JOURNAL OF NANO- AND ELECTRONIC PHYSICS
Vol. **7** No 2, 02010(5pp) (2015)

ЖУРНАЛ НАНО- ТА ЕЛЕКТРОННОЇ ФІЗИКИ
Том **7** № 2, 02010(5cc) (2015)

Investigation of the Field and Temperature Dependences of the Resistance of Nanocarbons Modified with Nickel and Cobalt

T.A. Len*, I.V. Ovsiienko, L.Yu. Matzui, V.Ya. Tkachuk

Taras Shevchenko National University of Kyiv, Volodymyrska Str., 64, 01601 Kyiv, Ukraine

(Received 17 December 2014; published online 10 June 2015)

The work is devoted to the study of the effect of modifying with magnetic metals of structurally different nanocarbon structures on their electrical and magnetotransport properties. The experimental temperature and field dependences of the resistivity in a wide temperature and magnetic field ranges are considered, and the analysis of their features and formation mechanisms is performed. Modification of nanocarbon by magnetic metals with the concentration of 10 wt. % almost does not influence the value and behavior of the temperature dependence of the resistivity of modified nanocarbon. The temperature dependence of the resistivity of modified nanocarbon is determined by the same mechanisms as for the initial (before modification) nanocarbon. We have revealed the difference in the effect of modifying by magnetic metals on the magnetotransport properties of different types of nanocarbon associated with the features of interaction of the magnetic metal particles with particles of nanographite and CNT.

Keywords: Modification multiwalled carbon nanotubes, Electrical resistance, Magnetoresistance.

PACS numbers: 61.48.De, 65.80. – g

1. INTRODUCTION

Carbon nanotubes (CNT) and carbon materials possess a complex of unique physical and chemical properties and find a wider practical application [1-3]. Direct regulation of their properties is an important problem. Modification of nanocarbon structures is of significant interest, since it allows to influence the electron structure of nanocarbon and change its properties associated with the charge transfer and magnetic properties. Use of modified carbon nanostructures in polymer composites allows to expand the boundaries of their application. Therefore, the questions of development of the methods of modification of nanocarbon and establishment of the influence of modification on the nanocarbon properties are a topical problem.

The aim of the present work is to establish the influence of modification of CNT and nanographite with nickel and cobalt on the mechanisms of electric and magnetic conductivity.

2. DESCRIPTION OF THE OBJECT AND METHODS OF STUDY

As the initial materials for modification, the following two types of nanocarbon were chosen: multi-walled CNT obtained by catalytic pyrolysis of carbohydrates (chemical vapor deposition (CVD) method) and nanographite obtained by thermochemical treatment from thermally expanded graphite.

Modification of nanocarbons with metals was performed by the metal reduction method from salt during impregnation of the initial nanocarbon with water-salt solution [4]. Cobalt and nickel were chosen as the modifying metals. Modification was carried out by the reduction method from water-salt solution in hydrogen stream. As a result, the samples of nanocarbon with the content of the modifying component of 10 wt. % were obtained.

Aqueous solution of cobalt acetate $Co(CH_3COO)_2$ with the salt concentration of 80 wt. % was used for impregnation of the carbon material. Impregnation occurred at the temperature of 350 K during 48 hours. Reduction of the carbon material/$Co(CH_3COO)_2$ powders to the state carbon material/metal was performed in hydrogen stream at $T = 350$ °C during 15 hours [5, 6].

Measurements of the electrical transport properties were carried out by the standard four-probe technique [7]. The samples were produced by cold pressing method. The obtained samples were marked as follows: sample # 1 – nanographite + Ni, sample # 2 – CNT + Ni, sample # 3 – nanographite + Co, sample # 4 – CNT + Co.

3. DESCRIPTION AND ANALYSIS OF THE RESULTS

In Fig. 1 we present the fragments of the diffraction patterns obtained for the modified nanocarbon samples.

The following parameters of the nanographite samples are determined according to the X-ray study: multiwalled CNT of the diameter of 40 nm with the internal cavity to 10 nm, $d_{002} = 3.35$ nm, $L_c = 10$ nm; flat scales of nanographite of the diameter to 10 μm, $d_{002} = 3.36$ nm, $L_c = 20$ nm (here L_c is the crystallite size along the basal plane c).

