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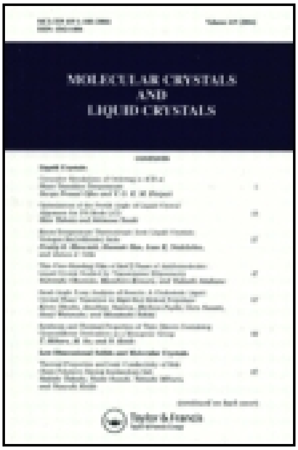

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Resistance of a Nanocarbon Material Containing Nanotubes

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The results of the experimental studies of resistivity of a nanocarbon material (NCM), which contains carbon nanotubes (CNT), and also the amorphous carbon particles and nanographite are presented. The main efforts were aimed at the ascertaining the mechanism of NCM conduction with regard to their phase composition.

Keywords: electric resistivity; luttinger liquid; nanocarbon material

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INTRODUCTION

Nanocarbon material (NCM) is the complex system which contains not only carbon nanotubes (CNT), but also amorphous carbon particles, nanographite, and the particles of a metal catalyst, whose content is determined by the method of NCM synthesis.

There is no consensus on the character of NCMs conduction. It has been known that the ideal (non-defect) single-walled CNT is a one-dimensional (1-D) conductor, whose transport properties can be well described within the Luttinger liquid theory [1]. Such a type of conduction is observed experimentally only in the case of a unit single-walled CNT [2]. However, the integral conduction of bulk (macro-) NCM specimens is studied usually. Such specimens are consisted either of the rope of separate CNT up to 30 nm wide or of mats of the CNT rope. Different models have been developed for the description of the temperature dependence of resistivity for bulk NCM specimens. Thus, the model for the description of the conduction of films consisted of anisotropically ordered single-walled CNT has been proposed in Ref. [3]. This model accounts the conduction of separate tubes as 1-D conductors and the conduction of CNT assemblies that is described within the non-interacting Fermi liquid model: $\rho(T) = aT^{-\alpha} + bT$. The possibility of the influence of the localization effect, contact resistance between tubes, and defects in a separate tube on the temperature dependence of resistivity has been analyzed in Ref. [4]. In order to describe the electrical transport of bulk NCM specimens, all the cited references present the models that involve the additive contribution of each mechanism. Meanwhile, Ref. [5] reported that the temperature dependence of the resistivity of CNT mats can be described within the model of hopping conduction with a variable hopping length being applied to the 2-D case (i.e., $\rho \sim T^{-1/3}$). Moreover, the thermo-chemical purification of specimens that leads to the removal of a metal catalyst and amorphous carbon particles was shown to have no effect on the temperature dependence of resistivity.

So, the problem of the electrical transport of NCM containing not only single-walled CNT of different degrees of imperfection but also certain amounts of amorphous carbon and a metal catalyst is still far from solving. In addition, the main factors that govern the dominant role of a certain mechanism of NCM conduction were not determined exactly.

Thus, this article presents the results of experimental studies of the resistivity of NCM of different structures and phase compositions. The main efforts were aimed at ascertaining the mechanism of NCM electrical transport with regard to their phase composition.

EXPERIMENTAL RESULTS

NCM "AP-SWNT" (As-Prepared Single-Walled Carbon Nanotube) synthesized by the "Carbonsolution" firm by the catalytic deposition of a carbon-containing gas (CO) using the (Ni/Y) catalyst has been used for experimental studies. According to the information of the firm-manufacturer, this material contains about 80 % of carbon.

