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INFLUENCE OF CURVATURE OF GRAPHENE LAYERS OF MULTI-WALLED CARBON NANOTUBES ON ELECTRICAL PROPERTIES

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We investigated temperature and magnetic field dependences of conductivity of multi-walled carbon nanotubes (MWNTs) with different average outer diameter. We separated out the quantum corrections to magnetoconductivity for interaction electrons and determined the dependence of constant of electron–electron interaction λ versus curvature of graphene layers in MWNTs.

Keywords: MWNTs; curvature; electron–electron interaction; conductivity; magnetoconductivity.

1. Introduction

Owing to the small sizes of nanostructures, the graphene layers forming there are always curved with radius of curvature of the order of internuclear distance. Curvature of graphene layers changes physical properties of a material and leads to occurrence of the unique properties which are not observed in plane structure. Physical properties of carbon nanotubes essentially depend on graphene layers curvature. This influence was shown on superconducting properties single-walled carbon nanotubes (SWNTs). The temperature of superconducting transition T_c increases in process of increase of graphene layers curvature (decreases of radius of nanotubes). In SWNTs with diameter $\overline{d} = 10\,Å$ (radius of curvature $r = 5\,Å$), $T_c \approx 1\,K$,[1] with diameter $\overline{d} = 4\,Å$ (radius of curvature $r = 2\,Å$), $T_c \approx 16\,K$[2] are observed. In multi-walled carbon nanotubes (MWNTs), similar researches were not carried out. In this article, we present the results of research of electron transport in MWNTs with different curvature of graphene layers (with different $\bar{d}$).

2. Result and Discussion

MWNTs were synthesized by chemical vapor deposition (CVD) methods via catalytic pyrolysis of ethylene at 950 K on FeCo-based catalysts

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supported on MgO or $CaCO_3$ or Al_2O_3. The structure of MWNTs was investigated using transmission electron microscopy (TEM, Fig. 1).

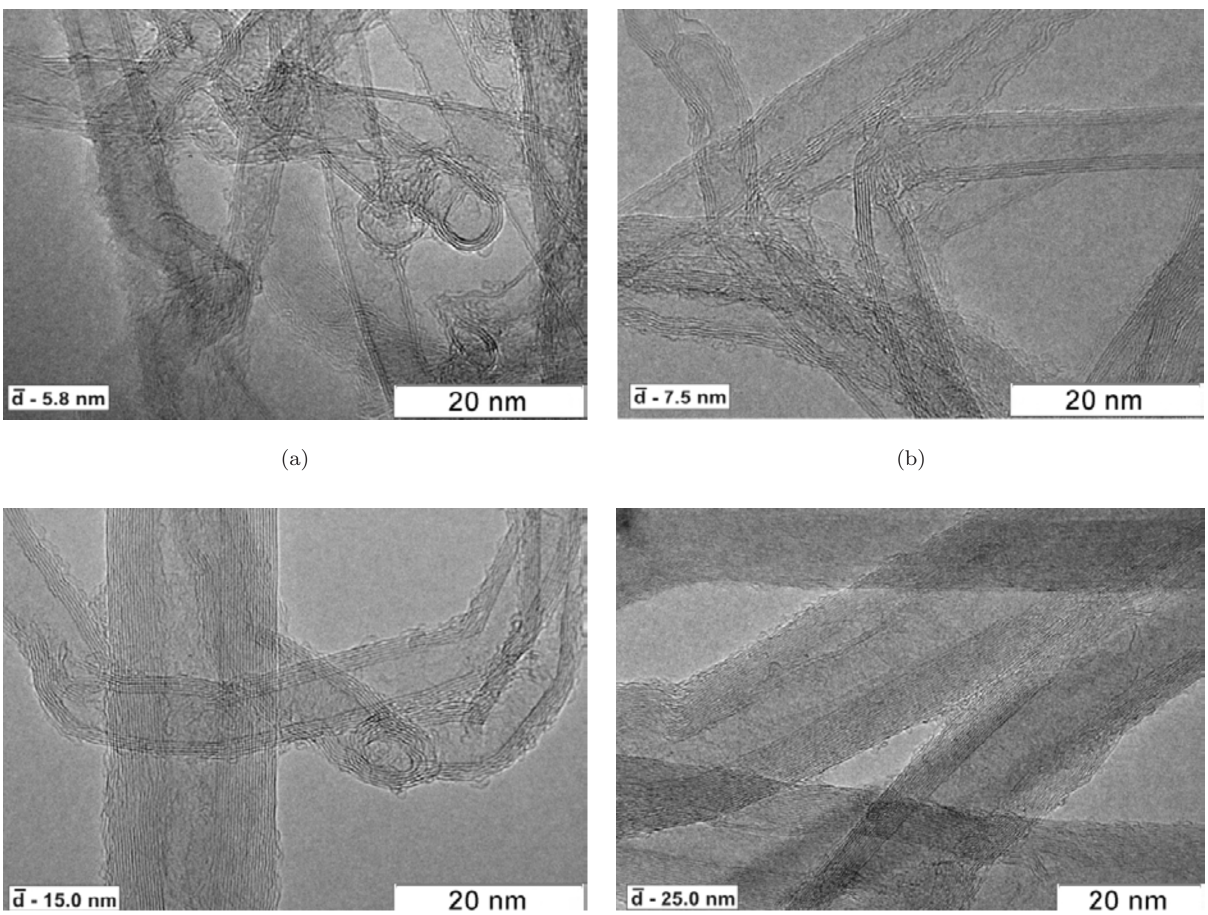
According to TEM investigation, the synthesized nanotubes material consisted of MWNTs with defective structure and did not contain amorphous carbon. MWNTs have narrow distributions of average outer diameter $\bar{d}$: 5.8 ± 0.8 nm; 7.5 ± 2.2 nm; 8.8 ± 3 nm; 11.5 ± 5.1 nm; 15.0 ± 8.6 nm; 17.0 ± 5.1 nm; 25.0 ± 11.1 nm and depended on synthesis conditions. For electrical measurements, the powder of MWNTs was pressed in a glass cylinder. The electrical contacts were made by 0.1 mm silver wires. The temperature dependences of the conductivity $\sigma(T)$ and magnetoconductivity $\sigma(B)$ were measured by four-point-probe technique. $\sigma(T)$ were measured in the temperature range 4.2–300 K. $\sigma(B)$ were measured in the field range B from 0 to 6 T at temperature 4.2 K. Our previous researches of powder carbon nanostructures carried out by this method[3–6] showed stability and reproducibility of results of the conductivity measurements.

