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## Temperature Dependences of Conductivity and Magnetoelectricity of Multiwall Carbon Nanotubes Annealed at Different Temperatures

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*Temperature (in range 4.2–300 K) and magnetic field (in fields up to 10 kG at 4.2 K) dependences of the conductivity of two sets of multiwall carbon nanotubes with different average diameters (8–10 nm and 20–22 nm) heated at various temperatures (1600, 2200, 2600, 2800 °C) were investigated. Temperature dependences for nanotubes with average diameter 20–22 nm is typical for quantum corrections to conductivity of the systems with interaction electrons in two dimensional conductors with local disorder. For nanotubes with average diameter 8–10 nm temperature dependences corresponds to one-dimensional variable range hopping conductivity (VRHC). The variation of annealing temperature of MWNTs influence on the contribution of corrections to conductivity and parameters of VRHC. The magnetoelectricity of MWNTs also depends on the annealing temperature and is less than that of highly oriented pyrographite. Annealed MWNTs with average diameter 20–22 nm has a positive magnetoelectricity.*

*Keywords: conductivity, magnetoelectricity, annealed multiwall carbon nanotubes, one-dimensional variable range hopping, quantum corrections to conductivity.*

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## Introduction

Electron transport properties (conductivity and magnetoelectricity) in conducting materials are the basic characteristics defining their fundamental and applied properties. In carbon multiwall nanotubes (MWNTs) these properties depend on a state of surface atoms because in nanostructures materials the surface atoms are an appreciable part of full quantity of atoms in

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nanostructures. Investigation of the electrical characteristics of carbon nanotubes is interesting both from a practical point of view and from the standpoint of studying the fundamental properties of solids. According to transmission electron microscopy (Fig. 1) the synthesized nanotubes have defects in the outer layers. It was shown that high temperature annealing decrease number of defects on a surface of nanotubes, while increasing the annealing temperature nanotubes tends to the ideal: fewer defects, straighten a tube, a surface becomes smoother. Outer layers of nanotubes participate in conductivity, because layers contact with each other. We can assume that the temperature processing affects electric properties of matter.

The goal of this study was to investigate influence of heat treatment on the conductivity and magnetoconductivity. We investigated the electrical properties of nanotubes with different outer diameters, as the initial, and after heat treatment up to 2800°C.

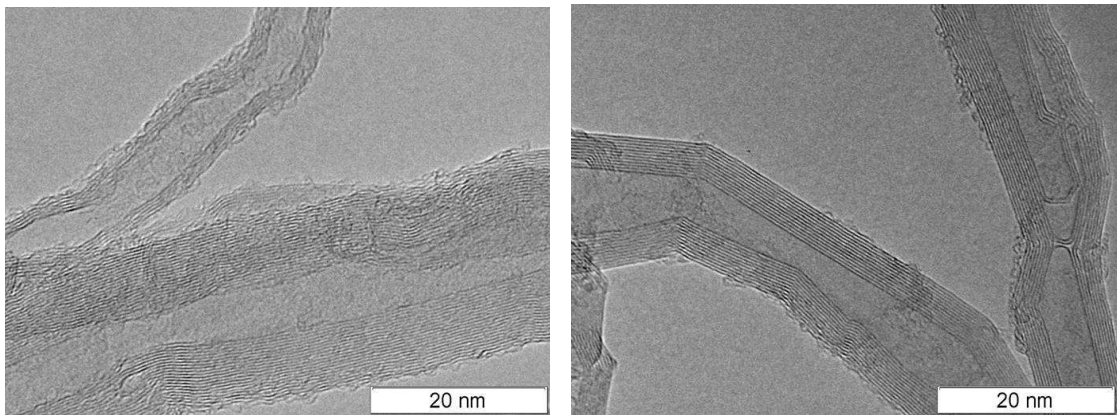


Fig. 1. The data from transmission electron microscopy. Initial nanotubes (left) and annealed nanotubes (right)

## 1. Experimental

Multiwall carbon nanotubes of two types (with the average external diameter of 8–10 nm and 20–22 nm) were obtained by pyrolysis of ethylene in a flow reactor for highly Fe-Co catalysts at temperatures of 650–750°C, obtained by the polymerization of complex predecessors. MWNTs samples obtained at the first stage were purified by boiling in 15% hydrochloric acid solution with subsequent washing with water. In the final product contained about 0.2–1.5 wt. % of metal impurities. The structure of MWNTs was investigated using transmission electron microscopy (TEM, Fig. 1). Ignition of the samples was carried out in a stream of high-purity argon at 1600–2800°C, resulting in a multilayer nanotubes with the content of metallic impurities less than 1 ppm.