The electric resistivity of NCM has been studied in the temperature range of 4.2–293 K using a standard four-probe technique. Bulk NCM specimens have been prepared for these experiments either by the cold compacting without binder (specimen #1) or by using polyvinyl acetate (PVA) (25 mass.%) as a binder (specimen #2). In order to change the ratio of CNT and amorphous carbon contents, the source NCM has been also subjected to the thermo-chemical treatment according to the scheme: three-fold boiling in a 2.5 M solution of nitric acid for 2 h and the subsequent annealing for 20 min in air. According to the data of transmission electron microscopy (TEM) [6] experiments, such a treatment leads to a damage of the CNT structure and to the fining of amorphous carbon particles, *i.e.*, to an increase of the amorphous carbon phase content. A bulk specimen has been prepared from the treated material by cold compacting with a PVA binder (25 mass.%) (specimen #3).

The temperature dependences of the resistivity $\rho(T)$ for these three specimens are presented in Figure 1.

Evidently, the similar character of $\rho(T)$ curves was observed for all these specimens: a sharp decrease of resistivity at temperatures less

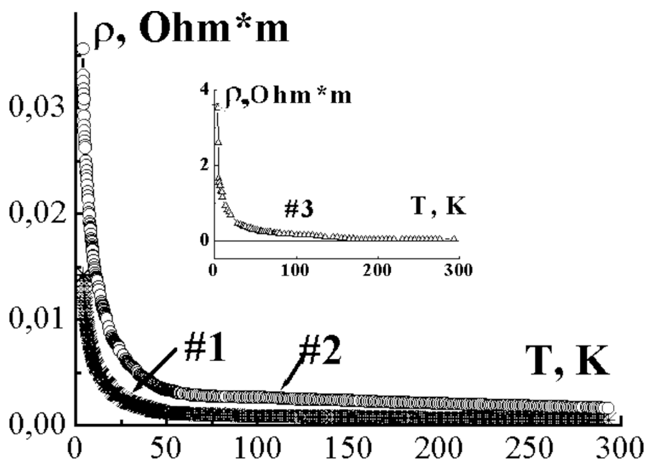

FIGURE 1 ρ(T) dependence for NCM specimens of different structures and phase compositions.

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than 50 K and then a weak dependence of ρ with the temperature rise. However, the values of resistivity at room temperature (ρ_r) are $\sim 5 \cdot 10^{-4}$ ohm*m for specimen #1, $\sim 1.5 \cdot 10^{-3}$ ohm*m for specimen #2, and $\sim 3 \cdot 10^{-2}$ ohm*m for specimen #3. The values of $\rho_{4.2}/\rho_r$ were found to be also different. This ratio is equal to ~ 110 for specimen #3, while $\rho_{4.2}/\rho_r \sim 29$ for specimen #1 and ~ 22 for specimen #2. It should be noted that the resistivity is somewhat lower and the ratio $\rho_{4.2}/\rho_r$ is somewhat higher for the NCM specimen prepared without binder (#1) as compare to those for the NCM specimen prepared using PVA as a binder (#2).

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DISCUSSION

As was stated earlier, the investigated NCM contains several phases differing by structure. Each of them is characterized by a peculiar type of conduction. CNT are the interacting 1-D systems, and their electronic properties, electric conduction in particular, are usually described within the theory of a Luttinger liquid with the power type of temperature dependence $\rho \sim aT^{-\alpha}$. Here, the exponent α is related with the Luttinger parameter g as: $\alpha = (g + g^{-1} - 2)/8$. In addition, the metallic type of conduction is inherent to the junctions of tubes, as was shown in a series of earlier articles. The hopping mechanism of conduction with a variable hopping length is inherent to amorphous carbon. In this case, the resistivity can be expressed as $\rho = \rho_0 \exp(T_0/T)^{1/n}$, where $n = 3$ for the 2-D case, $n = 4$ for the 3-D case, T_0 and ρ_0 are certain constants that increase on "worsening" the amorphous carbon structure. Just this type of dependence has been used in Ref. [4] to fit the resistivity of CNT mats.

Let us analyze the applicability of these mechanisms to the description of the temperature dependences of the resistivity of the investigated NCM.

Figure 2 displays the temperature dependences of the resistivity for the studied specimens on a logarithmic scale $\ln\rho = f(\ln T)$.

