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LOW-TEMPERATURE THERMOPOWER IN DISORDERED CARBON NANOTUBES

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Low-temperature thermopower in disordered carbon nanotubes was calculated while taking into account multiple elastic electron scattering on impurities and short-range structural inhomogeneities. A possible explanation is presented for the low-temperature behavior of thermopower which depends on defect structure, impurities and chirality.

Keywords: Carbon nanotube, thermopower, structural disordered, low-temperature.

1. Introduction

Thermopower S in multi-walled carbon nanotubes (CNTs) and bundles of single-walled CNTs is found to be high (much higher than in metals) and characterized by nonlinear temperature dependence at low temperatures. In disordered, unannealed CNTs, thermopower is positive and the curve $S(T)$ has a maximum or a bend at $T \sim$ 30–100 K. However, after degassing or high-temperature annealing of CNTs, the thermopower changes sign and $S(T)$ weakly deviates from linear dependence without any minimum or bend [1–11].

In [1], the large value of thermopower is explained by the proximity of chemical potential to the boundary of electronic band. The change of thermopower sign is connected with the location of chemical potential relative to the center area of electronic band in CNTs. However, other researchers have postulated that the peculiarities of band structure in CNTs cannot be the only reason for the low-temperature behavior of thermopower. In bundles of single-walled carbon nanotubes (SWNTs), the electron-hole symmetry is broken and charge transfer between single-walled nanotubes takes place. This may become another reason for the considered low-temperature features in thermopower.

Previously, the thermopower of multi-walled CNTs (MWNTs) mats synthesized using spark plasma sintering technique has been investigated [3]. The authors explained the singularities in low-temperature thermopower by electron-phonon interaction. In [4], the contributions to thermopower from the electron transport in a clean tube and impurity scattering have been considered. The authors believe that the contribution of the impurity scattering resulted in a deviation from linear dependence of $S(T)$, and note that the nitrogen saturation of the same tube resulted in a change of sign of the thermopower.

The non-linear $S(T)$ has been described by competing contributions from phonon drag and diffusive electron transport, the former dominating at very low temperatures and the latter predominating at high T [5].

The thermopower in bundles of multi-walled CNTs about 20 nm in diameter has been investigated in the framework of the two-band model [6]. However, at $T < 30$ K, the results

of calculations in [6] were not in agreement with the experimental data and thus, the authors assumed that the effect of weak localization may be a reason for the divergence between their theoretical and experimental data.

The low-temperature thermopower in the long bundles of multi-walled CNTs (length $\sim$ 1 mm and diameter $\sim$ 30 nm), has been investigated and the following expression has been proposed: $S(T) \sim T \log T$ at $T < 20$ K [7]. The authors presume that the deviation of $S(T)$ from linear dependence was caused by the repulsive interaction between electrons in a disordered local environment. The change of thermopower sign and the type of its temperature dependence were shown to be determined by the chirality angle and the ratio of the overlap integrals for electron transport along the cylindrical axis of the helix and the base spiral of CNTs [8, 9].

There is a number of studies of low-temperature thermopower in nanotubes, where the role of other factors such as annealing temperature, nanotube chirality or diameter, was consider [6, 10, 11]. For example, in [10], the influence of annealing temperature on electron transport properties in long multi-walled CNTs with 10–12 nm diameter was investigated. The electrical resistivity and heat conductivity were found to increase when temperature rises. At the same time, the thermopower decreased and may even change sign from positive to negative. The latter may be associated with decreased oxygenation after annealing. There are also data on the value of low-temperature thermopower in CNTs which decreases with the increased nanotube diameter, and the deviation from linearity becomes more pronounced [2, 4, 6].

