Low temperature charge transport in arrays of single-walled carbon nanotube bundles with radiation induced defects

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Abstract. Electric transport properties and magnetoresistance (MR) of the array of metallic single-wall carbon nanotube bundles irradiated by the electron flux with the energy close to 1 MeV or Co^{60} gamma quanta have been investigated within the temperature range T = 1.8…200 K and in the magnetic fields up to 5 T. The power-law behavior of the conduction *vs* temperature was observed within the range 50 to 200 K, which is typical for conduction of quasi-one-dimensional systems in the model of the electron gas as the Luttinger liquid. The change in power exponent α with the radiation dose and its deviation as compared to α for the non-irradiated samples is related with changing the number of conduction channels in the bundles as a consequence of the radiation defects appearance. At the temperatures below 50 K, the Mott three-dimensional hopping conduction is realized. Using the measured dependence of conduction on the temperature and electric field, the density of electron states in the vicinity of the Fermi level, which participate in the hopping charge transport, and the localization length of charge carriers in these states have been determined. These parameters determining the hopping mechanism of the charge transport are noted to depend on the radiation dose. The magnetoresistance in the Mott-type hopping conduction region was negative in the whole range of magnetic fields, while at the large fields an upturn to the positive change was observed. The mechanisms both of the negative and positive MR components are discussed.

Keywords: metallic single-wall carbon nanotube bundles, electric transport, radiation, magnetoresistance, hopping conduction, localization length.

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1. Introduction

In recent years, the charge transport in carbon nanotube (CNT) arrays in electric and magnetic fields has been intensively investigated because of its importance for possible applications of these structures in nano-electronics and sensors [1, 2]. These studies have been carried out using various types of CNT arrays (carbon nanotubes bundles, aligned fibers, networks, films, mats, *etc*.), and there was found that the electrical properties strongly depend on morphology of arrays and the quality of contacts between individual nanotubes (see, for example [3-7]). In fact, since CNT arrays are formed by randomly distributed nanotubes, the contacts play the role of insulating barriers along the conduction path. Therefore, the conduction mechanism acquires the character relevant for disordered materials – the mechanism of variable range hopping and tunnel mechanism or the fluctuation induced tunneling. Both of these mechanisms of charge transport have been observed in the oriented arrays of the single-wall nanotube (SWCNT) bundles and aligned SWCNT fibers at temperatures below 50 K [4]. In the SWCNT network, the hopping conduction was observed within the wide temperature range from 4 up to 300 K [6].

In the case when the role of contact barriers is diminished, the phenomena inherent to individual CNT nanotube, being a quasi-one-dimensional conductor, are observed. These are the quantum corrections to conductivity due to the weak localization [8] and Luttinger liquid behavior [9]. The Luttinger liquid conductivity mechanism was observed in the oriented and non-oriented arrays of the SWCNT bundles within the temperature range 20 to 200 K [3]. The temperature dependence of conductivity, which is characteristic for contribution of the quantum corrections to conductivity under the conditions of weak localization of charge carriers, was found in the arrays of aligned multi-wall CNT [10].

The transport properties of CNT arrays depend on the defectiveness extent that may be changed, for example, by radiation treatment. In practice, the influence of various irradiation types on the charge transport in the CNT arrays is still poorly known. Modification of functionality of the metallic SWCNT [11] and changes of the Luttinger liquid conductivity in the arrays of bundles of the metallic SWNTs under the Co^{60} γ-radiation have been investigated in [12].

In this paper, we present the charge transport properties of the array of the metallic SWCNT bundles irradiated by the electron flux with the energy close to 1 MeV or Co^{60} gamma quanta. Mainly, our attention was paid to low temperatures where the conduction, as a consequence of the random spatial location of nanotubes, was caused by hops of charge carriers. The parameters characterizing the transport properties, such as the density of electronic states in the vicinity of the Fermi level g_F participating in the charge transport and the localization length of charge carriers in these electron states ξ, have been determined. These parameters are noted to depend on the radiation doze and used to explain features of the magneto-transport in the structures under study. The discussion on possible types of radiation defects and the dependence of g_F and ξ parameters on the radiation dose will be published later.