As seen from Fig. 1, only Ni lines are revealed in the samples of nanocarbon modified with Ni, while for nanocarbon modified with Co both lines of pure cobalt and lines corresponding to cobalt oxides are identified by the X-ray data.

In Fig. 2 we illustrate the fragment of the electron microscopic image obtained using transmission electron microscope – TEM images of the samples of nanocarbon modified with Ni.

As seen from Fig. 2, there is a rather uniform distribution of Ni particles on the CNT surface and, obviously, partly in the internal cavity of CNT.

* talen148@gmail.com

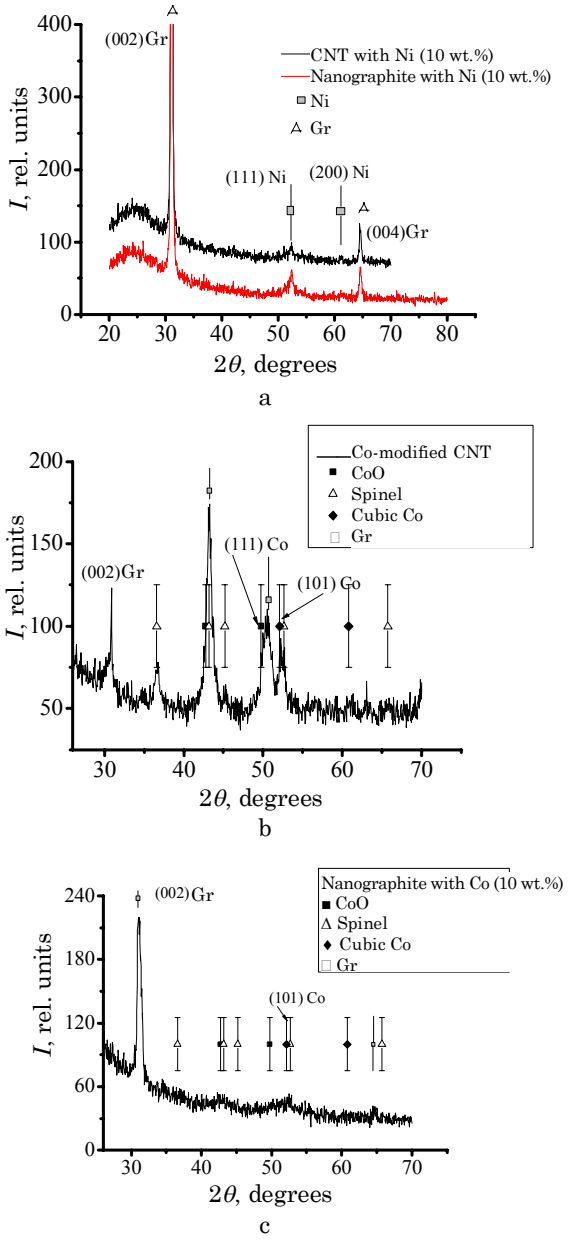

Fig. 1 – Diffraction patterns of nanographite samples: (a) CNT modified with 10 wt. % Ni, (b) CNT modified with 10 wt. % Co, (c) nanographite modified with 10 wt. % Co

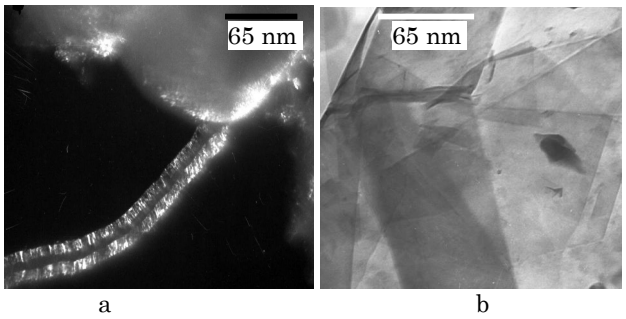

Fig. 2 – Fragment of the TEM-image of Ni-modified: CNT (a) and nanographite (b)

Separate nickel particles of size not more than 5 nm are visualized. Individual Ni particles of size to 50 nm are observed on the surface of nanographite particles.