Thus, we may conclude that the origin of low-temperature thermopower peculiarities in CNTs is not understood and still attracts the attention of investigators. The following features in the behavior of thermoelectric power in disordered carbon nanotubes may be emphasized:

- The value of thermopower in CNTs is on the order of 5–50 μV/K, which is much larger than in metals.
- In disordered (gas saturated) and unannealed CNTs, the thermopower is always positive, while it is always negative in clean (degassed) nanotubes.
- The positive thermopower increases nonlinearly with increasing temperature (at $T <$ 100 K) and the curve $S(T)$ has a maximum or bend at $T \sim$ 30–100 K. The negative thermopower decreases nonlinearly with increasing temperature (at $T <$ 100 K) but the curve $S(T)$ has no minimum or bend.
- Saturation of the CNTs with nitrogen or oxygen changes the sign of thermopower, and the subsequent degassing of nanotubes by annealing at high temperatures again leads to a change in the sign of the thermopower.
- Changing the concentration of the impurities, the structural defects or the diameter of the nanotube, which is directly proportional to the chirality of the CNT, leads to the deviation of temperature dependence from linearity, which may be pronounced to different degrees.

The significant influence of the factors mentioned above (chirality or diameter of nanotubes, concentration of impurities and defect structure) on the low-temperature behavior of thermopower requires further study. Previously, we showed that at low temperatures, the electrical properties of SWNTs and MWNTs bundles, including thermopower, display similar properties to metallic alloys with short-range order and amorphous metals [12]. That is why we proposed to use the approach developed to describe the low-temperature anomalies of the electrical properties in amorphous metals for the investigation of disordered CNTs [13, 14]. Using the Green functions (GF) method, we calculated the electron relaxation time [15] and found a single-electron and a multiple-electron contribution to thermopower [12] which took into account the multiple elastic electron scattering by defects, the interference of inelastic

electron-electron interactions and the elastic scattering by defects. The expression obtained for thermopower gave good qualitative agreement with experimental data and explained behaviors of thermopower in the 'dirty' metallic nanotubes.

However, in [12] we did not take into account the chirality of the nanotubes. In [16] we could develop and supplement our theory by considering the electronic spectrum of CNTs in its dependence on the chirality. This allowed us to calculate the contribution to thermopower for the disordered (20,20) CNTs and gave a possible explanation for the changing sign of the thermoelectric power, the emergence of a bend or a maximum in $S(T)$ depending on chirality of nanotube, the concentration of defects and type of short-range ordering in the structure of nanotubes. When taking into account the electronic spectrum, which depends on nanotube chirality, we were able to calculate the contribution to electronic density of states (DOS), and obtain the conditions for electrical conductivity under which the nanotubes behave as metal or as semiconductor [17, 18].

In the present work, we would like to analyze the low-temperature behavior of thermopower for bundles of single-walled CNTs and individual multi-walled CNTs with hilarities (10,10) and (16,16). The second aim of this paper is to investigate the derivative of thermopower and to find conditions when $S(T)$ has a maximum or bend. Finally, we hope here to understand how annealing influences the structure of CNTs and why the thermopower becomes negative.

2. Thermopower: results and discussion

In [16] we have obtained the expression for thermopower of the disordered carbon nanotubes. However, in calculating $S(T)$, we neglected a summand which is not important at low temperatures ($T < 50$ K) but, as we found later, plays a role in the formation of the maximum in $S(T)$ at higher temperatures ($T > 50$ K). So, the more exact expression for thermopower is the following:

$$S(T) = -\frac{\pi^2 k^2 T}{3e}\left[\left(\frac{\pi a\gamma_0}{\sqrt{3}C_h} - 2\pi kT\right)^{-1} - \left\{2\pi kT\left(1 + \frac{1}{BT^{1/2}}\right)\right\}^{-1}\right], \tag{1}$$