2. Samples and experimental details

We investigated the samples consisted of compressed SWNTs powder containing bundles. The original powder was compressed at the room temperature by applying the uniaxial pressure of 1 GPa. The powder was provided by Cheap Tubes Inc. Company, USA, and contained 90% of SWCNT having metallic conductivity with the tube diameters of 1.1 and 2 nm, and with initial bundle lengths within the range 5…30 μm.

According to the results of Ref. [13], the structures formed at the above pressure were bundles mainly oriented in the plane perpendicular to the axis of the applied pressure. Nanotubes are bound together by weak van der Waals forces. The high-resolution electron microscopy images show the structure consisting of twisted and crossed bundles that form a SWNT array with a large number of inter-tube contacts.

The samples to measure the dependences of the resistance on the temperature and the applied electric or magnetic field had the electric contacts fabricated by silver paste applied to the sample surface cut out of the structure. Irradiation of the samples was carried out at 300 K in the hydrogen ambient at the normal atmospheric pressure. The γ-radiation dose was varied up to $1.7\cdot10^7$ rad, the fluence magnitude of the high-energy electrons was chosen in the range of $3\cdot10^{14}$ up to $6\cdot10^{14}$ e/cm^2. Measurements of the electric transport under weak electric fields were carried out using the dc regime (~ 10 μA). In measurements at high (heating) fields, the pulsed regime was used with the applied voltage pulse duration ~ 100 ns. In the magnetoresistance (MR) measurements, the magnetic field strength up to 5 T was used.

3. Experimental results and discussion

The measured temperature dependences of conduction for the samples with different kinds and doses of irradiation manifest the similar behavior. Shown in Fig. 1 with both axes in the logarithmic scale are curves for the cases of irradiation by the high-energy electrons with the fluences of $3\cdot10^{14}$ and $6\cdot10^{14}$ e/cm^2 (samples S1 and S2, respectively) and γ-irradiation with the dose of $1.7\cdot10^7$ rad (sample S3).

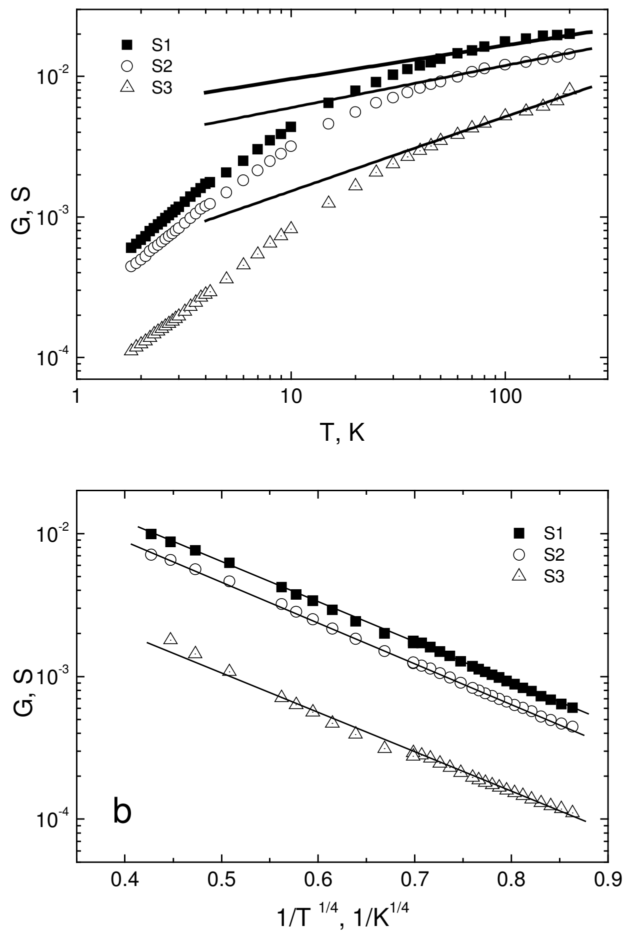

Fig. 1. The conductance (G) *vs* temperature (T) dependences of the carbon nanotube bundles in the double logarithmic coordinates; the solid line corresponds to the power function $G \sim T^{\alpha}$ (a), and *vs* the reciprocal temperature to the ¼ power in the range 1.8 up to 50 K (b).