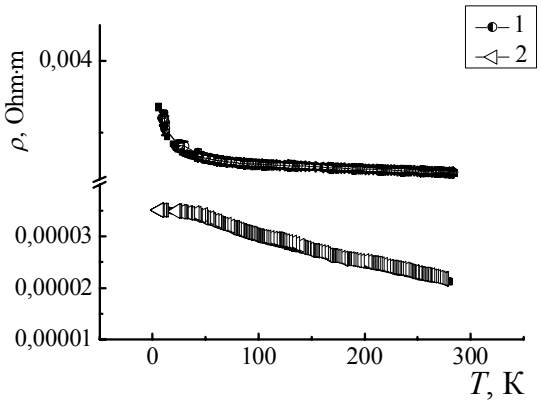

Fig. 3 – Experimental dependences $\rho(T)$ for the following samples: (1) Ni-modified CNT and (2) Ni-modified nanographite

So, the samples are heterogeneous systems composed of multi-walled CNT or nanocarbon and nickel particles.

Temperature and field dependences of the electrical resistance and magnetoresistance of nanocarbon samples modified with metals were investigated.

In Fig. 3 we present the dependences $\rho(T)$ for nanographite and CNT samples modified with Ni.

As seen from Fig. 3, dependence $\rho(T)$ is decaying. In contrast to the modified nanographite sample, for Ni-modified CNT sample one observes an anomalous increase in the resistance with decreasing temperature to 4.2 K.

$\rho_{4.2\ K}/\rho_{277\ K}$ ratio for the sample # 1 is equal to 1.61 and for the sample # 2 – 3.09. $\rho_{4.2\ K}/\rho_{277\ K}$ ratio is almost 2 times more for the sample # 2 (in comparison with the same ratio for the sample # 1).

A substantial difference in the temperature dependences of the resistivity for these two samples is observed at low temperatures: a horizontal shelf is observed for modified nanographite, while for modified CNT – an anomalous increase in the electrical resistance. Such behavior of the temperature dependence of the electrical resistance is typical for the ordered graphites. A weak dependence of the resistance on the temperature is also observed for modified CNT at high temperatures, although the value of the resistivity is considerably larger. However, at low temperatures there is an anomalous increase in the resistivity typical for fine-crystalline weakly ordered graphite. We should note that character of the temperature dependence of the resistivity for modified nanocarbon is absolutely the same as the temperature dependence of the electrical resistance for the initial (before modification) nanocarbon samples. So, the influence of modification on the value and dependence of $\rho(T)$ is not revealed. Metal particles do not form a continuous cluster through the whole nanocarbon sample.

A weak dependence of the electrical resistance on the temperature for the studied samples of modified nanocarbon is associated with the fact that temperature-independent scattering at the boundaries of crystallites is the main carrier scattering mechanism in the given material that leads to a weak temperature dependence of the charge carrier mobility. A small overlap of the valence and conduction bands takes place for ordered nanographites leading to the situation when charge carrier concentration is not changed with temperature at low temperatures. This fact explains a horizontal shelf in the dependence $\rho(T)$ for nanographite.

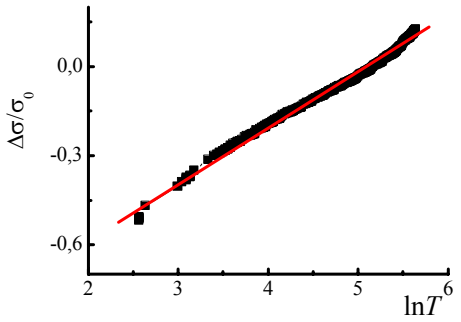

Fig. 4 – Dependence of the correction to the conductivity on the logarithm of temperature $\Delta\sigma/\sigma_0 \sim f(\ln T)$ for Ni-modified CNT

In contrast to nanographite, in modified CNT at low temperatures one can observe an anomalous increase in the value of the electrical resistance that is, obviously, associated with the manifestation in these materials of the quantum effects of weak localization and the electron-electron interaction of charge carriers. In Fig. 4 we represent the calculated dependence of the correction to the conductivity on the logarithm of temperature $\Delta\sigma/\sigma_0 \sim f(\ln T)$ for Ni-modified CNT.