where k is the Boltzmann constant, the chirality $C_h = a\sqrt{n^2 + mn + m^2}$ is related to the diameter of nanotube d as follows: $C_h/\pi = d$, (n, m) are the indexes of chirality. Then a is the lattice constant and γ_0 is the transfer integral between the first neighbor p_z orbitals. Finally $B = \dfrac{2\sqrt{2\pi}(1-c)m^{3/2}k^{1/2}}{\nu_0 N}\sum\limits_i \alpha_i$, where α_i are the short-range order coefficients ($\alpha_0 = 1$) [19], N is the number of atoms inside the structure inhomogeneity of the short-range order type, m is mass of electron and $\nu_0 = \dfrac{p_0}{\pi^2\sqrt{3}a\gamma_0}\sqrt{p_0^2 - \left(\dfrac{2}{3d}\right)^2}$ is the density of states at the Fermi level and p_0 is the Fermi momentum for an ideal CNT.

The first term in (1) is connected with the contribution from DOS and the second term is connected with the contribution from the electron relaxation time. These contributions have different signs; one of them increases while the other one decreases when temperature rises. That is why in the $S(T)$ curve there is a maximum which takes place when the velocities of change of these contributions are equal.

The contributions to thermopower, calculated using the formula (1) for the (10,10) CNT, are represented in Fig. 1. The full $S(T)$ is the sum of the contribution from electron scattering on structural defects of CNTs (S1) and the linear contribution to thermopower of ideal CNTs

(S2). As is seen in Fig. 1, the deviation from linearity of $S(T)$ may be due to the electron scattering on the short-range ordered domain structure of the nanotube. The dependences obtained here were confirmed by the experimental data [4].

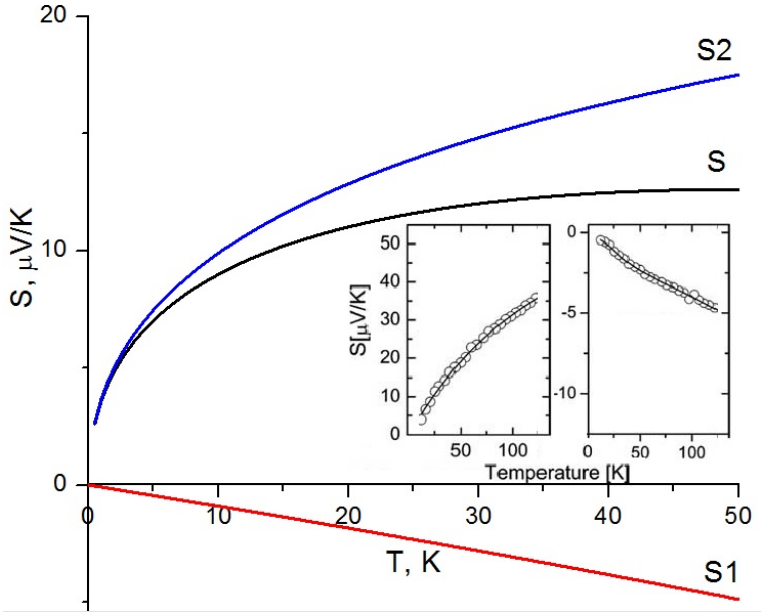

FIG. 1. Contribution to thermopower of a 'metallic' CNT calculated for the tube chirality (10,10) and $\sum_i \alpha_i \approx 0.1$. n insert [4]: (a) thermopower of pure MWNT mat; (b) thermopower of N-doped MWNT mat

Thermoelectric power $S(T)$ calculated for the (10,10) CNT for the different values of short-range order parameters and concentration of impurities, is shown in Fig. 2. As mentioned above, the sum of parameters of short-range order is determined by the different types of structural defects of the CNT and may be positive or negative, depending on what coordination sphere (the first or the second one) will be occupied by atoms of the impurity or defects. From our data, the thermopower is positive when the defects are located mainly in the first coordination sphere and thermopower becomes negative at $\sum_i \alpha_i \leq 0.1$ when most defects are pushed out of the first coordination sphere.