The samples had narrow distributions of average outer diameter of MWNTs with diameter depends on synthesis conditions. For electrical measurements the powder of MWNTs was pressed in a glass cylinder for as long as its resistive properties cease to depend on the degree of compression. The electrical contacts were made by 0.1 mm silver wires. The temperature dependences of conductivity  $\sigma(T)$  and magnetoconductivity  $\sigma(B)$  were measured by four-point-probe technique.  $\sigma(T)$  was measured in the temperature range 4.2–300 K.  $\sigma(B)$  was measured in the field  $B$  range 0–10 kG at temperature 4.2 K.

## 2. Experimental Results and Discuss

Temperature dependences of normalized conductivity  $\sigma(T)/\sigma(T_{room})$  — conductivity at room temperature) of MWNTs with average outer diameters 20–22 nm are shown in Fig. 2. Logarithmic dependences take place at temperature below 100 K:

$$\sigma(T) = \sigma_1 + A \ln(T), \quad (1)$$

where  $\sigma_1$  and  $A$  are constants. This dependence is typical for quantum corrections to conductivity of the systems with interaction electrons in two dimensional conductors with local disorder [1]. Similar dependence has a Coulomb gap.

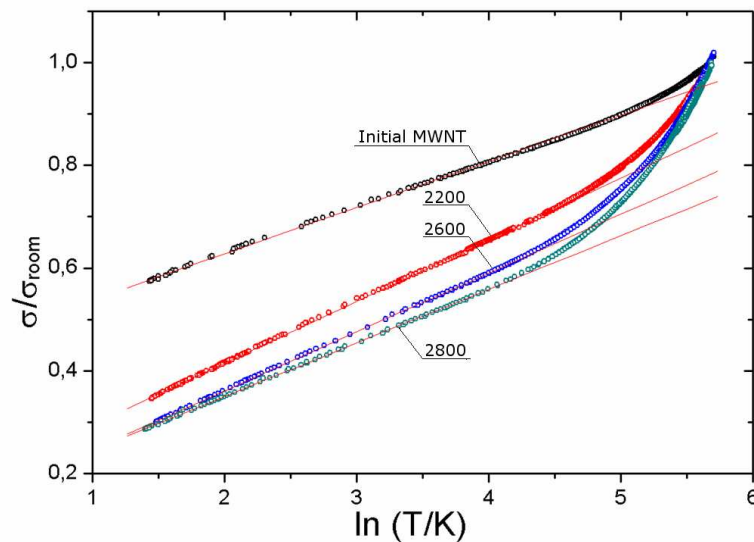


Fig. 2. Temperature dependences of relative conductivity  $\sigma/\sigma_{room}$  ( $\sigma_{room}$  — conductivity at room temperature) of multiwall carbon nanotubes with average diameters 20–22 nm (initial and with different annealing temperature) in the  $\sigma/\sigma_{room} - \ln(T)$  axes. Numbers on the figure are showing annealing temperature in  $^{\circ}\text{C}$

Angle of approximation line depends on annealing temperature of initial samples of nanotubes. Slope increases with increasing annealing temperature. This suggests that the contribution of quantum corrections change in temperature annealing.

Fig. 3 shows the temperature dependence (normalized at room temperature) of logarithm of conductivity of the samples of nanotubes with average diameter of 8–10 nm in the  $\ln[\sigma(T)/\sigma(T_{room})] - T^{-1/2}$  axes in temperature range 4.2–300 K. In these axes the dependence of conductivity is linear. In temperature range 4.2–50 K the electrical conductivity can be described by one-dimensional variable range hopping conductivity with variable length of hops between localized states located in a narrow energy range close to the Fermi level. This is proven by the experimental observation of relation (2) (Mott's law) [2]. In [3] experimentally demonstrated that the carbon structure can be described by the theory of one-dimensional hopping conductivity with variable hopping length. Conductivity in this case is described by the following formula:

$$\sigma(T) = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{1+d}} \right], \quad (2)$$