As seen from Fig. 4, linear dependence $\Delta\sigma/\sigma_0 \sim f(\ln T)$ is observed that really implies the possibility to realize the quantum effects of weak localization and electron-electron interaction for the obtained modified CNT and two-dimensional behavior of the conductivity in them.

In Fig. 5 and Fig. 6 we show the relative change in the magnetoresistance $\Delta\rho/\rho$ for the sample # 1 of nanographite with Ni and sample # 2 of CNT with Ni, respectively, in two configurations: current I passing through the sample is directed perpendicular to the magnetic field induction B (0º) $I \perp B$ and current through the sample is parallel to the magnetic field induction (90º) $I \| B$ at the temperatures of $T = 77$ K and 300 K.

It is seen from Fig. 5 that a substantial increase in the magnetoresistance $\Delta\rho/\rho$ up to 2% is observed for the perpendicular orientation, while for the parallel orientation $\Delta\rho/\rho$ increases only by 0.4 %. For Ni-modified CNT one observes a loop-shaped positive magnetoresistance at room temperature and a negative magnetoresistance at low temperatures (Fig. 6).

In Fig. 7 and Fig. 8 we present the dependence $\Delta\rho/\rho$ at $T = 293$ K and 77 K at the perpendicular $I \perp B$ and parallel $I \| B$ orientations for Co-modified CNT.

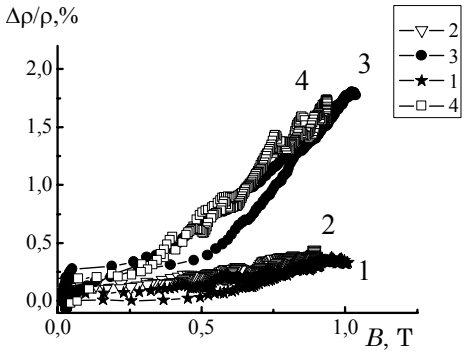

Fig. 5 – Experimental dependences of the magnetoresistance of Ni-modified nanographite at: 1 – (0º, 300 K), 2 – (0º, 77 K), 3 – (90º, 300 K) and 4 – (90º, 77 K)

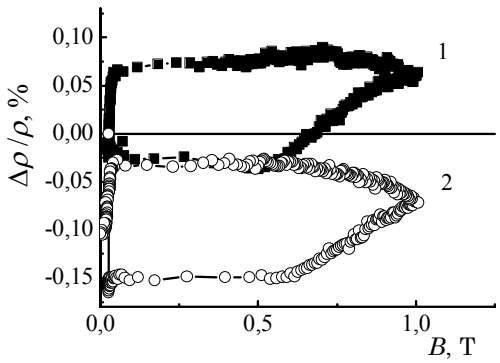

Fig. 6 – Experimental dependences of the magnetoresistance of Ni-modified CNT at: 1 – (90º, 300 K), 2 – (0º, 300 K)

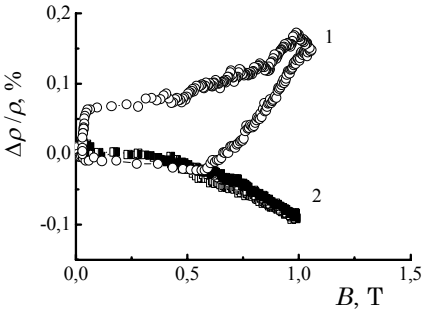

Fig. 7 – Experimental dependences of the magnetoresistance of Co-modified CNT at $I \perp B$, curve 1 – $T = 293$ K, curve 2 – $T = 77$ K

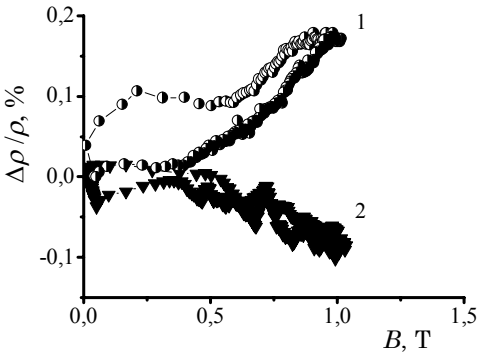

Fig. 8 – Experimental dependences of the magnetoresistance of the sample # 4 at $I \| B$, curve 1 – $T = 293$ K and curve 2 – $T = 77$ K

For Co-modified CNT, magnetoresistance is positive in absolute value at $T = 293$ K and value of $\Delta\rho/\rho$ decreases and becomes negative with decreasing temperature. A loop-shaped dependence $\Delta\rho/\rho$ (B) is observed at room temperature.