In particular, this takes place in the case of annealed and degassed nanotubes [1, 2]. In reality, annealing resulted in decrease in the concentration of impurities, structural defects and sorbed gas; the higher annealing temperature, the lower concentration of defects (of all types as impurities as structural inhomogeneities of short-range order) and thus, lower thermopower.

Finally in the fully-degassed samples , thermopower becomes negative [10]. However, when we distinguished the calculated contributions to thermopower depending on concentration of impurities and short-range order parameters we found that the tendency of $S(T)$ to decrease takes place only for decreasing short-range order parameter. As for the concentration of the impurities, then the opposite effect occurs: $S(T)$ is higher for CNTs with the lower concentration of impurities. However, the change in the thermopower value does not exceed 5%. This would seem to indicate that annealing regulates the short-range ordered structure of CNTs more strongly than the concentration of impurities.

It is interesting that the same effect is found in nitrogen-doped multiwalled carbon nanotubes [4], although boron doping results in a positive thermopower of MCNT. We can

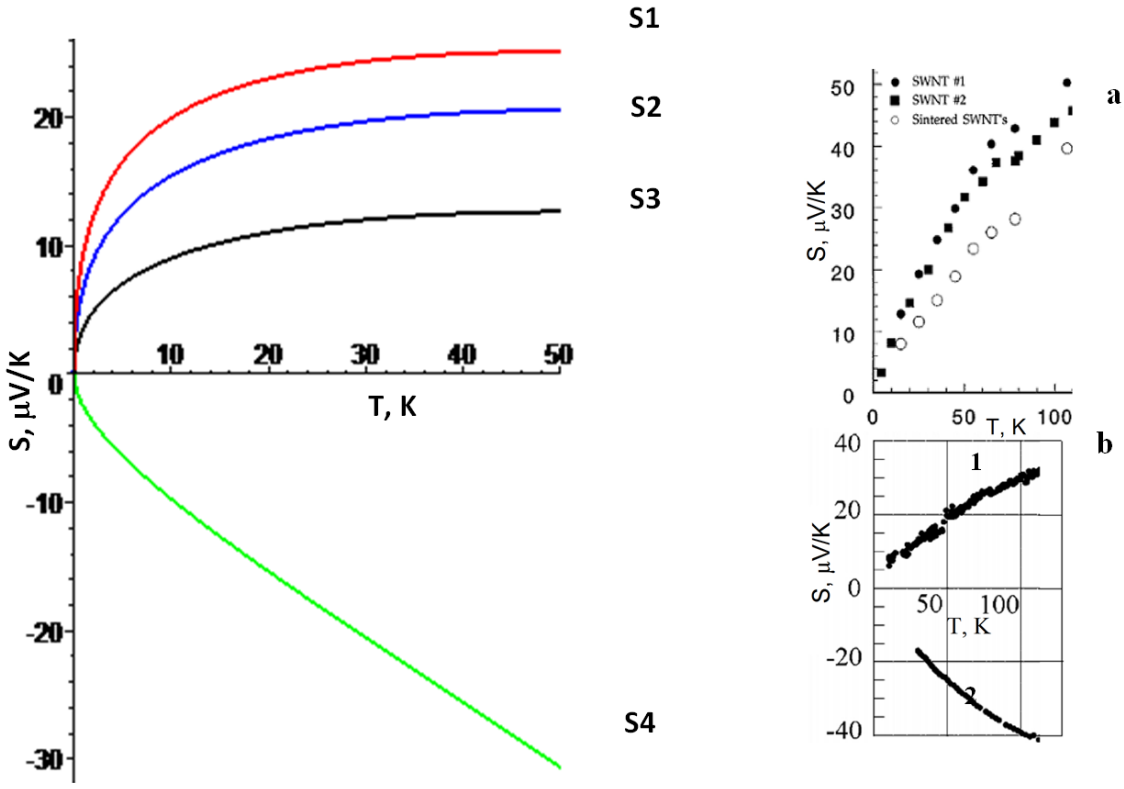

FIG. 2. Temperature dependence of thermopower of the CNT (10,10), calculated for different values $S(T)$ of short-range order: $\sum_i \alpha_i = 0.3$ (S1), $\sum_i \alpha_i = 0.2$ (S2), $\sum_i \alpha_i = 0.1$ (S3) and $\sum_i \alpha_i = -0.1$ (S4). On insert the experimental data: (a) temperature