It is seen that within the range 50 to 200 K the results are well described by the power dependence $G \sim T^{\alpha}$ (the solid line in the figure), the power exponent equals to 0.24, 0.3, and 0.53, respectively. This behavior of conduction in the weak electric field is typical for conduction of the quasi-one-dimensional systems in the model of the electron gas as the Luttinger liquid, which differs as compared to the Fermi model by the presence of Coulomb interaction resulting in correlated movement of charge carriers [9]. The change of the power exponent α with the irradiation dose and its deviation as compared to $\alpha \approx 0.42$ for the non-irradiated samples [12] is related with changing the number of the conduction channels in the CNT bundles as a consequence of appearance of radiation defects.

In the low temperature range from 50 down to 1.8 K, the conduction quickly decreases with lowering temperature, and the temperature dependence bears well pronounced exponential character $G = G_0 \exp(-T/T_0)^{1/4}$. It is indicative of the variable range hopping (VRH) conduction mechanism described by the Mott law [14]. The characteristic temperature T_0 is determined by the independent of energy density of electron states in the vicinity of the Fermi level, which participate in the charge carriers transport, g_F, and the localization length of electrons in these states, ζ, that is, $T_0 = C_T / (k_B g_F \varsigma^3)$, where C_T is the constant. Note, the localization length in CNT is generally considered as anisotropic. Then, the localization length is geometrically averaged over directions along and transverse to the nanotube axis [15].

The data shown in Fig. 1 enable to estimate the values of T_0: 1874, 1677, and 2346 K for the samples S1, S2 and S3, respectively. To determine the localization length, one needs to know the density of states g_F, which, as it is known, depends on structure morphology and should be determined separately for each sample. For this purpose, we carried out measurements of the hopping conduction under the conditions of heating charge carriers by the applied electric field. The obtained dependences of the current in the sample on the electric field strength are depicted in Fig. 2.

It is seen that at the electric field strength higher than approximately 100 V/cm the dependences measured at different temperatures practically coincide. It is indicative of the fact that at these field strengths the hopping conduction is defined only by heating the charge carriers in the electric field. The current J *vs* the electric field strength E dependence in this case is as follows

$$J = \exp\left[-\left(\frac{E_0}{E}\right)^{0.25}\right], \quad E_0 = \frac{C_E}{e g_F \varsigma^4}.$$

Here, e is the electron charge, C_E – constant.

As one can see in Fig. 2, this dependence describes well the experimental results with the characteristic field E_0 values equal to $5.8 \cdot 10^5$, $5.2 \cdot 10^5$, and $1.4 \cdot 10^6$ V/cm for the samples S1, S2 and S3, respectively. Using the obtained values of E_0 and T_0, one can calculate the localization length of charge carriers:

$$\varsigma = \frac{a k_B T_0}{e E_0}, \text{ where } a = \frac{C_E}{C_T}.$$

The published papers give different values for the constant a. We determined the values of the localization length and density of the electron states for the samples S1, S2 and S3 by using the values of $C_E = 9.6$ and $C_T = 18.5$ [16, 17]. They are listed in the table.

Note, the obtained values of the localization length within the range 8 to 10 nm are typical for the strong localization of charge carriers. Both the density of states and localization length manifest dependence on the radiation dose and type, which may be interpreted as a dependence on the kind and amount of created radiation defects.