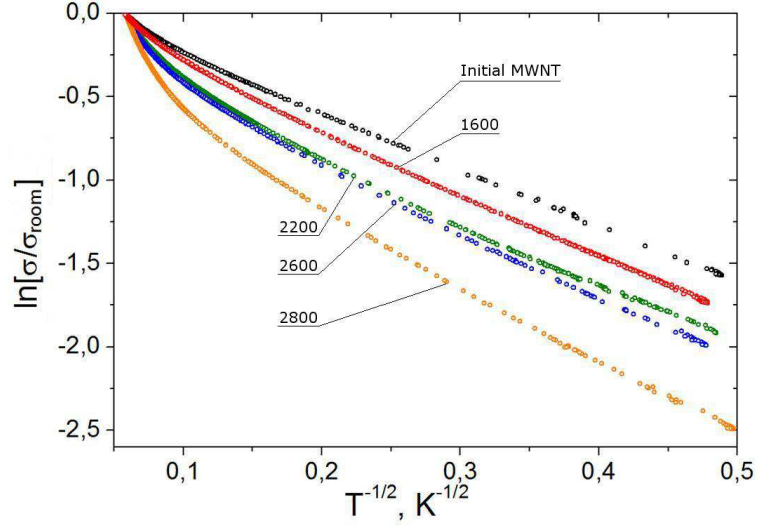


Fig. 3. Temperature dependences of relative conductivity  $\sigma/\sigma_{room}$  ( $\sigma_{room}$  — conductivity at room temperature) of multiwall carbon nanotubes with average diameters 8–10 nm (initial and with different annealing temperature) in the  $\ln[\sigma/\sigma_{room}] - T^{-1/2}$  axes. Numbers on the figure are showing annealing temperature in °C

where  $T_0 = \frac{\beta}{a_{loc}^d k_B N(E_F)}$ ,  $\beta$  is a constant depending on the dimension,  $a_{loc}$  is a localization radius of electron wave function,  $d$  is the movement dimension of the current carriers,  $k_B$  is the Boltzmann constant,  $N(E_F)$  is the density of states at the Fermi level. The experimental data are well described by the formula (2) with  $d = 1$ .

The physical meaning of hopping conduction — electron tunneling between localized states, accompanied by energy exchange with phonons. Variable hopping length means tunneling over long distances with small change in energy or a small distance with a large change in energy. In other words, when the temperature becomes energetically favorable tunneling over long distances.

Fig.4 shows normalized magnetoconductivity of samples (initial and annealed) and magnetoconductivity of pyrolytic graphite in the  $\delta\sigma_{int}(B^2)/\sigma_0 - B^2$  axes for MWNTs at  $T = 4.2$  K, where  $\delta\sigma_{int} = \delta\sigma_{exp} - \sigma_0$ ,  $\delta\sigma_{exp}$  are the experimental results of measurement of conductivity in magnetic field  $B$ .

Quantum corrections for weak localization effects [4]  $\delta\sigma_{WL}(T)$  are not observed, but quantum corrections for interaction electrons (QCIE) to magnetoconductivity [5]  $\delta\sigma_{int}(T)$  take place. Magnetic field  $B$  suppresses this QCIE [5]. Low field asymptotic behavior for  $\delta\sigma_{int}(B)$ :

$$\frac{\delta\sigma_{int}(B)}{\sigma_0} = -\sigma_2 g(T) \left( \frac{B}{B_{int}} \right)^2, \quad \frac{B}{B_{int}} \ll 1, \quad (3)$$

where  $\sigma_0$  is the conductivity at  $B = 0$ ,  $\sigma_2$  is constant,  $B_{int} = \pi c T / 2eD \approx 6$  T at  $T = 4.2$  K,  $D \approx 20$  cm<sup>2</sup>/s for MWNTs (diffusion coefficient) [6]. The interaction constant  $g(T)$  is given by

$$g(T)^{-1} = 1/\lambda + \ln \left( \frac{\gamma\eta}{\pi k_B T} \right), \quad (4)$$

where  $\lambda$  is the constant of electron-electron interaction (at attraction of electron the temperature of superconducting transition  $T_c = \theta_D \exp[1/\lambda]$ ,  $\eta = E_F$  at repulsion and  $\eta = \theta_D$  at attraction of electrons,  $\theta_D/k_B$  is the Debye temperature. As can see from eq. (3) the  $\delta\sigma_{int}(B)$  is positive when