dependence of thermopower of bundles of SWNTs: the samples 1 and 2 are not annealed and the sintered SWNT is annealed at 1000 ° [2] and (b) the temperature dependence of thermopower of the oxygenated CNT (curve 1) and deoxygenated one (curve 2) [1]

explain this phenomenon by occupation of the first and second coordination spheres by nitrogen and boron, respectively .

Equation (1) may be rewritten in a way which may be more convenient for the interpretation of the experimental data:

$$S(T) = -\frac{\pi k}{6e}\left[\left(\gamma_h + B^2\right)T + \gamma_h^2 T^2 - BT^{1/2}\right], \tag{2}$$

where $\gamma_h = \dfrac{\sqrt{3}C_h k}{a\gamma_0}$.

Analyzing (2), we found that when thermopower is negative, the derivative does not have real (physical) roots. Hence, there are no any bending points in the negative $S(T)$. This result is in good agreement with the experimental data [10] – the negative thermopower never has a maximum or minimum in its temperature dependence!

In the case of positive thermopower, which takes place at $\sum_i \alpha_i > 0$, the derivative $\dfrac{\partial S(t)}{\partial T}$ has two real roots, one of which is in the range of low temperatures ($T < 100$ K) and the other one is in the high-temperature region (above 5000–6000 K). Since we studied

only the low-temperature behavior of thermopower, we found out that the second derivative of thermopower in the low-temperature thermopower was negative. So the positive $S(T)$ has a maximum. This fact is also consistent with the experimental date [3] presented in the insert (a) in Fig. 3.

