

Macroscopic thermoelectric efficiency of carbon nanocompositesE. D. Eidelman^{1,2}, A. P. Meilakhs¹¹Ioffe Physical Technical Institute, 26 Politekhnicheskaya, 194021 Saint Petersburg, Russia²Saint Petersburg State Chemical-Pharmaceutical Academy, 14 Professora Popova, 197376 Saint Petersburg, Russia

eidelman@mail.ioffe.ru, mejlaxs@mail.ioffe.ru

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The subject of this study is the thermoelectric efficiency (Z) and the thermoelectric parameter (ZT) of carbon nanocomposites, namely, the structures consisting of graphite-like (gr) and diamond-like (d) regions made of sp^2 and sp^3 hybridized carbon atoms, respectively. The impact of heat transfer across the boundary between sp^2 and sp^3 areas is analyzed for the first time. It is shown that the interfacial thermal resistance (Kapitza resistance) is not lower than the thermal resistance in the macroscopic gr region. The influence of various factors on the Kapitza resistance is analyzed. The value of $ZT \approx 3.5$ at room temperature, taking into account the interfacial thermal resistance, is significantly higher than it would be in gr films ($ZT \approx 0.75$).

Keywords: carbon nanostructures, thermoelectricity.*Received: 28 October 2016***1. Introduction**

In recent years, a lot of attention has been paid to the influence of size on transport phenomena in solids and, in particular, on thermoelectric effects [1–5]. Currently, attention is focused on the creation of new materials with the highest possible thermoelectric figure of merit (quality factor) Z , which makes it possible to use this material in refrigerators or generators [2,5]: $Z = S^2\sigma/\chi$. Here, S is the thermoelectric coefficient or the Seebeck coefficient (V/K), σ is the conductivity ratio ((Ohm·m)⁻¹), and χ is the thermal conductivity (J/(m·s·K)).

The higher the value of the parameter ZT (where T is the temperature in Kelvin) is for any material, the more useful this material is for thermoelectric conversion. Therefore, ZT is used as a dimensionless quantity that characterizes thermoelectric materials.

Serious efforts were made to increase Z , both by selecting an appropriate semiconductor and by determining its optimal layer thickness [3, 4]. To the best of the authors' knowledge, the highest value $ZT = 2.6$ at room temperature is reported in [6] for SnSe crystals.

Part of this effort is the study of thermoelectric phenomena in carbon nanostructures [3–5]. In these nanostructures, hybridized carbon atoms coexist. The coexistence of regions with very different electrical and thermal properties at such small distances from each other is a unique feature of these structures. The gr areas are semimetallic with a high electrical conductivity but a relatively low thermal conductivity. The d areas are wide bandgap semiconductors, dielectrics in fact, but with a high thermal conductivity. The corresponding kinetic coefficients differ in value by many orders of magnitude.

The article deals with the Z values of the composite produced from 4 nm diamond nanoparticles generated by detonation synthesis. Such diamond nanoparticles were prepared by milling [7–9] and before long by purification techniques [10, 11] from agglomerates about 100 nm in size. Then, solid composite was produced from 4 nm particles by sintering at high pressure and high temperature (HPHT). Regions with sp^3 hybridization, as determined by areas of coherence, reached sizes of up to 4–12 nm. The composite consists of such particles with a d core, which can be covered by up to four layers of the sp^2 phase, but may have no coating at all. The composite is completely free from the separate gr phase. The average particle size becomes 4–35 nm [12]. Then, the size of gr regions can be assumed at an average of $l \approx 10$ –30 nm. The thermoelectric effect and mechanisms that contribute to the increase in the thermoelectric coefficient S , the main component of the Z , were discussed in [13, 14] for carbon nanostructures.

As for the ratio of electrical and thermal conductivity coefficients σ/χ being part of Z , it is always considered to be proportional to the temperature according to the Wiedemann - Franz law (see, e.g., [15] §78). Of course, there may be limitations associated with the possible flow of heat in the gr areas. Let us further assume that the percolation threshold (see, eg, [16]) is reached [9], but the heat carried by electrons is small compared with the lattice vibrations heat transfer.

It was recently shown that the presence of borders between the *gr* and *d* regions greatly influences the thermal conductivity of carbon nanostructures [17,18]. In this paper, we examine the effect of borders on the thermoelectric efficiency.