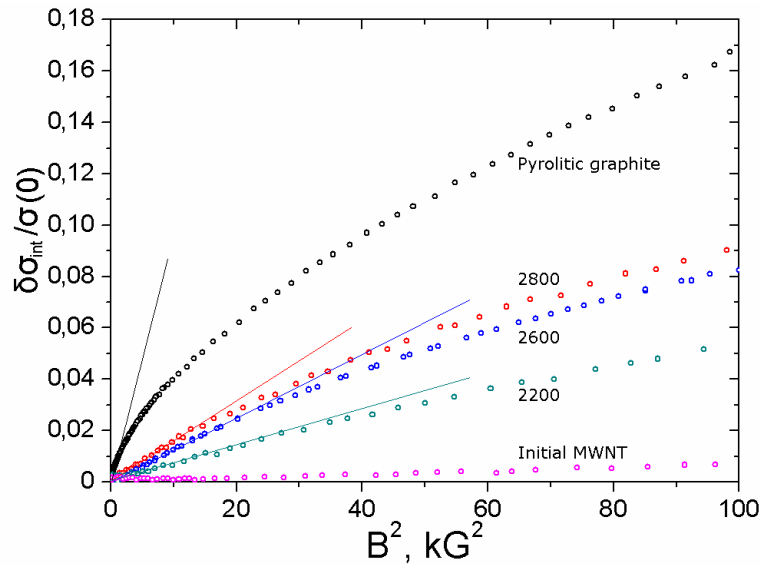


Fig. 4. Dependences of relative conductivity  $\delta\sigma_{int}/\sigma(0)$  (where  $\delta\sigma_{int} = \delta\sigma_{exp} - \sigma(0)$ ,  $\delta\sigma_{exp}$  — the experimental data of conductivity measurements,  $\sigma(0)$  — conductivity of samples without field) of the samples in magnetic field: multiwall carbon nanotubes with average diameters 20–22 nm in the  $\delta\sigma_{int}(B^2)/\sigma(0) - B^2$  axes. Also magnetoconductivity of pyrolytic graphite is shown. Numbers on the figure are showing annealing temperature in  $^{\circ}\text{C}$

$g(T)$  is negative. Fig. 4 shows that the dependence of magnetoconductivity at low fields is linear in the  $\delta\sigma_{int}(B^2)/\sigma_0 - B^2$  axes. At the field  $B_{min}$  magnetoconductivity behaves logarithmically depending on the external field [5]. For samples annealed at high temperatures requires less external fields for entering the logarithmic behavior of dependence. You can see that with increasing annealing temperature, angle of magnetoconductivity increases and the dependence tends to characteristic dependence of pyrolytic graphite.

## Conclusion

In this paper we studied the electrical characteristics of multiwall carbon nanotubes annealed at different temperatures. It was shown that the conductivity of nanotubes with different average diameters has different mechanism of the conductivity. Dependence of conductivity for nanotubes with average diameter 20–22 nm is typical for quantum corrections to conductivity of the systems with interaction electrons in two dimensional conductors with local disorder. For nanotubes with an average outer diameter 8–10 nm temperature dependence of conductivity corresponds to one-dimensional variable range hopping conductivity. It was shown that annealing changes the contribution of quantum corrections to conductivity and parameters of VRHC. At the same diameter of MNWTs and different annealing temperature type of characteristic dependences does not change.

It was shown that magnetoconductivity of annealing nanotubes is positive. Asymptotic approximation of the magnetoconductivity in weak fields is square, in strong is logarithmically dependent on the magnetic field. While increasing the annealing temperature dependence of magnetoconductivity of the nanotubes tends to dependence of magnetoconductivity of pyrolytic graphite. Perhaps this is due to the fact that during the annealing defects in nanotubes decreases and the behavior of carriers of MNWTs tend to the ideal crystalline state.

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## Температурные зависимости проводимости и магнетопроводимости отожженных многослойных углеродных нанотрубок

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*Представлены температурные зависимости проводимости (в диапазоне 4.2–300 K) и магнетопроводимости (в полях до 10 кГ при 4.2 K) многослойных углеродных нанотрубок со средним внешним диаметром 8–10 и 20–22 нм, отожженных при различных температурах (1600, 2200, 2600, 2800 °C). Показано, что зависимость проводимости для нанотрубок со средним диаметром 20–22 нм характерна для квантовых поправок к проводимости взаимодействующих электронов в двумерных проводниках с локальным беспорядком. Для нанотрубок со средним диаметром 8–10 нм имеет место одномерная прыжковая проводимость с переменной длиной прыжка. Показано, что при температурной обработке многослойных углеродных нанотрубок изменяется вклад квантовых поправок в проводимость, а также параметры прыжковой проводимости, что отжиг образцов влияет на магнетопроводимость. Многослойные углеродные нанотрубки со средним диаметром 20–22 нм имеют положительную магнетопроводимость.*

*Ключевые слова: проводимость, магнетопроводимость, отожженные многослойные углеродные нанотрубки, одномерная прыжковая проводимость с переменной длиной прыжка, квантовые поправки к проводимости.*