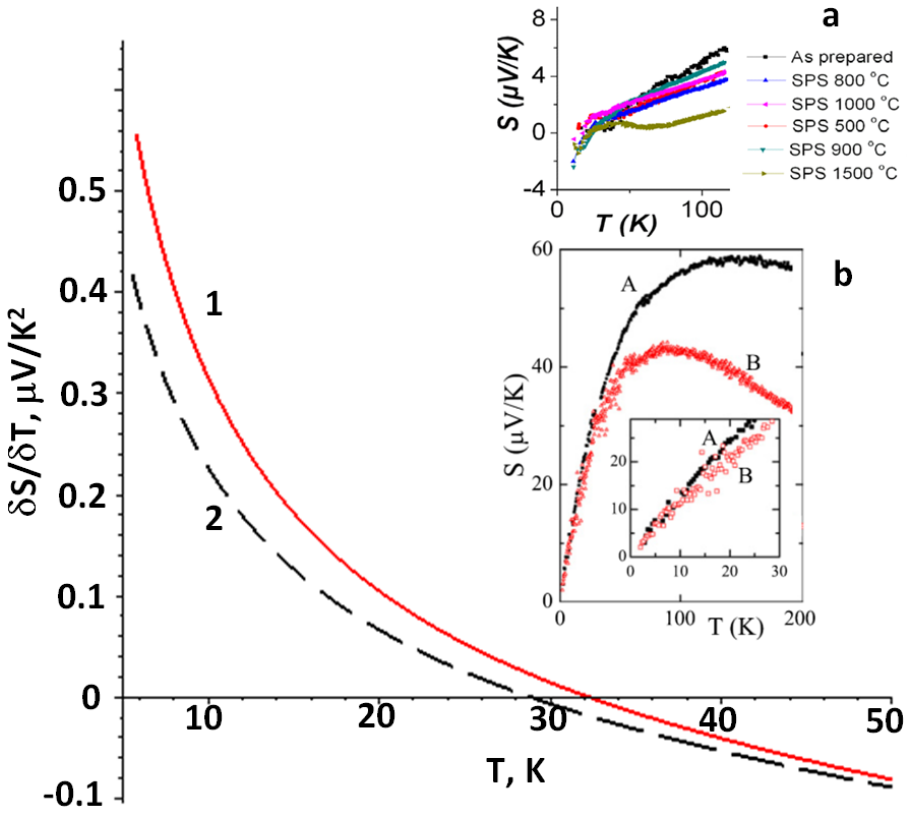

FIG. 3. $\dfrac{\partial S(T)}{\partial T}$ in metallic (16,16) CNT for $\Sigma\alpha = 0.15$ (curve 1) and $\Sigma\alpha = 0.1$ (curve 2). Inserts: (a) temperature dependence of thermopower in MCNTs synthesized at different temperatures [3]; (b) temperature dependence of thermopower in unannealed (A) and annealed (B) boundless of SWNTs [11]

Insert (b) shows the temperature dependence of thermopower for unannealed (A) and annealed (B) boundless of SWNTs [11] . Indeed, from this insert, one may see that the annealed sample has a lower T_{max} than the unannealed one.

Now, let us analyze the temperature dependencies of thermopower (1) as a function of the short-range order coefficients. We shall consider the CNTs with the following parameters: chiral indices equal to (10,10), temperature varies from 0.1 to 80 K, $\nu_0 \approx 0.1$ eV [13] and $U_0 = 0.05$ eV; sum of short-range order parameters $\sum_i \alpha_i$ is varied from -0.5 to 0.5. The latter corresponds to the different types of short-range order: when the short-range order parameter is negative, the defects are located in the second coordination sphere, and when positive, the defects are in the first sphere [19].

The temperature of the maximum in $S(T)$ differs for different CNTs and depends upon the chirality and short-range order parameters, as shown in Table 1.

From Table 1, one may see that the value of the temperature at maximum T_{max} decreases dramatically when the index of chirality increases at the fixed $\sum_i \alpha_i$ and T_{max} increases more

TABLE 1. Temperature of maximum in $S(T)$, in Kelvin, depending on parameter of short-range order (the first line of the table) and index of chirality (the first column of the table) n (here we assume $c = 0, 1$)

n \ $\sum_i \alpha_i$	0.05	0.1	0.15	0.2	0.25
6	70	87	88	85.6	82.1
8	48.3	63.7	66.4	65.4	63.4
10	35.8	49.8	52.9	52.8	51.6
12	27.9	40.5	43.8	44.1	43.5
14	22.4	33.8	37.2	37.9	37.6
16	18.5	28.9	32.2	33	33

slowly when $\sum_i \alpha_i$ rises at the fixed n. This means that the negative "structure" contribution defined by chirality, increases more quickly than the contribution determined by the short-range ordering.

3. Conclusion

In the present paper we have described the low-temperature peculiarities of thermopower in disordered carbon nanotubes in the framework of the short-range ordered structure model and thus explained the influence of different factors (chirality or diameter of nanotubes, concentration of impurities and structural defects, annealing temperature) on the low-temperature behavior of thermopower, taking into account only multiple elastic electron scattering on structure defects (without electron-electron correlations) and concluded the following:

- The non-linear temperature dependence of thermopower is due to electron scattering on structural defects of CNTs. In an ideal CNT the dependence $S(T)$ is linear.
- A decrease in the short-range order parameters results in a smaller slope of the $S(T)$ curve and even in a changed thermopower sigh. These results agree with the experimental data [2, 5, 10, 11].
- Position of the bend or maximum with a subsequent change in the slope of the $S(T)$ curve to the temperature axis is determined by the chirality of and the types of structural defects present in the CNTs .

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