the thermal chamber. The whole structure was then placed in a vacuum chamber pumped to 10^{-6} mmHg. The chamber was heated to 750°C.

As a result, carbon film 8 mm in diameter and 3 μm in thickness (Fig. 1, *a*) formed on the substrate.

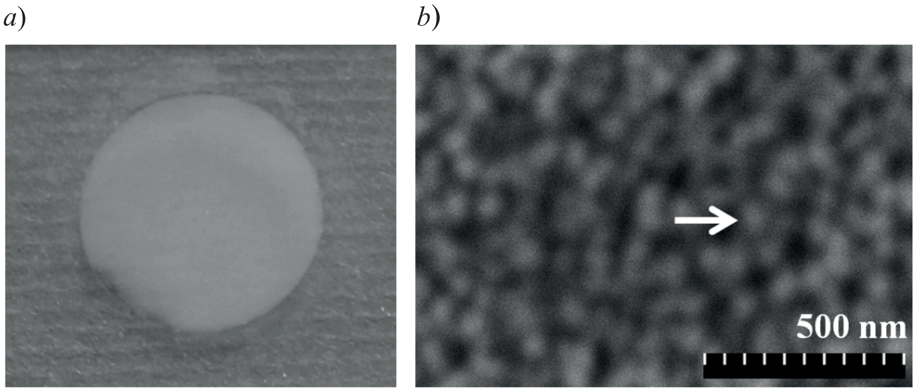

Fig. 1. Photograph (*a*) and SEM image (*b*) of the carbon film synthesized (diameter 8 mm and thickness 3 μm); the arrow points to one of the nanoparticles

The size of carbon nanoparticles forming the thin film was 50–100 nm.

Experimental procedure

It is well-known that the specific behavior of the current-voltage characteristic and the diamagnetic response are indicators of a material's superconductivity [7].

In this study, we used two well-developed experimental procedures: recording the *I–V* curve and measuring the diamagnetism of thin films.

Nanosecond voltammetry [8] is based on recording the incident (U_i) and reflected (U_r) voltage pulses for the sample.

The sample's voltage *U*, current *I* and resistance *R* are calculated by the following formulae:

$$U = U_i + U_r, I = (U_i - U_r) / Z,$$

$$R = Z \frac{U_i + U_r}{U_i - U_r},$$

where *Z* is the wave impedance of the coaxial line ($Z = 50\ \Omega$).

The technique for measuring the diamagnetic response [9] was based on imbalance in the frequencies of quartz oscillators (the generation frequency of each was 1 MHz) due to a change in the diamagnetic properties of the sample. A ferromagnetic film magnetized in a constant magnetic field of 59 mT was used as a means of contact between the sample and the first quartz resonator.

The relative change in the frequency *df/f* depends linearly on the quartz mass, which allows using quartz as an indicator of contact with the film.

The change in *df/f* allowed to obtain data on the behavior of magnetic susceptibility, analyzed in the temperature range from 78 to 220 K, at a rate of temperature change of 0.1 K/min.

The probability density distribution for the transition temperature T_c (50 thermal cycles of cooling) for carbon film in the range from 78 to 220 K was calculated by a known method described in [10].

Homogeneity of carbon films and their thickness were initially measured with a VK-9700K Color 3D Laser Microscope (by Keyence) where the light source was a 0.9 mW semiconductor laser operating at 408 nm.

The structural features of the obtained carbon films were studied by scanning electron microscopy (SEM) using an SU1510 microscope (by Hitachi) with an electron probe microanalyzer (EPMA) and by Raman spectroscopy using a Nicolet Almega XP dispersive Raman spectrometer (by Thermo Scientific). The Raman spectra were recorded at a wavelength of 532 nm, with a spectral window from 100 to 3500 cm^{-1}; the