2. Statement of the problem of heat transfer through the interface between phases

Let us assume that the *gr* area is heated or cooled on one side and contacts with a *d* area on the other side. In this case, the *gr* phonons migrate into *d* or *d* phonons migrate into *gr*. In accordance with Fourier's law, this heat source lowers or raises the temperature of the *gr* lattice. The heat of the electron gas from the *gr* area is not directly transferred to the *d* area. However, the electrons can heat or cool the crystal lattice in *gr*. An increase in the phonon flux component takes place, and then the heat is transferred from this component to the *d* area. This nonlinear process occurs due to the temperature difference between the electronic and phonon subsystems in *gr*. It appears as a result of presence of the boundary with *d*. The ideal structure would be the one with plane borders perpendicular to the direction of heat propagation. Any possibility of heat flow bypassing the border increases the thermal conductivity, and thus reduces the thermoelectric efficiency *Z*.

The temperature at the border undergoes a jump ΔT , which is proportional to the heat flux q (W/m²). Such dependence makes it possible to use the electrothermal analogy. The proportionality coefficient r (m²·K/W) between the ΔT and q is called interfacial thermal resistance (Kapitza resistance). The Kapitza resistance is a characteristic of the interface; in the heat transfer theory the reciprocal value of $1/r$ is called the heat transfer coefficient.

The process being considered is a special case of heat transfer through the metal – dielectric boundary. The Kapitza resistance at the metal-dielectric interface has been widely studied (see, e.g., [17]). It was found that the Kapitza resistance, as calculated considering the nonlinearity of the process, does not depend on the dielectric characteristics and is fully determined by the properties of the metal. This thesis was experimentally confirmed in [19].

In fact, each subsystem in *gr* is characterized by its set of values: electron T_e ; q_e ; χ_e , and phonon T_{ph} , q_{ph} , χ_{ph} . Each triplet of values is related according to the Fourier law.

The interaction coefficient θ (W/(m³·K)) characterizes the efficiency of heat transfer between subsystems and relates the heat flux to the difference $T_e - T_{ph}$.

It should be noted that in experiments, the temperature is measured far away from the boundary. At this location, the temperature is $T_e = T_{ph} = T$, and the thermal conductivity $\chi = \chi_e + \chi_{ph}$ can be attributable to the general heat flow in *gr*: $q = q_e + q_{ph}$. In *gr*, it can be assumed that $\chi_e \gg \chi_{ph}$ and heat transfer through the electronic subsystem dominates.

Only phonons can pass from *gr* to *d*, hence $q_{ph} = q$; $q_e = 0$ at the boundary.

According to [19], the problem is posed so that the properties of *d* do not affect the T_e and T_{ph} temperature in *gr*.

3. Temperature and thermal resistance alignment at the boundary between *gr* and *d*

The solution of the problem is completely similar to that provided in [17]. The result is that the characteristic distance λ , at which the temperatures of the electron and phonon subsystems in *gr* are actually aligned, is related to the system characteristics as:

$$\lambda = \sqrt{\frac{\chi_e \chi_{ph}}{\theta \chi}} \simeq (\chi_{ph}/\theta)^{1/2}. \quad (1)$$

The components of the thermal resistance are determined by the jumps of the subsystems temperatures, $T_e(0)$ and $T_{ph}(0)$, relative to the temperature T_d in *d*, which is equal to $T_d(0)$ at the boundary (Fig. 1). In the course of the experiment, the temperature gradient from a region far from the boundary is usually extrapolated linearly to the boundary. This temperature T_{gr} is considered to be the *gr* temperature; accordingly, it is $T_{gr}(0)$ at the border, and the temperature jump is considered equal to $\Delta T = T_{gr}(0) - T_d(0)$. However, almost always $T_{gr}(0) \approx T_e(0)$.

The Kapitza thermal resistance caused by the measured jump ΔT can be divided into r_{ph} , arising due to the temperature jump ΔT_{ph} of phonons in *gr* and *d* areas, and r_r , arising because the electronic and phonon subsystems in *gr* are heated unequally near the border. Therefore, $r = r_{ph} + r_r$.