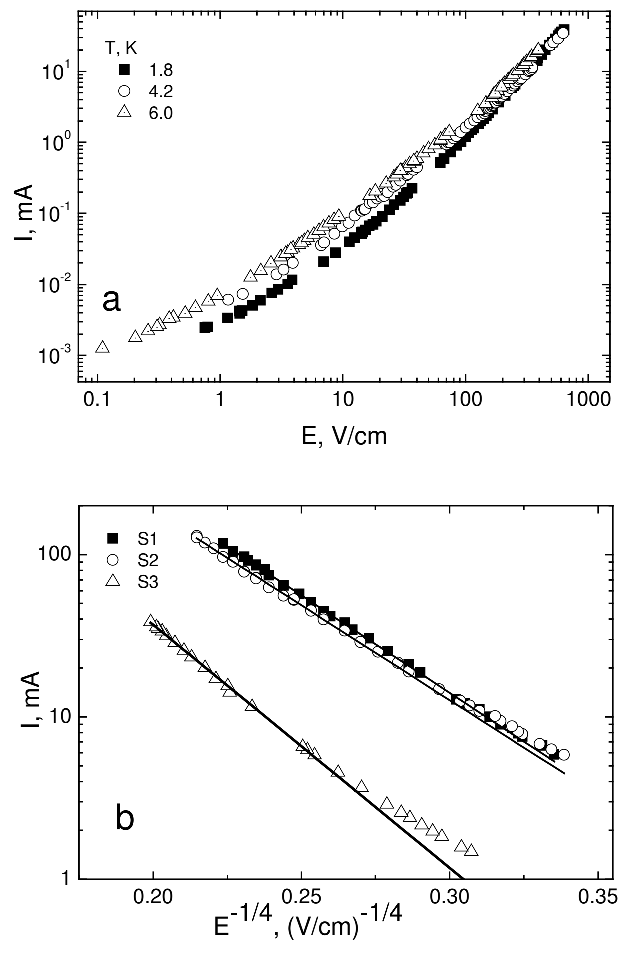

Fig. 2. Current *vs* electric field strength dependences for the sample S1 at different temperatures (a) and the current *vs* reciprocal value of the electric field to the ¼ extent for different samples in the electric field range corresponding to charge carriers heating up (b).

Sample	T_0, K	E_0, V/cm	ζ, cm	g_F, $eV^{-1}cm^{-3}$	*b*	*n*	*c*	*m*	C_{calc}
S1	1874	$5.8\cdot10^5$	$9.31\cdot10^{-7}$	$5.9\cdot10^{19}$	0.018	1.48	0.0066	2.01	0.0042
S2	1677	$5.2\cdot10^5$	$1.08\cdot10^{-6}$	$4.2\cdot10^{19}$	0.010	1.34	0.0065	1.91	0.007
S3	2346	$1.4\cdot10^6$	$8.2\cdot10^{-7}$	$6.9\cdot10^{19}$	0.015	1.31	0.0045	1.96	0.003

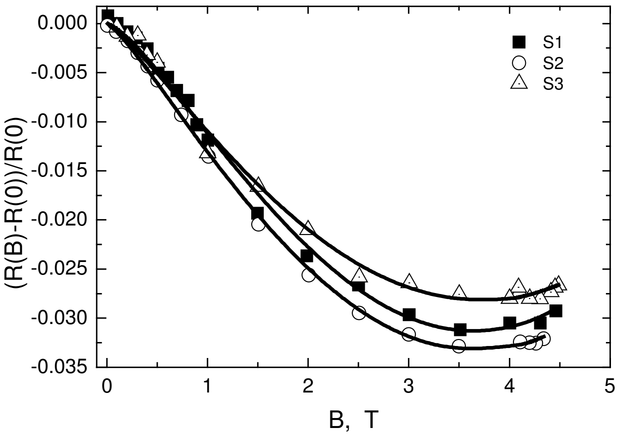

Fig. 3. Dependence of the relative magnetoresistance on the magnetic field at 4.2 K. Solid lines – fitting by the formula (1).

Now we consider the transverse magnetoresistance that is observed under the conditions of hopping conduction. Fig. 3 illustrates the dependence of the relative MR of the samples $(R(B) - R(0))/R(0)$ on the magnetic field B measured at 4.2 K, where $R(0)$ and $R(B)$ are the electrical resistance measured in zero field and at a given field B, respectively.

We can see that MR is negative in the whole range of magnetic fields, while at the large fields an upturn to the positive change is observed.

In analysis of the experimental data on the Mott kind hopping conduction in the magnetic field, we assumed the resistance changes to be caused by two contributions. They describe different mechanisms that influence on the electron wave function in the localization regime when a magnetic field is applied [18]:

$$\frac{R(B) - R(0)}{R(0)} = -bB^n + cB^m . \quad (1)$$

As shown in Fig. 3, the measured MR is well fitted by Eq. (1) in the whole range of data. The values of n, m, b and c obtained by fitting are reported in Table.