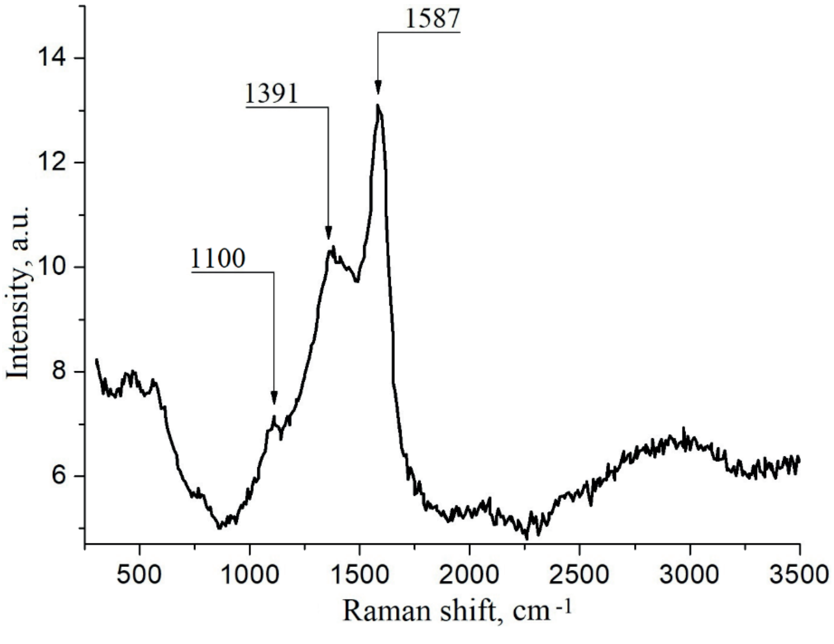

Fig. 2. Raman spectrum for the carbon film obtained

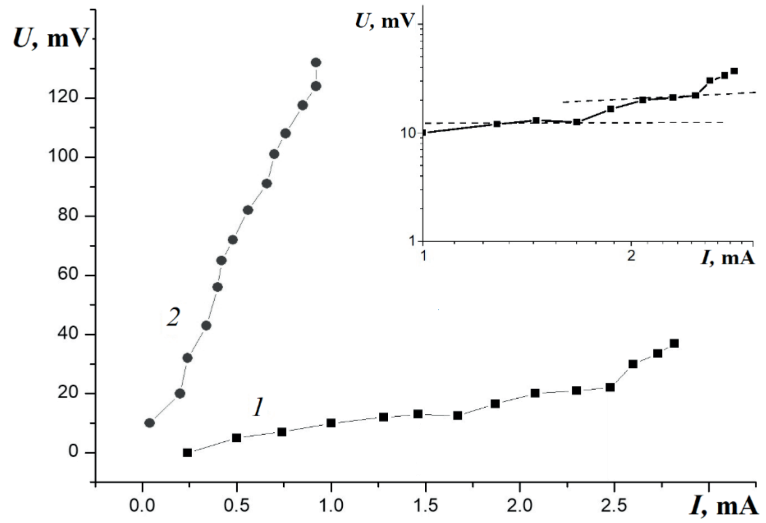

Fig. 3. Current-voltage characteristics for carbon film at 78 K (*1*) and 220 K (*2*)
The inset shows a fragment of curve *1* in a logarithmic scale; the dashed lines indicate the descending branches

obtained spectra were then analyzed using the Omnic software.

Structural studies were carried out at the Center for Collective Use of the Institute of Geology of the Karelian Research Center RAS (Petrozavodsk, Russian Federation) and at the Department of Information-Measuring Systems and Physical Electronics of the Petrozavodsk State University.

The conductive properties of the samples were studied using the equipment of the Fullerene Group of the Peter the Great St. Petersburg Polytechnic University (St. Petersburg, Russian Federation).

Experimental results and discussion

Raman spectra. First-order *D* and *G* bands characteristic for noncrystalline carbon materials were observed in the spectrum of the film at wavenumbers of 1391 and 1587 cm^{-1}, respectively, before the temperature experiments started (Fig. 2).

In contrast with the Raman spectrum of the initial shungite carbon powder, the second harmonic (2*D* and 2*G*) is absent in the spectrum of the given sample, but a D_4 band or a *T* band appears at a frequency of 1110 cm^{-1}. Opinions

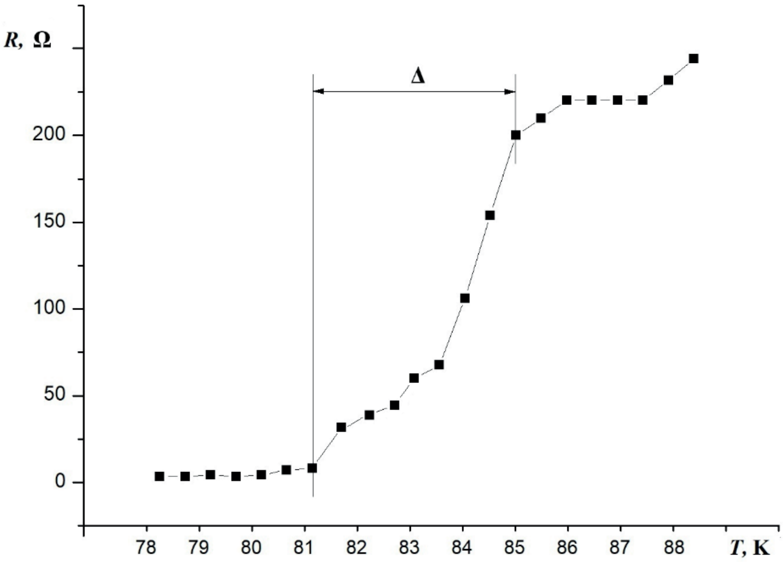

Fig. 4. Resistance as a function of temperature for carbon film;
Δ is the transition width (region with the change in conductivity)