In Fig. 9 we illustrate the dependence $\Delta\rho/\rho$ (B) at $I \perp B$ for Co-modified nanographite at $T = 293$ K.

A small increase in the magnetoresistance is observed at the parallel orientation of magnetic field, and at the perpendicular orientation of B and I, magnetoresistance is slightly higher and is equal to 2.35 %.

The value of the magnetoresistance for Co-modified nanographite at $T = 77$ K and at the perpendicular and parallel orientations of B and I is presented in Fig. 10.

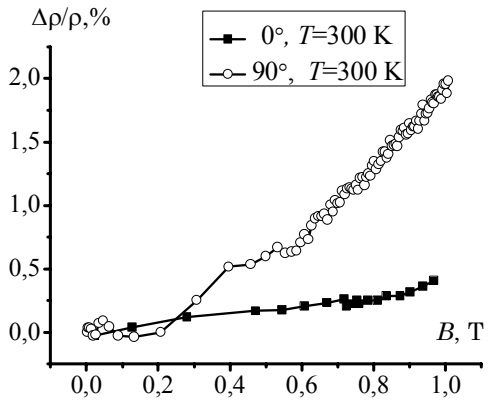

Fig 9 – Experimental dependences of the magnetoresistance for Co-modified nanographite at $I \perp B$ and $I \| B$ and $T = 293$ K

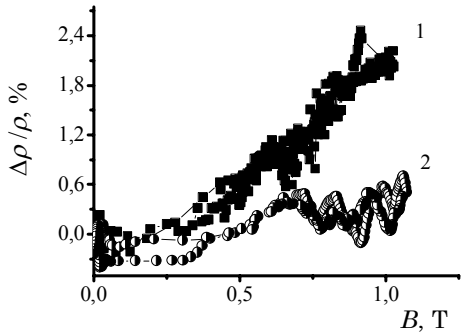

Fig. 10 – Experimental dependences of the magnetoresistance for Co-modified nanographite at nitrogen temperature: curve 1 – $I \perp B$, curve 2 – $I \| B$

As seen from Fig. 10, magnetoresistance of Co-modified nanographite at nitrogen temperature is positive and is equal to 2.4 %. Magnetoresistance at $T = 77$ K is positive for both the parallel and perpendicular orientations of B and I. The absolute value of the magnetoresistance is slightly lower and is equal to 0.6 %. In the case of the perpendicular orientation of magnetic field and current one can observe a positive, quadratic in field, magnetoresistance of ~ 2-2.5 % in the maximum field. Moreover, with decreasing temperature magneto-resistance is almost not changed, the resistance remains positive. Such character of the dependence of the magnetoresistance is typical for the ordered graphites.

Dependence of the magnetoresistance of the ordered graphite materials on magnetic field can be written as

$$\frac{\Delta\rho}{\rho} = \frac{p}{n}\bar{\mu}^2 B^2, \qquad (1)$$

where p, n and $\bar{\mu}$ are the concentrations of holes and electrons and, respectively, their average mobility. The relative magnetoresistance depends quadratically on the value of the magnetic induction.

In Fig. 11 we represent the dependences of the magnetoresistance on the square of the magnetic field induction for the samples of nanographite modified with nickel (a) and cobalt (b).

Indeed, a linear dependence of the magnetoresistance on the square of the magnetic induction for nanographite modified with both Ni and Co is observed (see Fig. 11). Considering that mobilities of electrons and holes are approximately equal and p/n ratio is equal to 1.2, we have estimated by the formula (1) the averaged value of the mobility μ, which is equal to 0.114 m²/V·s for Ni-modified and 0.119 m²/V·s for Co-modified nanographites. With decreasing temperature, the value of the magnetoresistance slightly increases due to the insignificant increase in the mobility [8-10].