It is clearly seen that the linear part of the $\ln\rho = f(\ln T)$ curves is observed only in a narrow temperature range from 4.2 to 40 K. The values of a, α, and g parameters determined from the experimental data are summarized in Table 1.

Figure 3 presents the temperature dependences of the NCM resistivity in the $\ln\rho = f(T^{-1/4})$ coordinates.

Evidently, the linear parts of these dependences also are not observed in the whole experimental temperature range. The values of T_0 and ρ_0 obtained from the linear parts of $\ln\rho = f(T^{-1/4})$ curves are presented in Table 1.

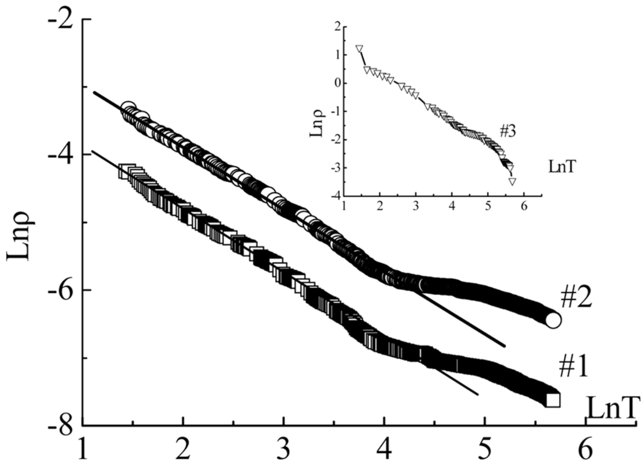

FIGURE 2 Temperature dependence of resistivity for the studied specimens on the logarithmic scale $\ln\rho = f(\ln T)$.

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So, none of the conduction mechanisms proposed in Ref. [4,5] describes the temperature dependences of the NCM resistivity in the whole experimental temperature range. This is thought to be evidence for the complexity of the structure and phase composition of the investigated NCM specimens that results in a combination of different mechanisms of conduction.

Thus, the model involving the conduction mechanism for each phase constituent of NCM with regard for the percolation effect is necessary for the adequate description of transport properties of such complicated systems.

In Ref. [7], we have proposed the model of serial junction of elements with different types of conduction in order to describe the electric properties of carbon materials containing the parts of metallic and hopping conduction. Within the proposed model of electrical transport, the equivalent network of NCM can be presented as a serial junction of effective resistant elements that correspond to carbon phases with

TABLE 1 Values of a, α, g, ρ_0, and T_0 Parameters for NCM Specimens

Specimen	a	α	g	ρ_0, Ohm*m	T_0, K
#1	0.056	0.960	0.105	$1.54 \cdot 10^{-4}$	$1.79 \cdot 10^{3}$
#2	0.137	0.936	0.107	$5.7 \cdot 10^{-4}$	$1.2 \cdot 10^{3}$
#3	0.490	0.927	0.108	$8.07 \cdot 10^{-3}$	$7.71 \cdot 10^{3}$

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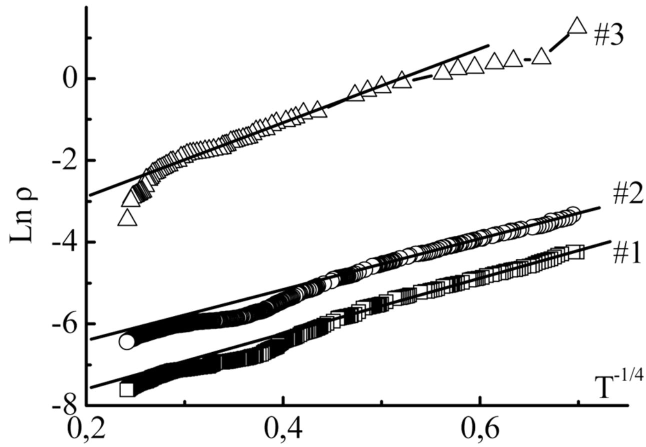