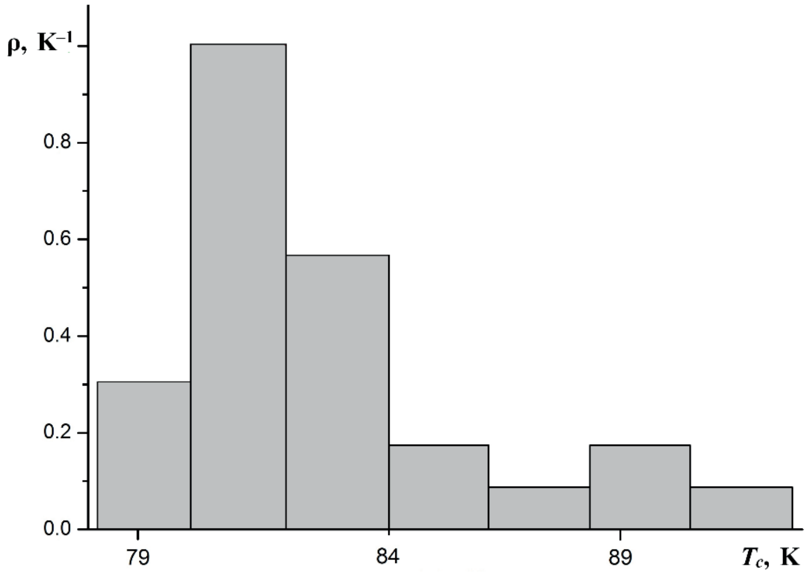

Fig. 5. Diagram of probability density distribution for transition temperature T_c (50 thermal cycles of cooling) for carbon film in the range from 78 to 220 K; the mean value of T_c = 81 K

differ regarding the nature of this band; some studies attribute it to deformation of graphene planes [13].

Analysis of Raman spectra in our earlier study [5] lead us to conclude that graphene fragments are present in the given films.

Current-voltage characteristics. Descending branches found at 78 K on the obtained $I-V$ curves (see the inset in Fig. 3) are one of the signs of anomalous conductivity and may indicate that the sample exhibits superconducting properties.

Nonlinear behavior of the $I-V$ curve in this state at 78 K may also indicate that the conductivity of the channels in the carbon film, is due, for example, to contact effects not associated with superconductivity.

The descending branches are partially compensated by normal current flow in an inhomogeneous structure. These branches disappear with subsequent increase in current, taking a normal

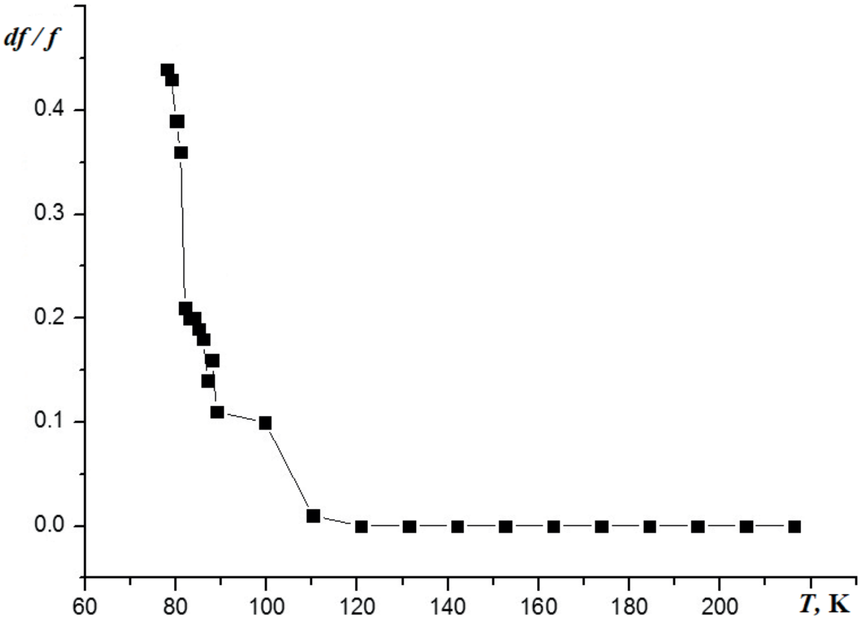

Fig. 6. Temperature dependence of the relative frequency change of two quartz resonators for carbon film

shape (see Fig. 3, segment of curve *1* at currents above 2.5 mA).