Temperature dependences of relative conductivity $\sigma(T)/\sigma_{290}$ (σ_{290} — conductivity at room temperature) of MWNTs with average outer diameters $\bar{d}$ from 5.8 to 25 nm are shown in Fig. 2. Logarithmical dependence of $\sigma(T)/\sigma_{290}$ takes place for $\overline{d}$ from 8.7 to 25 nm (Fig. 3(a)) at temperature below 50 K (Eq. (1))

$$\sigma(T) = \sigma_1 + A\ln(T)\,, \tag{1}$$

where σ_1 and A are constants. This dependence is typical for quantum correction to conductivity for interaction electrons (interaction effects (IE)) in two-dimensional conductors with local disorder.[7]

Exponent dependence $\ln[\sigma(T)/\sigma_{290}]$ from $T^{-1/4}$ takes place for $\overline{d} = 5.8$ and 7.5 nm (Fig. 3(b)). This type of dependence is typical for variable range hopping conductivity (VRHC) $\sigma_{\mathrm{VRHC}}(T)$ for three-dimensional conductor.[8] The temperature



(a) (b) (c) (d)

Fig. 1. TEM micrographs of MWNTs samples with narrow distributions of average outer diameter $\bar{d}$: (a) 5.8 ± 0.8 nm; (b) 7.5 ± 2.2 nm; (c) 15.0 ± 8.6 nm; and (d) 25.0 ± 2.2 nm.

