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Electrical Resistance and Magnetoresistance of Modified Carbon Nanotubes

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The paper presents the results of the experimental studies of the magnetoresistance and electrical resistance of carbon nanotubes modified with iron and iron oxide. A comprehensive study of the processes occurring with change in the temperature of modified CNTs is performed. Joint analysis of the structural studies and electrical transport characteristics is enabled to explain new and interesting results. It is established that modification with iron has little effect on the electrical resistance. On the other hand, modification is strongly reflected on the ferromagnetic resistance anisotropy. It is shown that the localization mechanism and anisotropic magnetoresistance are manifested in magnetoresistance. Anisotropic magnetoresistance arises due to the features of magnetization of ferromagnetic phase in an external magnetic field.

Keywords: Multi-walled carbon nanotubes, Electrical resistance, Magnetoresistance.

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1. INTRODUCTION

Year after year scientists discover and explore new interesting properties of carbon nanotubes (CNT). Among them a new magnetometer created based on CNT and intended for the investigation of the properties of separate atoms and molecules. For example, joint group from the USA, Germany and Japan gave the evidence that three-walled CNT can be even more interesting than single-walled ones. All this because the internal layers of the structure are shielded from external influence [1]. CNT and CNT-based composite materials are of great scientific and practical interest, primarily due to the unique combination of their physical characteristics. CNT are an extremely interesting class of materials both from the point of view of practical use and from the point of view of theoretical notions about the nature of nano-sized systems. Electrical transport properties belong to these interesting properties [2-3].

However, a question of the interconnection between the production conditions, structural characteristics and their electrical transport properties is poorly studied at present. This question is sufficiently important from the point of view of new possibilities of CNT use.

The key objective of the work was to reveal the conduction mechanisms of multi-walled CNT and establish connection with their magnetoresistive characteristics.

2. DESCRIPTION OF THE OBJECT AND INVESTIGATION METHODS

Modified multi-walled CNT, obtained by the carbon oxide conversion method [4] using iron oxide Fe_3O_4 catalyst, were the object of the investigation.

In Fig. 1 we present the electron-microscope image of a CNT obtained by the above mentioned method.

As seen from the figure, the average CNT diameter is equal to ~ 40 nm, iron particles of the size of 3-5 nm are located on the surface and partly in the CNT interlayer space. Based on the data of X-ray diffraction (see Fig. 2), lines which correspond to 002-reflexes of graphite (d_{002} = 0.337 nm), iron and iron oxide are identified in the CNT sample.

Structure of modified CNT, which were investigated, is described in detail in the work [5].

Fig. 1 – Electron-microscope image of a CNT modified by iron

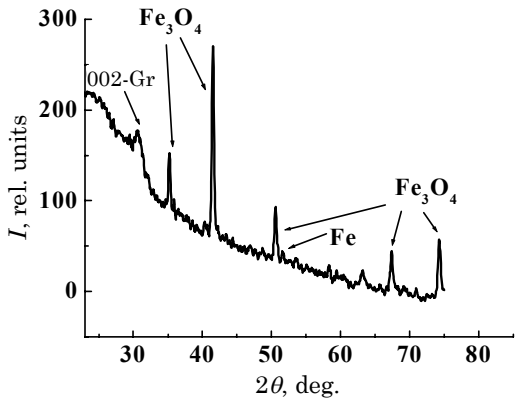

Fig. 2 – Fragment of the diffraction pattern of modified CNT

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3. EXPERIMENTAL PART AND ANALYSIS OF THE RESULTS

3.1 Temperature dependence of the electrical resistance

In Fig. 3 we illustrate the temperature dependence of modified CNT.