As the critical temperature T_c = 81 K is reached, the sample makes a transition to a normal state characterized by ohmic behavior (see Fig. 3, curve *2*). The resistance of the sample increases up to one and a half orders of magnitude (Fig. 4).

Similar *I*–*V* curves were previously observed [14] for the Cu_nC_{60} system.

Resistance as a function of temperature. Fig. 4 shows a typical curve for electrical resistance of the sample versus temperature in the range from 78 to 89 K. A region Δ = 4 K where the conductivity varies (transition width) is marked with straight lines.

Notably, a similar change in resistance was observed in [15] for highly oriented pyrolytic graphite intercalated with Cu – O monolayers, but the effect was unstable and vanished after several thermal cycles.

Fig. 5 shows a diagram for the distribution of the probability density ρ for the transition temperature T_c (50 thermal cycles of cooling) in the temperature range from 78 to 220 K, with a mean value of T_c = 81 K.

Fig. 6 shows the relative change in the frequency *df/f* of two quartz resonators as a function of temperature for carbon film.

The value of T_c = 81 K is close to that obtained in [3] for shungite rocks of the Chebolaksha deposit. A similar result was previously found for a membrane based on the C_{60} and C_{70} fullerenes doped with copper [4]. However, such a membrane was characterized by the presence of a diamagnetic “well” (manifestation of diamagnetic properties in a certain temperature range). The diamagnetic state was disrupted in strongly inhomogeneous regions of the sample. In addition, the diamagnetic effect did not persist at all in repeated cycles of cooling and heating fullerene membranes [4].

Our findings confirm the practically important properties of carbon film, such as the temperature-induced changes in conductivity and the presence of diamagnetism, persisting in the samples for 50 thermal cycles.

Conclusion

The carbon films that we have synthesized are characterized by a conductivity anomaly, with the diamagnetic effect persisting the temperature range of 78–110 K for all thermal cycles.

These practically important properties of carbon films have been obtained by using specially prepared shungite carbon powder as the initial carbon material.

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REFERENCES

[1] **V.F. Masterov, F.A. Chudnovsky, S.V. Kozyrev, et al.**, Microwave absorption in schungites containing fullerenes, Superconductivity. 6(9) (1993) 1848–1851.

[2] **V.F. Masterov, A.V. Prichodko, O.I. Konkov**, The metal-insulator transition and superconductivity in allotropes of carbon intercalated with copper: Prediction and experiment, Fullerene Science and Technology. 6(3) (1998) 481–497.

[3] **V.V. Kovalevski, A.V. Prikhodko, P.R. Buseck**, Diamagnetism of natural fullerene-like carbon, Carbon. 43(2) (2005) 401–405.

[4] **A.V. Prikhodko, O.I. Konkov**, V.F. Masterov’s school and fullerene research at the department of experimental physics, St. Petersburg State Technical University, Semiconductors. 36(11) (2002) 1204–1208.

[5] **O.I. Konkov, A.A. Mikhaylina, A.V. Prikhodko, N.N. Rozhkova**, Nanostructured membranes based on a natural carbon material, Journal of Optical Technology. 83(5) (2016) 286–289.

[6] **A.A. Kovalchuk, A.V. Prikhodko**, Proyavlenie diamagnetizma v novykh uglerodnykh nanomaterialakh Exhibition of diamagnetism in new carbon nanomaterials., Materials of the 24th All-Russian Scientific Conference of Physics for Students and Young Scientists, Tomsk (2018) 81–82.

[7] **K.Yu. Arutyunov**, Nanoscale Superconductivity: physics and applications // Physics, Chemistry and Applications of Nanostructures: Reviews and Short Note. Minsk: World Scientific. 2013. Pp.191–194.

[8] **W. Jantsch, H. Heinrich**, A method for subnanosecond pulse measurements of I-V characteristics, Review of Scientific Instruments. 41 (2) (1970) 228–230.

[9] **A.V. Prikhodko, O.I. Konkov**, The Meissner effect in copper-containing fullerides, Semiconductors. 35 (6) (2001) 659–661.

[10] **B. Ramachandran**, Advanced theory of characteristic functions, Publishing Society, Calcutta, 1967.