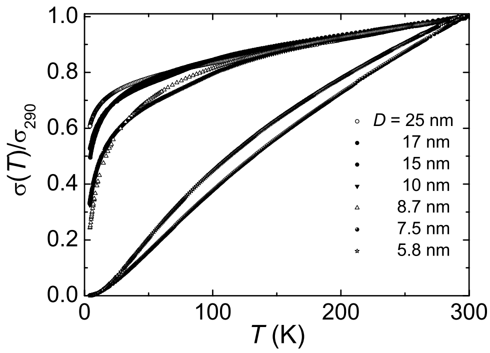
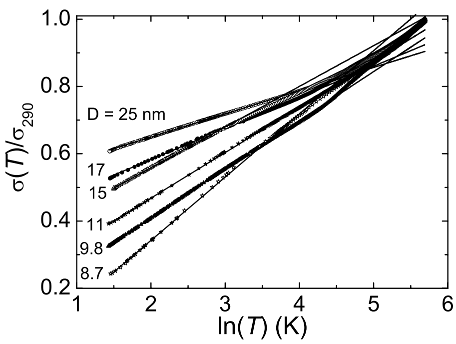
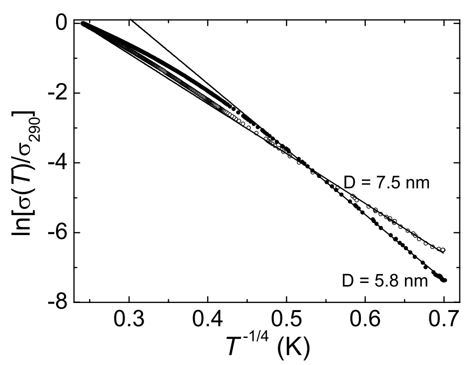


Fig. 2. Temperature dependence of relative conductivity $\sigma(T)/\sigma_{290}$ of MWNTs with $\bar{d}$ from 25 to 5.8 nm.



(a)



(b)

Fig. 3. (a) Logarithmical dependence of relative conductivity $\sigma(T)/\sigma_{290}$ of MWNTs with average outer diameter $\bar{d}$ from 8.7 to 25 nm. (b) $\sigma(T)/\sigma_{290}$ in the $\ln[\sigma(T)/\sigma_{290}]-T^{-1/4}$ axis of MWNTs with $\bar{d} = 5.8$ and 7.5 nm.

dependence of conductivity $\sigma(T)$ may be described by Eq. (2) for such systems.

$$\sigma_{\mathrm{VRHC}}(T) = C\exp\left[-\left(\frac{T_0}{T}\right)^{1/n}\right], \qquad (2)$$

where C is constant, the value of n is determined by dimensionality d of the motion of current carriers as $n = 1 + d$,[8] $T_0 = C_{\mathrm{T}}a^{-3}/k_{\mathrm{B}}N(E_{\mathrm{F}})$, $C_{\mathrm{T}} = 24/\pi$ for three-dimentional VRHC,[8] a is the length on which the amplitude of wave function fall down ($a \approx 10\,\text{Å}$), $N(E_{\mathrm{F}})$ is the density of localized states at the Fermi level, k_{B} is the Boltzmann constant.

We discovered the absence of amorphous carbon in MWNTs produced via CVD method. As a result, only quantum correction to magnetoconductivity $\delta\sigma(B)$ for interaction electrons $\delta\sigma_{\mathrm{int}}(B)$ takes place,[9] and quantum corrections for weak localization effects $\delta\sigma_{\mathrm{WL}}(B)$ is not observed.[10] Magnetic field B suppresses this quantum correction for interaction electrons.[9] As a result, the magnetoconductivity $\delta\sigma_{\mathrm{int}}(B)$ takes place. Low-field asymptotic behavior for $\delta\sigma_{\mathrm{int}}(B)$ is

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

where σ_0 is the conductivity at $B = 0$, σ_2 is constant, $B_{\mathrm{int}} = \pi cT/2eD \approx 6\,\mathrm{T}$ at $T = 4.2\,\mathrm{K}$, $D \approx 1\,\mathrm{cm}^2/\mathrm{c}$ for MWNTs (diffusion coefficient).[11] The interaction constant $g(T)$ is given by

$$g(T)^{-1} = \frac{1}{\lambda} + \ln\left(\frac{\gamma\eta}{\pi k_{\mathrm{B}}T}\right), \qquad (4)$$

where λ is the seed constant of electron–electron interaction (at attraction of electron the temperature of superconducting transition $T_{\mathrm{c}} = \theta_{\mathrm{D}}\exp(1/\lambda)$), $\eta = E_{\mathrm{F}}$ at repulsion and $\eta = \theta_{\mathrm{D}}$ at attraction of electrons, E_{F} is the Fermi energy, $\theta_{\mathrm{D}}/k_{\mathrm{B}}$ is the Debye temperature and k_{B} is the Boltzmann constant. As can be seen from Eq. (3), the $\delta\sigma_{\mathrm{int}}(B)$ is positive when $g(T)$ is negative. Figure 4 shows relative magnetoconductivity $\delta\sigma_{\mathrm{int}}(B)/\sigma_0$ as a function of the magnetic field B for MWNTs at 4.2 K. The inset of Fig. 4 shows relative magnetoconductivity of MWNTs in the