The thermal resistance (relative!) r_r arises due to the difference in temperature jumps of the electron ΔT_e and phonon ΔT_{ph} subsystems: $\Delta T_r = T_e - T_{ph} = \Delta T_e - \Delta T_{ph}$. In practice, the temperature in *gr* is determined by the electronic subsystem temperature. So, the measured jump $\Delta T \approx \Delta T_e$ and ΔT_r can be calculated as $\Delta T_r = \Delta T - \Delta T_{ph}$.

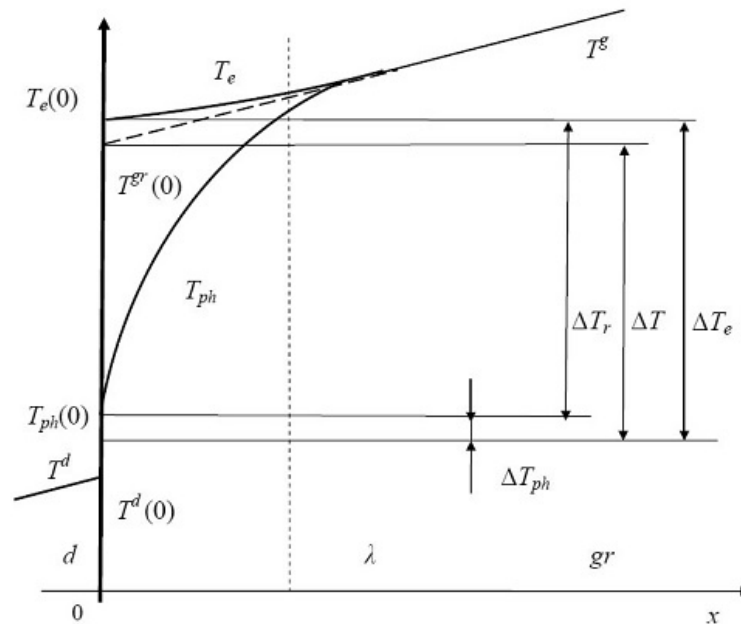


FIG. 1. This figure presents the temperatures in the graphite-like (*gr*) area T_{gr} (on the right) and the diamond-like (*d*) area T_d (on the left), near the boundary located at $x = 0$. At the boundary, the temperatures are, respectively, $T_{gr}(0)$, $T_d(0)$, $T_e(0)$ and $T_{ph}(0)$. Also shown are values of the corresponding temperature jumps ΔT_{ph} and ΔT_e at the border to the temperature $T^d(0)$. The jump $\Delta T = T_{gr}(0) - T^d(0)$ is measured experimentally. Finally, the temperature differences in *gr* subsystems were shown to be caused by the Kapitza resistance due to the presence of the boundary ΔT_r .

The value of the jump ΔT_{ph} determines the proportion of phonons reflected from the boundary back into *gr*. This proportion was determined in [13] for a system very similar to the carbon nanocomposites under study. There, it was found to be usually small. Therefore, $\Delta T_{ph} \ll \Delta T_r$ and accordingly $r_{ph} \ll r_r$. This inequality is the major, roughest approximation that is used for the solution of the problem. The values in Fig. 1 are provided using this approximation.

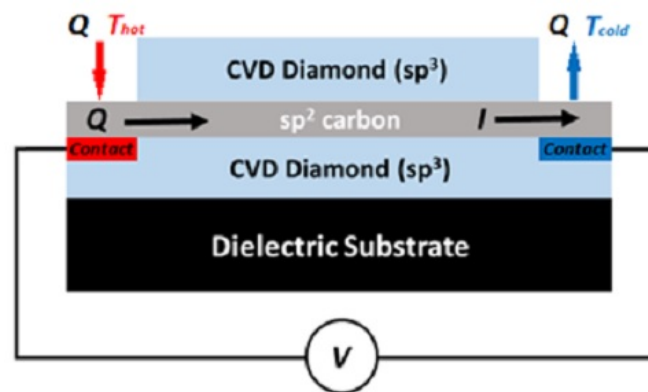


FIG. 2. A possible thermoelement design, where the heat Q and the temperature difference $T_{hot} - T_{cold}$ provide the conditions (see [13]) under which the quasi-ballistic drag of electrons by phonons prevails in the carbon nanostructure

Next, it will be assumed that the Kapitza resistance in carbon nanostructures and, in particular, carbon nanocomposites produced by HPHT, is determined by the relative temperature jump, which is approximately equal to the measured temperature jump $\Delta T_r \approx \Delta T$, and therefore, the thermal resistance is determined approximately by the relative thermal resistance $r \approx r_r$.