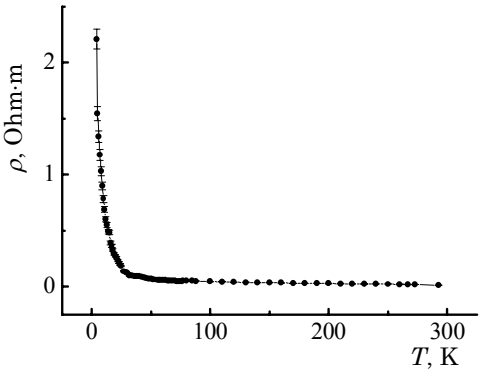

Fig. 3 – Temperature dependence of the electrical resistance of modified multi-walled CNT

As it is seen from Fig. 3, view of the temperature dependence of the electrical resistivity is typical for disordered carbon materials: dependence $\rho(T)$ is almost linear in the temperature range from 300 K to 62 K. A sharp increase in the electrical resistance is observed with further temperature decrease. Ratio $\rho_{4.2K} / \rho_{300K}$ for the given sample amounts to $\rho_{4.2K} / \rho_{300K} = 163.70$. The value of electrical resistivity is considerably larger in comparison with the samples of non-modified CNT [6]: $\rho_{4.2K} = 221 \cdot 10^{-2}$ Ohm·m and $\rho_{300K} = 1.35 \cdot 10^{-2}$ Ohm·m. This is, obviously, connected with both the defect structure of CNT themselves and sufficiently high content of iron oxide which prevents the formation of continuous conducting channels through the whole CNT sample.

We will analyze which conduction mechanisms are realized in the given sample of modified CNT. As it follows from the above presented data of the structural and phase analysis of the sample [5], the considered material is a complex heterosystem, whose composition consists of the ordered (multi-walled CNT and, possibly, nanographite) and disordered carbon phases, and also of the particles of iron and iron oxides, and the latter do not form continuous cluster in the sample. Each carbon phase, which is present in the sample, is characterized by own conduction mechanism [6]. Heterogeneous model, which takes into account different conduction mechanisms of separate phases entering the sample composition, is proposed for the analysis of the electrical resistance of the nanomaterial containing CNT. Such models were proposed for the description of the conduction of complex systems containing a polymer matrix and a nanocarbon filler [7-9].

In the framework of the proposed model, resistance of the sample containing CNT can be represented as a sum of coupled effective resistances which correspond to different phases in the sample [5]

$$\rho(T) = \sum_{i=1}^{n} C_i \rho_i(T) = C_1\rho_1(T) + C_2\rho_2(T) + \\ + C_3\rho_3(T) + C_4\rho_4(T), \quad (1)$$

where ρ_1 is the resistance of single-walled CNT or CNT with a small amount of layers; ρ_2 is the resistance of the ordered or weakly ordered carbon phase (multi-walled CNT with different degree of structural perfection, nanographite); ρ_3 is the resistance of disordered carbon phase (amorphous carbon, structurally deficient tube-like formations); ρ_4 characterizes metallic conduction. Each effective resistance is characterized by own weighting coefficient C_i, which shows the relative content of the phase in the sample. It is obvious that the given CNT sample does not contain single-walled CNT and, as it was mentioned above, metal particles do not form a continuous cluster there.

Thus, of all the possible mentioned mechanisms of electrical resistance for the given material, mechanisms which contribute to the total conduction of the sample are those mechanisms which form the resistance of the ordered carbon phase (the second term) and mechanisms which form the resistance of the disordered carbon phase (the third term). Electrical resistance of weakly ordered materials, in which the effects of weak localization and interaction of charge carriers are realized and to which multi-walled CNT can be related, in two-dimensional case is written in the form [9]

$$\Delta\rho_{zp} = \left\{ -\frac{e^2}{2\pi^2\hbar}\frac{\nu_1^2\lambda_1\rho(T_0)}{d_{002}} \times \right. \\ \left. \times \left[(\nu p + \gamma) \ln\frac{T}{T_{4.2}} + \gamma \ln\frac{2\pi k_B \tau_0}{\hbar} + \nu \ln\left(\frac{\tau_0}{A^*}\right) \right] \right\} + \rho_0, \quad (2)$$

where

$$\frac{1}{A^*} = \frac{k_B}{2E_F\tau_0} \ln\left(\frac{E_F\tau_0}{\hbar}\right), \quad (3)$$