The negative contribution into the magnetoresistance with the exponent $n = 1$ is usually explained by interference of the electron wave functions. However, our values of n considerably differ from unity ($n = 1.38\ldots1.41$). It cannot be explained by now within the frames of known theories.

The positive component of hopping magnetoresistance is usually related with shrinkage of the envelop wave function for the localized electron state in the magnetic field. The accompanying reduced wave function overlap results in a decrease of the hopping probability. For this mechanism of MR, the VRH theory predicts a quadratic dependence of MR on the magnetic field at low fields, when the magnetic length is larger and of the order of the localization length. In our case, this condition is satisfied. The obtained value of the parameter m is close to 2. A small deviation from 2 may be caused by contribution of the spin-polarization mechanism, which is explained by accounting for the Zeeman splitting of the energy band in the Fermi level vicinity, where the hopping conduction occurs. In fact, it accounts for the double filled localized states and dependence of the hopping probability on the polarization extent of the spin part of the wave function in the magnetic field.

For MR related with the electron wave function shrinkage mechanism, the parameter C in (1) is given by [4, 18]:

$$c = \frac{\alpha e^2 \varsigma^4}{\hbar^2} \cdot \left(\frac{T_0}{T}\right)^{3/4} , \quad (2)$$

where $\alpha = 0.00248$ [4], e and $\hbar$ are the electron charge and the reduced Planck constant, respectively, and $T = 4.2$ K is the temperature of measuring the magnetoresistance.

The values of C_{calc} calculated by (2) are presented in the table. It can be seen that they coincide by the order of magnitude with the values of C obtained by fitting the experimental data by using the expression (1).

4. Conclusion

In summary, we report the electrical and magnetotransport measurements of the array of metallic single-wall carbon nanotube bundles irradiated with the flux of fast electrons or Co^{60} gamma quanta. For the temperatures below 50 K, the low-field conduction shows the temperature dependence that is characteristic for the Mott three-dimensional hopping conduction. Using the measured dependence of conduction on the temperature and electric field, the energy density of electron states in the vicinity of the Fermi level, which participate in the hopping charge transport, and the localization length of charge carriers in these states have been determined. They manifest variation with changing the radiation dose or irradiation type, which may be interpreted as changes of the kind and amount of radiation defects. In the Mott-type hopping conduction region, MR is negative in the whole range of magnetic fields, while at the large fields an upturn to the positive change is observed. The positive component may be explained by shrinkage of the localized electron envelop wave functions. At the same time, the negative component nature cannot be explained within the frames of existing theories and requires further studies.