Then the solution obtained in [17] can be written for the simplest one-dimensional heat propagation as:

$$\begin{aligned} T^{gr} - T_e &= \frac{1}{\chi}qx + \frac{\lambda q}{\chi}e^{-x/\lambda}; \\ T^{gr} - T_{ph} &= \frac{1}{\chi}qx - \frac{\lambda q}{\chi} \frac{\chi_e}{\chi_{ph}} e^{-x/\lambda}. \end{aligned} \tag{2}$$

Then the thermal resistance:

$$r \simeq r_r = \frac{\lambda \chi_e}{\chi \chi_{ph}} \approx \frac{1}{\sqrt{\theta} \chi_{ph}} \tag{3}$$

is expressed in terms of the thermal conductivity of the phonon subsystem in gr and heat transfer efficiency between the electron and phonon subsystems in the same area.

4. Thermoelectric efficiency

The thermoelectric efficiency Z_b of the system at the boundary between *gr* and *d* can be represented now as:

$$Z_b = \frac{S^2 \sigma}{\chi_{ef}} \approx S^2 \sigma \left(\frac{1}{\chi} + \frac{r}{l} \right). \tag{4}$$

This formula is stated using the electrothermal analogy. The magnitude of the thermoelectric efficiency is expressed through the effective thermal conductivity χ_{ef} of the system that takes into account the thermal conductivity in the *gr* area with the overall size of *l*, and the thermal resistance of the boundary.

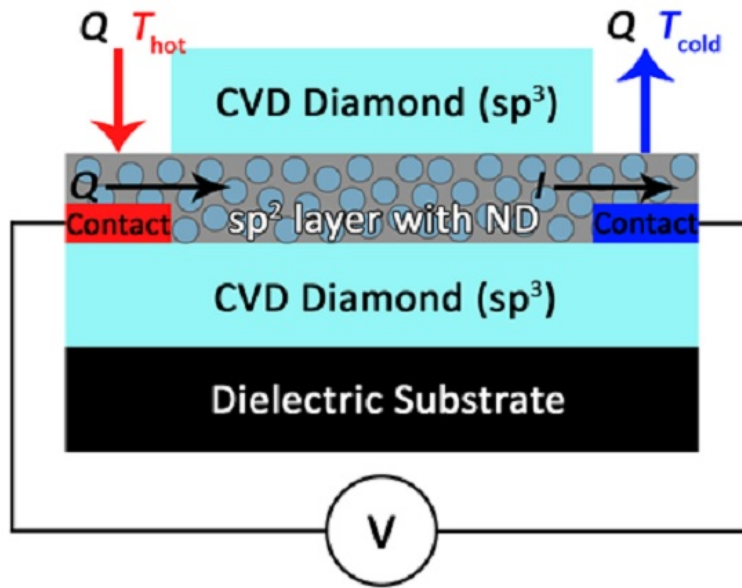


FIG. 3. A possible thermoelement design. In addition to the conditions corresponding to the structure shown in Fig. 2, the Wiedemann – Franz law is violated because of the introduction of diamond nanoparticles (ND). The thermal conductivity is determined by the Kapitza thermal resistance, i.e. by heat transfer at the interface of sp^2/sp^3 areas

Of course, even for macroscopic and microscopic samples, this formula provides the value *Z* mentioned in the Introduction. For small values of $l \ll \lambda$ in nanosystems, the addition generated by a decrease in scattering due to heat transfer from the electron subsystem to the phonon subsystem, can significantly increase the thermoelectric efficiency.