E_F is the Fermi energy; λ_1 is the parameter which takes the values from 0.1 to 1 [9]; ν is the numerical coefficient which depends on the correlation between τ_φ and τ_0; $\tau_0 = L_a / V_F$ is the relaxation time of charge carriers at different scattering mechanisms; $\tau_\varphi = A^* T^{-m}$ is the relaxation time of the electron wave-function phase; m is the coefficient responsible for the type of charge carrier scattering ($m \sim 1$ for two-dimensional materials); γ is the numerical coefficient which reflects the measure of charge carrier screening; ν_1 is the constant which takes the value 1 in the case of turbostratic graphite and 0 in the case of highly oriented graphite; ρ_0 is the classical electrical resistance which for the turbostratic graphites according to the Wallace model is written as

$$\rho_0 = \frac{\pi\sqrt{3}\hbar a_0\gamma_0}{e^2}\frac{d_{002}}{k_F L_K} = \frac{\pi\sqrt{3}\hbar a_0\gamma_0 d_{002}}{e^2 k_F L_{ef}}, \quad (4)$$

where

$$\frac{1}{L_{ef}} = \frac{1}{L_{ph}} + \frac{1}{L_c} + \frac{1}{L_{def}} + \frac{1}{L_{imp}}, \quad (5)$$

$\gamma_0 = 2.8$ eV is the overlap integral which characterizes the interaction between atoms in graphite; a_0 is the lattice translation vector; k_F is the Fermi wave-vector; L_{ef} is the effective mean free path of charge carriers; L_{ph} is the mean free path of charge carriers (electrons and holes) at scattering by phonons; L_c is the mean free path

of charge carriers at scattering by crystal boundaries; L_{def} is the mean free path of charge carriers at scattering by defects; L_{imp} is the mean free path of charge carriers at scattering by impurities. Since L_c, L_{def}, L_{imp} do not depend on the temperature, then temperature dependence of the effective mean free path L_{ef} will be determined by the value of L_{ph}.

Resistance of the disordered carbon phase (the third term in (1)) is defined by the hopping conduction mechanism with variable jump distance for the three-dimensional case [10]

$$\rho_3 = \rho_{01/4} \exp\left[\left(\frac{T_{01/4}}{T}\right)^{1/4}\right], \quad (6)$$

where $T_{01/4}$ and $\rho_{01/4}$ are the coefficients varied in a wide range depending on the degree of order of the disordered carbon phase.

Formation of the Coulomb gap is typical for such materials at low temperatures. In this case, according to the Efros-Shklovskii model, electrical resistance depends on the temperature as [10]

$$\rho_{1/2} = \rho_{01/2} \exp\left[\left(\frac{T_{01/2}}{T}\right)^{1/2}\right], \quad (7)$$

where $T_{01/2}$ and $\rho_{01/2}$ are the constants.

Thus, in the case of modified CNT, which are investigated, (1) takes the view [2-3, 7]

$$\rho(T) = C_2\rho_2 + C_3\left(\rho_{1/4} + \rho_{1/2}\right). \quad (8)$$

In the framework of the proposed model using the experimental data on the temperature dependence of the electrical resistance, the values of the coefficients C_2 and C_3 for the studied CNT were estimated and the temperature dependences of the electrical resistance components, which are defined by the localization mechanism and hopping mechanism, were calculated (Fig. 4).

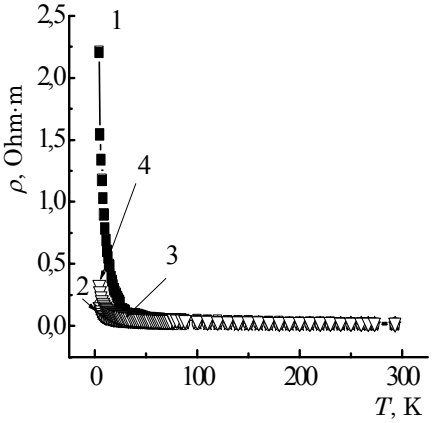

Fig. 4 – Calculated dependences of the components $\rho(T)$ according to the formula (1) for modified CNT (curve 1 – experimental values of ρ, curve 2 – $C_3\,\rho_3$, curve 3 – $C_2\,\rho_2$, 4 – theoretically calculated values of ρ)

Obtained values are equal to $C_2 = 0.31$, $C_3 = 0.69$. Thus, the hopping conduction mechanism is the main mechanism which forms the electrical resistance of the investigated CNT.