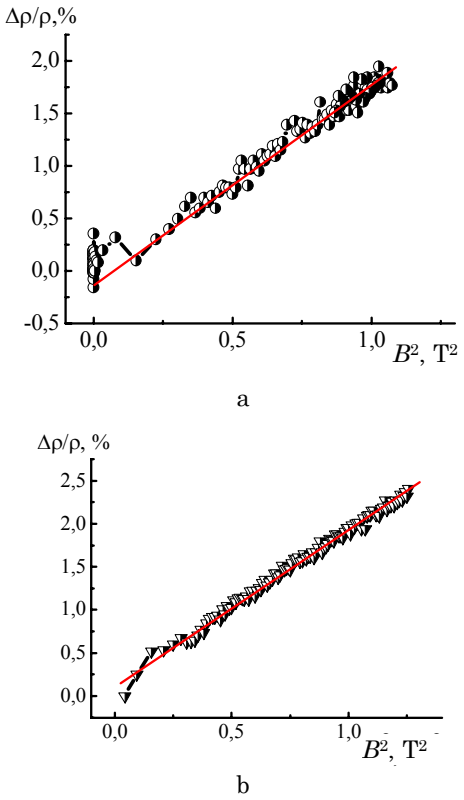

Fig. 11 – Dependence of the magnetoresistance on B^2 for nanographite modified with nickel (a) and cobalt (b)

We note that for the given samples one can observe a small in value quadratic longitudinal magnetoresistance, which should be absent in a graphite material for such mutual orientation of the magnetic field and current. To our opinion, this is connected with a certain disorientation of nanographite particles in the bulk sample and considerable difference in the values of the conductivity along the graphite layers and perpendicular to the graphite layers. This, obviously, leads to the appearance of a small in value longitudinal magnetoresistance. We note that presence of magnetic metal particles on the surface of nanographite particles does not influence the magnetoresistance of the sample.

An entirely different dependence of the magnetoresistance on the magnetic field and temperature is observed for the samples of modified nanotubes. As seen from Fig. 10 and Fig. 11, a complex view of the field dependences of the magnetoresistance for the samples of modified CNT is observed: hysteresis in the dependence of the magnetoresistance on the magnetic field is present both in the transverse and longitudinal magnetic fields. For the samples of Ni-modified CNT (Fig. 6) one can also observe a sign change of the magnetoresistance for different magnetic field orientations relative to the current through the sample. As it was established in the previous works [11, 13], during the study of the magnetoresistance

at different mutual orientations of magnetic field and current through the sample, the specified features in the dependences of the magnetoresistance for Fe-modified CNT are associated with the manifestation of two effects, namely, the giant magnetoresistance effect and anisotropic magnetoresistance. Giant magnetoresistance is observed in layered or cluster systems, in which magnetic and non-magnetic phases are combined, and this results in the spin polarization of charge carriers. Orientation of spins of magnetic metals in magnetic field leads to the substantial decrease of charge carrier scattering by them that, in turn, leads to the decrease in the electrical resistance of the system in general. Anisotropic magnetoresistance appears in magnetic metals under the condition that the easy magnetization axis does not coincide with the external magnetic field direction and is determined as $\rho = \rho_{\perp} + (\rho_{\perp} - \rho_{||})\cos^2\theta$, where $\rho_{\perp}$ and $\rho_{||}$ are the resistances in magnetic field, respectively, for the perpendicular and parallel orientations of the current density vector with respect to the magnetization vector, θ is the angle between the magnetization and current density vectors. Thus, a complex behavior of the field dependence of the magnetoresistance for modified CNT is explained by the manifestation of the effects of giant magnetoresistance and anisotropic magnetoresistance, and these effects are more pronounced for Ni-modified samples than for Co-modified ones. This difference is explained by the lower content of magnetic phase in CNT samples modified with Co compared with the samples modified with Ni. Moreover, as the comparative analysis of the results obtained for modified CNT and modified nano-graphite shows, the arrangement of particles of the nano-sized metal in nanocarbon is the determining factor for the presence of the effects of giant and anisotropic magnetoresistances. For CNT, magnetic metal particles are located over the CNT surface and, obviously, partly penetrate into the internal cavity of CNT. In this case, charge carriers in graphite layers and magnetic metal atoms interact with each other that leads to the appearance of the mentioned phenomena. For modified nanographite, metal particles are placed only on the surface of nanographite particles, do not interact with charge carriers in graphite layers, and, therefore, phenomena of the giant and anisotropic magnetoresistances are not observed for the given structures.