References

1. Stetter J.R., Maclay G.J. Carbon nanotubes and sensors: a review, in: *Advanced Micro and Nanosystems*. Vol. 1. Wiley-VCH Verlag GmbH & Co, Weinheim, Germany, 2004. P. 357–382.
2. Freitag M. Carbon nanotube electronics and devices in: *Carbon Nanotubes Properties and Applications*. Ed. M.J. O'Connell. Taylor & Francis Group, LLC, 2006.
3. Danilchenko B.A., Shpinar L.I., Tripachko N.A., Voitsihovska E.A., Zelensky S.E., and Sundqvist B. High temperature Luttinger liquid conductivity in carbon nanotubes bundles. *Appl. Phys. Lett.* 2010. **97**. P. 072106-3. https://doi.org/10.1063/1.3467464.
4. Salvato M., Lucci M., Ottaviani I. *et al.* Low temperature conductivity of carbon nanotube aggregates. *J. Phys.: Condens. Matter.* 2011. **23**. P. 475302-7. https://doi.org/10.1088/0953-8984/23/47/475302.
5. Ksenevich V., Shuba M., Paddubskaya A. Electric transport and magnetoresistance in single-wall carbon nanotubes films. *Mater. Sci.* 2014. **20**, No 2. P. 126–128. https://doi.org/10.5755/j01.ms.20.2.6311.
6. Fang Jing-Hai, Liu Li-Wei, Kong Wen-Jie, Cai Jian-Zhen and Lu Li, Hopping conductivity in a single-walled carbon nanotube network. *Chin. Phys. Lett.* 2006. **23**, No 4. P. 953–955. https://doi.org/10.1088/0256-307X/23/4/053.
7. Sheng L., Gao W., Ma X., Zhao X., Cao S., Zhang J. Electrical properties in magnetic field of macroscopic carbon nanotube objects. *J. Nanosci. and Nanotechnol.* 2010. **10**, No 6. P. 4049–4053. https://doi.org/10.1166/jnn.2010.1966.
8. Fuhrer M.S., Holmes W., Richards P.L., Delaney P., Louie S.G., Zettl A. Nonlinear transport and localization in single-walled carbon nanotubes. *Synthetic Metals.* 1999. **103**. P. 2529–2532. https://doi.org/10.1016/s0379-6779(98)00305-1.
9. Egger R., Bachtold A., Cobden D., McEuen P., Fuhrer M., Bockrath M. Luttinger liquid behavior in metallic carbon nanotubes. *Lecture Notes in Physics*. 2001. **579**. P. 125–146. https://doi.org/10.1007/3-540-45532-9_7.
10. Komissarov I.V., Svito I.A., Fedotov A.K., Prischepa S.L. Electron transport in arrays of aligned multi-walled carbon nanotubes. *The Doklady of the National Academy of Sciences of Belarus.* 2015. **59**. P. 31.
11. Miao M., Hawkins S.C., Cai J.Y., Gengenbach T.R., Knott R., Huynh C.P. Effect of gamma-irradiation on the mechanical properties of carbon nanotube yarns. *Carbon*. 2011. **49**. P. 4940–4947. https://doi.org/10.1016/j.carbon.2011.07.026.
12. Danilchenko B.A., Tripachko N.A., Voitsihovska E.A. *et al*. Stability of the Tomonaga–Luttinger liquid state in gamma-irradiated carbon nanotube bundles. *J. Phys.: Condens. Matter.* 2013. **25**, No 47. P. 475302-7. https://doi.org/10.1088/0953-8984/25/47/475302.
13. Bendiab N., Almairac R., Sauvajol J.-L. *et al.* Orientation of single-walled carbon nanotubes by uniaxial pressure. *J. Appl. Phys.* 2002. **93**. P. 1769–1773. https://doi.org/10.1063/1.1534905.
14. Shklovskii B.I., and Efros A.L. Electronic Properties of Doped Semiconductors. M. Cardona, P. Fulde, and H.-J. Queisser (Series Eds.). *Springer Series in Solid-State Sciences, Vol. 45, Chapter 9.* Springer–Verlag, Berlin, Heidelberg, New York, Tokio, 1984.
15. Maarouf A.A., Kane C.L., and Mele E.J. Electronic structure of carbon nanotube ropes. *Phys. Rev. B.* 2000. **61**, No 16. P. 11156–11165. https://doi.org/10.1103/PhysRevB.61.11156.
16. Wang D.P., Feldman D.E., Perkins B.R., Yin A.J., Wang G.H., Xu J.M., Zaslavsky A. Hopping conduction in disordered carbon nanotubes. *Solid State Communs.* 2007. **142**. P. 287–291. https://doi.org/10.1016/j.ssc.2007.02.028.
17. Apsley N. & Hughes H.P. Temperature- and field-dependence of hopping conduction in disordered systems, II. *Phil. Mag.* 1975. **31**. P. 1327–1339. https://doi.org/10.1080/00318087508228686.
18. Demishev S.V., Bozhko A.D., Glushkov V.V. *et al.* Scaling of magnetoresistance of carbon nano-materials in Mott-type hopping conductivity region. *Physics of the Solid State.* 2008. **50**. P. 1386–1391. https://doi.org/10.1134/S1063783408070329.

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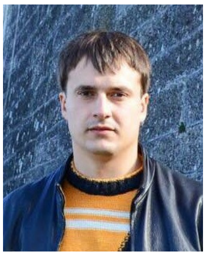

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