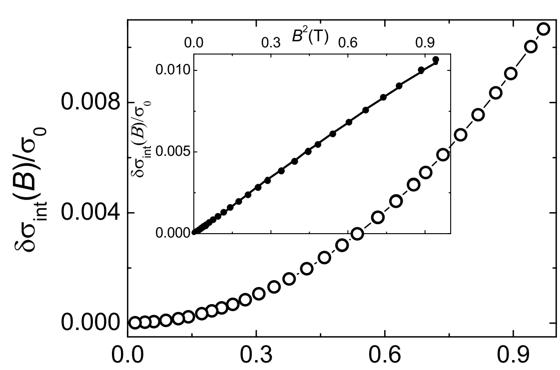


Fig. 4. Relative magnetoconductivity $\sigma_{\mathrm{int}}(B)/\sigma_0$ of MWNTs with average outer diameter $\bar{d} = 17.4$ nm which is typical for MWNTs with $\overline{d}$ from 8.7 to 25 nm.

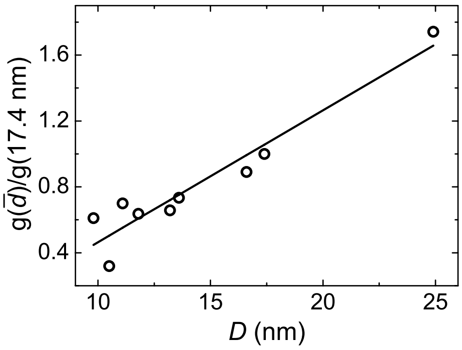


Fig. 5. Relative interaction constant $g(\bar{d})/g(17.4\,\mathrm{nm})$ which was estimated from magnetoconductivity $\sigma(B)$.

$\delta\sigma_{\mathrm{int}}(B)/\sigma_0 - B^2$ axes. In these axes, dependence is quadratically approximated in the magnetic range from 0 to 1 T (the straight line in the inset of Fig. 4). The quadratic increasing of magnetoconductivity shows that $g(T)$ is negative. Taking into account the value of $\ln(\gamma\eta/\pi k_{\mathrm{B}}T) \approx 6$ at $T = 4.2\,\mathrm{K}$ and $\eta = \theta_{\mathrm{D}}/k_{\mathrm{B}} = 1860\,\mathrm{K}$ for MWNTs like graphite[12] we may conclude that the constant of electron–electron interaction λ is negative (attraction of electrons) and $\lambda \geq -0.18$ (Eq. (4)).

From the data of quantum corrections to magnetoconductivity for interaction electrons, we estimated the relative interaction constant $g(\bar{d})/g(17.4\,\mathrm{nm})$ (Fig. 5). This constant is negative and monotonically decreases with decrease of MWNTs $\bar{d}$ (increase of curvature of graphene layers, Fig. 4).

This dependence takes place only for MWNTs with $\bar{d} \geq 8\,\mathrm{nm}$. For MWNTs with $\bar{d} = 5.8$ and 7.5 nm, the quantum correction to conductivity is not observed. We observed three-dimensional VRHC for these samples (Fig. 3(b)). As a result, we observed the square magnetic field dependence of magnetoconductivity (inset in Fig. 4) only for MWNTs with $\bar{d} \geq 8\,\mathrm{nm}$. Correspondingly, we may estimate $g(\bar{d})/g(17.4\,\mathrm{nm})$ only for MWNTs with $\bar{d} \geq 8\,\mathrm{nm}$ (Fig. 5).

3. Conclusion

We discovered the absence of amorphous carbon in MWNTs produced via CVD method. As a result in quantum corrections (QC) to $\sigma(B)$ take place only QC for interaction electrons $\delta\sigma_{\mathrm{int}}(B)$. From the data of QC to $\sigma(B)$ for interaction electrons we estimated the constant of electron–electron interaction $\lambda \geq -0.18$. This constant is negative (attraction between electrons) and monotonically decreases on the absolute value with decrease of average diameter of MWNTs (increase of curvature of graphene layers). This result is in opposite with experimental observation of superconducting state in SWNTs with diameter 1 nm at $T_{\mathrm{c}} \approx 1\,\mathrm{K}$[1] and with diameter 0.4 nm at $T_{\mathrm{c}} \approx 20\,\mathrm{K}$[2] but in agreement with data for MWNTs $T_{\mathrm{c}} \approx 16\,\mathrm{K}$.[13]

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