4. CONCLUSIONS

1. Modification of nanocarbon with ferromagnetic metals in the concentration of 10 wt. % almost does not influence the value and trend of the temperature dependence of the electrical resistance of modified nanocarbon. Temperature dependence of the electrical resistivity of modified nanocarbon is determined by the same mechanisms as for the initial for modification nanocarbon: for nanographite this is, mainly, grain boundary scattering of charge carriers, for CNT – mechanisms of weak localization and interaction of charge carriers.

2. Differences in the influence of modification with magnetic metals on the magnetic transport properties of different types of nanocarbon associated with the features of interaction of magnetic metal particles and particles of nanographite and CNT are revealed. It is established that modification with magnetic metals of nanographite does not change the classical mechanism of magnetoresistance, while modification with magnetic metals of CNT substantially influences the behavior of the dependence of the electrical resistance on the magnetic field. Magnetoresistance of CNT modified with magnetic metals is determined by the combination of two mechanisms: mechanism of giant magnetoresistance, which is typical for systems in which magnetic and non-magnetic layers are alternated, and anisotropic magnetoresistance.

3. It is established that structural and morphological features and distributional character of magnetic metal particles over the surface of nanocarbon particles is the determining factor, which defines the nature of the dependence of the electrical resistance on the magnetic field for nanocarbon modified with magnetic metals. For CNT, nanosized particles of the magnetic metal are located over the CNT surface and partly in the inner cavity of CNT that leads to the interaction of charge carriers in graphite layers and magnetic metal atoms. This induces the appearance of the giant and anisotropic magnetoresistance effects for the given modified structures. For modified nanographite, metal particles are placed only over the surface of nanographite particles and magnetic metal atoms do not interact with charge carriers in the graphite layers, therefore, the specified effects are not observed for these structures.

REFERENCES

1. A.L. Ivanovskiy, *Zhurnal neorganicheskoy khimii* **48** No 6, 945 (2003).
2. M.S. Dresselhaus, G. Dresselhaus, P. Eklund (Academic Press: 1996).
3. P. Kharris, *Uglerodnyye nanotrubki i rodstvennyye struktury* (M.: Tekhnosfera: 2003).
4. E.S. Choi , J.S. Brooks, D.L. Eaton, H. Garmestani, *J. Appl. Phys.* **94**, 6034 (2003).
5. Sarbajit Banerjee, Stanislaus S. Wong, *Nano Lett.* **2** No 1, 49 (2002).
6. Q. Li, Q.Z. Xue, X.L. Gao, Q.B. Zheng, *Polymer Lett.* **3**, No 12, 769 (2009).
7. L.Yu. Matzui, I.V. Ovsienko, T.A. Len, Yu.I. Prylutskyy, P. Scharff, *Fullerenes, Nanotubes and Carbon Nanostructures* **13**, 259 (2005).
8. I. Ovsienko, T. Len, L. Matzui, Yu. Prylutskyy, P. Eklund, F. Normand, U. Ritter, P. Scharff, *Physica E* **37**, 78 (2007).
9. T.A. Len, L.Yu. Matsui, I.V. Ovsienko, Yu.I. Prilutskyy, I.B. Berkutov, V.V. Andriyevskiy, G.Ye. Grechnev, Yu.A. Kolesnichenko, *Low Temp. Phys.* **37** No 9-10, 1027 (2011).
10. I. Ovsiyenko, T. Len, L. Matzui, O. Golub, Yu. Prylutskyy, P. Eklund, *Mater. Sci. Eng. C* **26**, 1180 (2006).
11. I.V. Ovsienko, Visnyk kyyivs'koho universytetu. Seriya fiz.-mat. nauk. 1, 267 (2014).
12. I.V. Ovsienko, L.Y. Matzui, I.V. Yatsenko, *Mat.-wiss. u Werkstofftech.* **44**, No 2-3, 161 (2013).
13. L.Yu. Matzui, T.A. Len, I.V. Ovsiyenko, *Nanosystemy, nanomaterialy, nanotekhnolohiyi* **7** No 2, 383 (2009).