FIGURE 3 Temperature dependence of the NCM resistivity in $\ln\rho = f(T^{-1/4})$ coordinates.

different types of conduction. Hence, the resistivity of NCM can be expressed as

$$\rho = \rho_t + \rho_{am} + \rho_m \quad (1).$$

Here, each of the terms corresponds to a certain mechanism of electrical transport: $\rho_t = cT^{-\alpha}$ is a "tube" resistivity, $\rho_{am} = \rho_0 \exp(T_0/T)^{1/4}$ is an "amorphous (hopping)" resistivity, $\rho_m = cT$ is a resistivity of tube junctions. a, c, and ρ_0 factors include the weighting coefficients that take into account the content of the appropriate phase constituent. Similar models of conduction have been considered in a series of papers (see, for example, Ref. [8,9], in which the conduction of CNT mats has been studied).

This model has been applied to calculate the temperature dependences of resistivity for three studied specimens using above Eq. (*). The values of a, α, g, c, T_0, and ρ_0 that lead to the best coincidence of the experimental and calculated resistivities are presented in Table 2. The results of the performed calculations are illustrated in Figures 4–6.

The dependences presented in Figures 4–6 evidence for a fairly correct description of the experimental $\rho(T)$ curves. Here, the low-temperature resistivity of specimen #1 is determined preferably by the resistivity of CNT. In the case of specimen #2, the resistivities of tube and amorphous constituents were found to be almost equal, and the total resistivity of specimen #3 is determined mainly by the contribution of amorphous carbon.

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TABLE 2 The Values of, a, α, g, ρ_0, T_0, and c Parameters for NCM Specimens

	ρ_t			ρ_{am}		ρ_m
Specimen	a	α	g	ρ_0, Ohm*m	T_0, K	c
#1	$5.7{\cdot}10^{-2}$	0.95	0.104	$3.0{\cdot}10^{-5}$	550	10^{-6}
#2	$8.0{\cdot}10^{-2}$	0.90	0.110	$3.0{\cdot}10^{-4}$	600	10^{-7}
#3	$5.0{\cdot}10^{-1}$	0.90	0.110	$2.0{\cdot}10^{-2}$	1967	0

As seen from the data listed in Table 2, the exponent in ρ_t remains almost invariable by evidencing for the "invariability" of the CNT structure. The factor a that includes, in particular, the weighting coefficients is also almost the same for specimens #1 and 2. Meanwhile, in a case of specimen #3, the factor a changes substantially indicating for a change of the ratio of the contents of phase constituents. If the "amorphous" contribution of resistivity is analyzed, one can see that the values of T_0 are almost the same for specimens #1 and #2 and differ from that for specimen #3, *i.e.*, for the specimen subjected to a thermo-chemical treatment. This factor characterizes the localization length in amorphous carbon. In other words, it is direct parameter of the amorphous phase. The values of ρ_0 were found to be different for different specimens. The difference in ρ_0 values for specimens #1

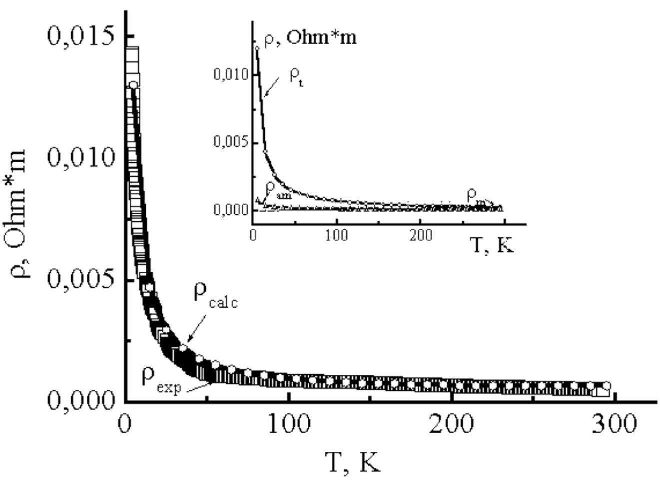

FIGURE 4 Temperature dependence of resistivity for sample #1.