3.2 Magnetoresistance of the modified CNT samples

In Fig. 5 we present the experimental dependences of the magnetoresistance $(R_B - R_0) / R_0$ for modified CNT on the value of the magnetic field for the perpendicular orientation of magnetic field with respect to the current through the sample (Fig. 5a, b) and for the parallel orientation of magnetic field (Fig. 5c).

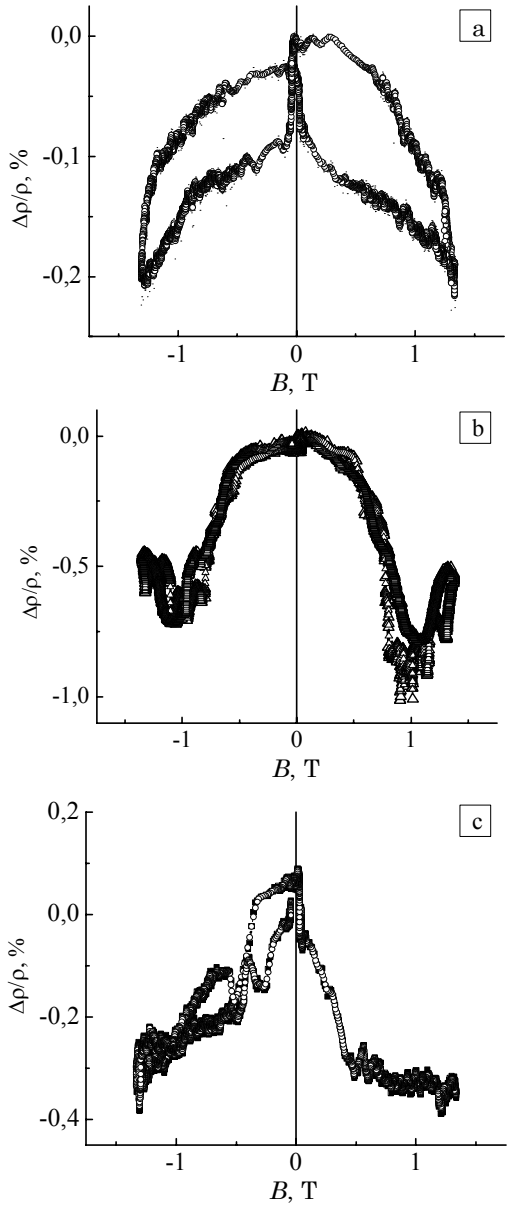

Fig. 5 – Dependence of the magnetoresistance of modified CNT on the magnetic induction for $B \perp I$ geometry at: (a) $T = 293$ K, (b) $T = 77$ K; for $B \parallel I$ (c) $T = 77$ K

As seen from Fig. 5, magnetoresistance is negative in all possible configurations, i.e. resistance of the sample decreases in magnetic field. At $T = 293$ K, hysteresis is observed in the field dependence of the magnetoresistance. The value of the magnetoresistance at maximum field is equal to – 0.20 %, and in this case saturation of the magnetoresistance is not achieved. At nitrogen temperature hysteresis in the dependence of the magnetoresistance is weakly expressed, and for the magnetic field

induction of ~ 0.5 T the magnetoresistance saturation is observed; the value of the magnetoresistance in the maximum field is equal to ~ – 0.4 %.