[11] **N.H. Chou, N. Pierce, Y. Lei, et al.**, Carbon-rich shungite as a natural resource for efficient Li-ion battery electrodes, Carbon. 130 (2018) 105–111.

[12] **N.N. Rozhkova**, Nanocarbon of schungites, Karelian Research Center of the RAS, Petrozavodsk, 2011.

[13] **A.C. Ferrari, J. Robertson**, Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond, Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences. 362(1824) (2004) 2477–2512.

[14] **V.F. Masterov, A.V. Prikhodko, O.I. Konkov, et al.**, High-temperture superconductivity in the carbon-copper system, Technical Physics Letters. 20(15) (1994) 614–615.

[15] **V.F. Masterov, A.V. Prikhodko, O.I. Konkov, A.A. Shaklan**, Electrical properties of Cu–O monolayers intercalated into crystalline graphite, Physics of the Solid State. 39(1) (1997) 84–86.

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СПИСОК ЛИТЕРАТУРЫ

1. **Мастеров В.Ф., Чудновский Ф.А., Козырев С.В., Зайденберг А.З., Рожкова Н.Н., Подосенова Н.Г., Стефанович Г.Б.** Микроволновое поглощение в шунгитах, содержащих фуллерены // Сверхпроводимость: физика, химия, техника. 1993. Т. 6. № 9-10. С. 1848–1851.

2. **Masterov V.F., Prichodko A.V., Konkov O.I.** The metal-insulator transition and superconductivity in allotropes of carbon intercalated with copper: Prediction and experiment // Fullerene Science and Technology. 1998. Vol. 6. No. 3. Pp. 481–497.

3. **Kovalevski V.V., Prikhodko A.V., Buseck P.R.** Diamagnetism of natural fullerene-like carbon // Carbon. 2005. Vol. 43. No. 2. Pp. 401–405.

4. **Приходько А.В., Коньков О.И.** Школа В.Ф. Мастерова и фуллереновые исследования на кафедре экспериментальной физики Санкт-Петербургского государственного политехнического университета // Физика и техника полупроводников. 2002. Т. 36. № 11. С. 1286–1290.

5. **Коньков О.И., Михайлина А.А., Приходько А.В., Рожкова Н.Н.** Наноструктурированные мембраны на основе природного углеродного материала // Оптический журнал. 2016. Т. 83. № 5. С. 24–28.

6. **Ковальчук А.А., Приходько А.В.** Проявление диамагнетизма в новых углеродных наноматериалах // Материалы 24-й Всероссийской научной конференции студентов-физиков и молодых ученых (ВКНСФ-24). Томск, 2018. С. 81–82.

7. **Arutyunov K.Yu.** Nanoscale superconductivity: physics and applications // Physics, Chemistry and Applications of Nanostructures: Reviews and Short Notes. Minsk: World Scientific. 2013. Pp. 191–194.

8. **Jantsch W., Heinrich H.** A method for subnanosecond pulse measurements of I-V characteristics // Review of Scientific Instruments. 1970. Vol. 41. No. 2. Pp. 228–230.

9. **Приходько А.В., Коньков О.И.** Наблюдение эффекта Мейснера в

медьсодержащих фуллеридах // Физика и техника полупроводников. 2001. Т. 35. № 5. С. 687–689.

10. **Рамачандран Б.** Теория характеристических функций. М.: Наука, 1975. 224 с.

11. **Chou N.H., Pierce N., Lei Y., Perea-Lypez N., Fujisawa K., Subramanian S., Robinson J.A., Chen G., Omichi K., Rozhkov S.S., Rozhkova N.N., Terrones M., Harutyunyan A.R.** Carbon-rich shungite as a natural resource for efficient Li-ion battery electrodes // Carbon. 2018. Vol. 130. Pp. 105–111.

12. **Рожкова Н.Н.** Наноуглерод шунгитов. Петрозаводск: Карельский научный центр РАН, 2011. 100 с.

13. **Ferrari A.C., Robertson J.** Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond // Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences. 2004. Vol. 362. No. 1824. Pp. 2477–2512.

14. **Мастеров В.Ф., Приходько А.В., Коньков О.И., Теруков Е.И.** Высокотемпературная сверхпроводимость в системе углерод – медь // Письма в Журнал технической физики. 1994. Т. 20. № 15. С. 17–21.

15. **Мастеров В.Ф., Приходько А.В., Коньков О.И., Шакланов А.А.** Электрические свойства монослоев Cu–O, интеркалированных в кристаллический графит // Физика твердого тела. 1997. Т. 39. № 1. С. 97–100.

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