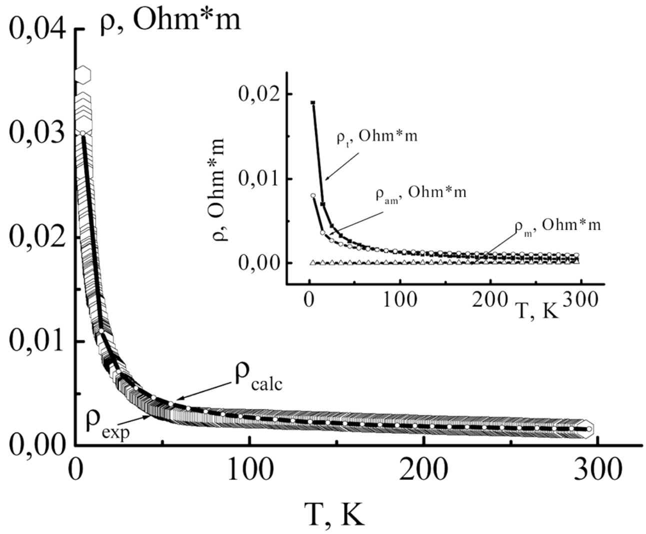

FIGURE 5 Temperature dependence of resistivity for sample #2.

and #2 can be, presumably, due to the neglect of the certain, rather small, influence of a binder. This also results in reducing the metal component contribution for specimen #3.

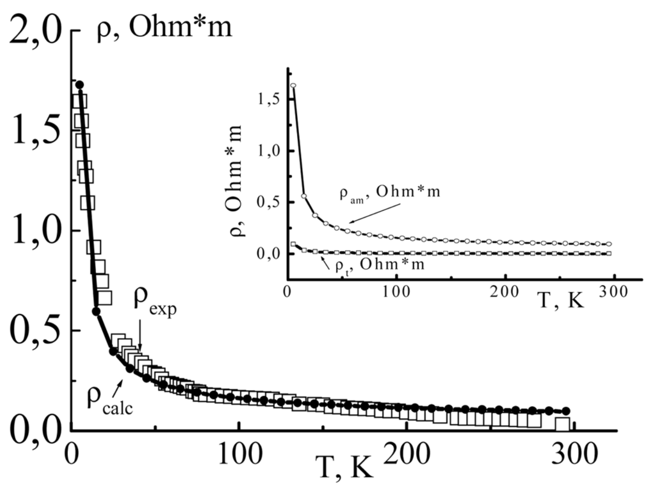

FIGURE 6 Temperature dependence of resistivity for sample #3.

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CONCLUSION

The studies of the conductivity mechanisms in NCMs, containing CNTs and particles of amorphous carbon, have been carried out in this article. The initial nanocarbon material was thermo-chemically treated (such a treatment leads to the destroying and amorphization of CNTs) in order to change the ratio of phases. This led to an increase in the relative percentage of the amorphous carbon phase.

The performed analysis showed that the electrical resistivity of the investigated specimens within the whole temperature range from 4.2 up to 300 K cannot be described only by the jump mechanism with a variable length of jumps or only by the 1-D Luttinger conductivity. This evidences for that none of the NCM phase constituents (amorphous carbon, CNT) forms the infinite circuit. The complex phase composition of NCM under investigation leads to the situation, when the electric transport is determined by several mechanisms simultaneously. To describe the mechanism of electric transport in NCMs containing several phases, the model of a serial junction of elements with different types of conductivity, accounting the phase content, has been proposed. The calculations performed within this model showed a good coincidence with the experimental results. The revealed variation of the fitting parameters reflects the real variation of the NCM phase composition during the thermo-chemical treatment.

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