As known, presence of the hysteresis in the dependence of the electrical resistance on the magnetic field in the systems, in which magnetic and non-magnetic phases are present, indicates a substantial contribution of the spin-dependent scattering to the scattering mechanisms of charge carriers. This scattering is maximum in the case of zero magnetic field, since, in this case, magnetic moments of particles of a magnetic metal are chaotically oriented. With increasing magnetic field, ordered orientation of the particles magnetic moments of magnetic metals takes place that leads to the decrease in the charge carrier scattering and, correspondingly, to the decrease in the system electrical resistance. Another mechanism, which leads to the appearance of the negative magnetoresistance, is the quantum effect of weak localization of charge carriers which is amplified in weakly ordered or disordered systems [10-12]. External magnetic field, as well as the presence of magnetic impurities in the material, leads to the loss of the phase coherence of electron waves and, as a result, to the attenuation of the weak localization effect [13].

As it is known from literature data, classical magnetoresistance in the configuration "magnetic field is parallel to the current" is absent for non-magnetic materials. However, as it follows from Fig. 5c, complex dependence of the electrical resistance on the magnetic field is observed for the given sample. Maximum value of the magnetoresistance is equal to ~ (– 0.7 ÷ – 0.8) %. A local minimum in the dependence of the magnetoresistance is observed for the field value $B \sim 1$ T.

Existence of the substantial longitudinal magnetoresistance in the studied CNT samples is connected with the presence of ferromagnetic phase [14]. Manifestation of the anisotropic magnetoresistance effect is typical for such systems. For ferromagnetic materials electrical resistance in magnetic field depends on the angle θ between the magnetization (M) direction and external magnetic field (B). Dependence of the magnetoresistance sign on the mutual orientation of the magnetic field M and current I is the feature of the anisotropic magnetoresistance or ferromagnetic resistance anisotropy (FRA)

$$\rho(\theta_{M,I}) = \rho_0 + \rho_\Delta \cdot \cos^2\left(\theta_{M,I}\right), \qquad (9)$$

where ρ_0 is the resistance in zero magnetic field, and FRA value is equal to $\rho_\Delta \equiv \rho_{||} - \rho_\perp$ [10]. The reason of the FRA appearance is the decrease in the symmetry of magnetized state of the material in comparison with its non-magnetic state induced by the presence of the magnetization and influence of the spin-orbit coupling [15-18]. Complex dependence of the anisotropic magnetoresistance is typical, if orientation of the easy magnetization axis of a magnetic impurity does not coincide with the direction of current flowing. Firstly, magnetization of ferromagnetic phase particles occurs at small fields along the easy magnetization axis which is, obviously, oriented at some angle to the current direction. Upon reaching the critical value of magnetic field, remagnetization of ferromagnetic phase particles occurs along the external field direction. Moreover, as shown when establishing the structural-phase composition of the studied material, CNT contain two ferromagnetic α-iron and iron oxide Fe_3O_4 phases with different coercive forces. Presence in the material of two ferromagnetic phases with different values of the coercive force leads to the appearance in the dependence of the magnetoresistance on the magnetic field of the local minima and maxima which represent the remagnetization processes of these different phases. Sizes of ferromagnetic particles themselves also influence the remagnetization processes of ferromagnetic particles. As known, $H_c \sim 1/d$, where d is the size of a ferromagnetic particle. That is, if material contains ferromagnetic particles of considerably different size, this also leads to the appearance of critical points in the dependence $\Delta\rho / \rho(B)$.

4. CONCLUSIONS

1. The performed investigations of the electrical resistance of the iron modified CNT samples have shown that the total CNT resistance is determined by relative correlation of separate carbon phases. Conduction mechanisms of separate carbon phases, which enter the sample composition, and relative weighting coefficients of the phase content are determined within the model of additive contributions of effective resistances with different conduction types.

2. The carried out investigations of the magnetotransport properties of the CNT samples modified with iron and iron oxide have revealed that the given materials are a complex heterogeneous system, in which simultaneous manifestation of different mechanisms of the magnetoresistance formation takes place.

3. Localization mechanism typical for the weakly ordered carbon phase (multi-walled CNT), giant magnetoresistive effect connected with the interaction of charge carriers of the carbon system with magnetic moments of the ferromagnetic phase, and anisotropic magnetoresistance appearing due to the features of magnetization of ferromagnetic phase particles in the external magnetic field are exhibited in the magnetoresistance.

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