The conductivity and the diamagnetic response of the graphene-like carbon films in the 80 – 120 K temperature range

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Abstract. The paper presents the results of conductivity and diamagnetic response studies in natural carbon films in the temperature range 77–220 K. The behavior of the current-voltage characteristic of carbon films containing graphene-like fragments was studied by nanosecond voltammetry. It is established that when the critical temperature is reached, the sample resistance increases sharply with the simultaneous disappearance of diamagnetism. Was proposed possible mechanism of high-temperature superconductivity based on synchronization of negative-U centres presumably exists in the carbon structure under study.

1. Introduction
The practical application of the effect of superconductivity is limited due to the need for low temperatures, the existence of critical fields and critical current. For a sufficiently long period of time, the efforts of many scientists working in the field of superconductivity have been directed to the search for materials with a high critical temperature. Such superconductors were obtained in the mid-80s of the last century and were called high-temperature superconductors (HTSC). Even before the start of HTS research, an alternative model to the Bardeen-Cooper-Schrieffer theory (BCS) was proposed with a strong static binding of electrons at localized centers and their extremely weak movement between centers [16].

In the 33 years since the discovery of high-Tc superconductivity [12] there have been many models proposed [13, 15] that might explain the nature of the ground state and the anomalous properties of HTSC compounds, but none of them are still logically closed and consistent.

Recently, much attention has been paid to studies of strongly correlated states, such as ferromagnetism and superconductivity, in various forms of carbon, including graphite (see, for example, [15, 17, 18]).

The superconducting properties of natural carbon-containing compounds with phase transition temperatures from 10 to 110 K were first observed in 1993 [3]. 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, [4]) reported on an anomaly observed for high-temperature superconductivity of C_{60}-Cu carbon structures. A 2005 study [5] 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 [5] that the observed effect is due to the peculiar structure of natural carbon.
The goal of this study has been to find conductivity anomalies in the temperature range of 77–220 K in films of natural carbon containing graphene-like fragments.

2. Experimental details
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 [6]. Carbon powder made from type I shungite from the Shunga deposit (Karelia, Russia) [7] used as the source was prepared by the technology described in [8]. The size of carbon nanoparticles forming the thin film was 50–100 nm.

It is well-known that the specific behavior of the current-voltage characteristic and the diamagnetic response are indicators of a material’s superconductivity [9]. In this study, we used two well-developed experimental procedures: recording the I–V curve and measuring the diamagnetism of thin films. Nanosecond voltammetry [10] is based on recording the incident (U₁) and reflected (U₂) voltage pulses for the sample. Pulse duration was 5 ns at voltages up to 1 V at a frequency of 100 Hz. The technique for measuring the diamagnetic response [11] was based on imbalance in the frequencies of quartz oscillators df (the generation frequency of each was f=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

3. Results
Descending branches found at 77 K on the obtained I–V curves (Figure 1a) are one of the signs of anomalous conductivity and may indicate that the sample exhibits superconducting properties.

![Figure 1(a, b). (a) Current-voltage characteristics for carbon film at 77 K (1) and 220 K (2); (b) Resistance as a function of temperature for carbon film.](image)

Nonlinear behavior of the I–V curve in this state at 77 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. As the critical temperature Tc = 81 K is reached, the sample makes a transition to a normal state. Figure 1b shows a typical curve for electrical resistance of the sample versus temperature in the range from 77 to 89 K. A region Δ = 4 K where the conductivity varies (transition width) is marked with straight lines.
Figure 2 shows the relative change in the frequency $\Delta f/f$ 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 [5] for shungite rocks of the Chebolaksha deposit. 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 5 thermal cycles.

![Graph showing temperature dependence of the relative frequency change of two quartz resonators for carbon film.](image)

**Figure 2.** Temperature dependence of the relative frequency change of two quartz resonators for carbon film.

The results presented suggest that the mechanism of conductivity of thin films of natural graphene-like carbon is comparable with conductivity in high-temperature superconductors. In this paper, we chose a superconductivity model based on the negative-U centres model, since it can explain high-temperature superconductivity in a wide temperature range (up to 500 K). This concept was first put forward by Anderson in 1975 to describe some properties of chalcogenide glassy semiconductors [1], later developed by Mott [2]. In this model, it is assumed that there are centers in the atomic lattice of a material that have a special property. The strong electron-lattice interaction leads to the fact that the binding energy of two electrons exceeds their Coulomb repulsion energy, that is, the effective correlation energy of the pair is negative. This effect is also observed under normal conditions, that is, electrons bound in a pair already exist at room temperature.

By analogy with the BCS theory [19], the attraction of two electrons with opposite spins on one node can result in a superconducting correlation between pairs. Moreover, the first term in the Habard Hamiltonian [14] corresponds to the interaction between electrons, the second to the kinetic energy of the band motion. This value is small compared with the first, and is considered as a perturbation. The difference between the concept of negative-U centres and BCS is that all electrons participate in superconductivity, and not just near the Fermi surface.

4. Conclusion

The carbon films that we have synthesized are characterized by a conductivity anomaly, with the diamagnetic effect persisting the temperature range of 80–120 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. To further describe the mechanism of conductivity of the objects under study, the negative-U centres model was selected.
Acknowledgments
This study was supported by a grant from the UMNIK program of the Foundation for Assistance to Small Innovative Enterprises in Science and Technology, Agreement No. 11094 GU/2016.

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