Let us estimate, first of all, the value of θ , the efficiency coefficient of heat transfer between the subsystems. As the primary heat flux is carried by electrons, we can assume that energy is transmitted from them to the crystal lattice. It is clear that energy can be transmitted by quanta only and the characteristic energy of the quanta is determined by the temperature of phonons: T_{ph} when $T_{ph} < T_D$, or Debye temperature T_D in case $T_{ph} > T_D$. Of course, the temperature difference between the subsystems is small compared with each subsystem temperature, it may be a few tenths of a degree or a few degrees, but the heat transfer occurs with the phonon transition. The phonons have the specified temperature $T_{ph} \approx T_D$ in the sp^2 region. On the other hand, the gradient of the thermal

flow of electrons is expressed in terms of the heat generated by the current, which would correspond to this heat flux. The result is:

$$\theta = a \frac{c^2 e^2 n_0^2}{\sigma T_D}. \tag{5}$$

Here, a is the order of unity factor, $c \approx 1.5 \cdot 10^3$ m/s is the speed at which the electrons move, because they captivate phonons, $n_0 \approx 10^{25} \text{m}^{-3}$ is the conduction electron density, $\sigma \approx 10^3 (\text{Om}\cdot\text{m})^{-1}$ is the conductivity coefficient, $T_D \approx 0.5 \cdot 10^3$ K, as already indicated, is the sp^2 region Debye temperature, and $e = 1.6 \cdot 10^{-19}$ Cl is the electron charge. The values of all variables, except, of course, the universal value of the electron charge, are given for graphite. All values are weakly dependent on the temperature and are borrowed from [20]. By substituting these values, we get $\theta \approx 10^{15}$ W/(m³ K). Apparently, smaller values should be selected in reality. Of course, this assessment is by the order of magnitude.

In [21] and [22] the following values of graphite thermal conductivity versus temperature are given (see. Tab. 1).

TABLE 1. Graphite thermal conductivity versus temperature

χ_{gr}	Bt/(m·K)	114	86	61	47	40	34	25
T	K	293	473	873	1173	1473	1774	2073

Data for diamond $\chi_d = 1000$ W/(m·K) at $T = 273$ and 42 W/(m·K) at 4323 K are also provided. It is obvious that the thermal conductivity for gr must be somewhat intermediate. In [23, 24] χ_{gr} values between 200 and 300 W/(m·K) are provided. On the other hand, the phonon part of thermal conductivity accounts for a small part of the total value. For further estimates, $\chi_{ph} \approx 5 - 10$ W/(m·K) will be taken (see [25]).

According to the formula (1) it turns out that $\lambda \approx 100$ nm, which confirms the above assumption on the size ratio of gr and the characteristic distance at which the temperatures of the electron and phonon subsystems can be regarded as being equal. Thus, the thermal conductivity in the carbon nanocomposites is no longer dependent on the size of the gr area, just like in the case where the interface is less than 4 nm thick (for oxides) the thermal conductivity is no longer dependent on the layer thickness [26–28].

Now, using the formulas (5) and (3) it is easy to estimate the thermal resistance. We obtain $r \approx 10^{-9}$ m²K/W. The same value of the thermal resistance is derived with an entirely different reasoning in [24]. Finally, let us find the relative thermoelectric efficiency:

$$\frac{Z_{ef}}{Z} - 1 = \frac{r\chi^{gr}}{l}. \tag{6}$$

As stated above (see Introduction), we can assume that if the size of the graphite-like area is on the order of $l \approx 10 - 30$ nm, it turns out that the thermoelectric efficiency of carbon nanocomposites is ten times higher than that of graphite. At room temperature, the thermoelectric parameter is 5-20 times higher than that of graphite.

5. Conclusion

As is known (see, for example, [20]), the Seebeck coefficient of graphite depends on its purity, but it is of the order of $S = 2 - 3 \mu\text{V/K}$. Thus, the graphite-like layer, whose surfaces have the temperature difference 100 K, produces the voltage of 0.3 mV. This value does not depend on the layer thickness, but the layer geometry affects the conditions of heating and heat dissipation and, consequently, the thermoelectric efficiency. At the surface with the lower temperature of 300 K, subject to the Wiedemann – Franz law, such a thermoelement would have the thermoelectric parameter $ZT = 3 \cdot 10^{-4}$. Materials from carbon nanostructures have $S = 10 - 20 \mu\text{V/K}$ [28] and they could produce the voltage of 1-2 mV with $ZT = 3 \cdot 10^{-2}$ with the same temperature differences. However, if such conditions are provided under which the quasi-ballistic drag of electrons by phonons prevails in the carbon nanostructure [13], it would be possible to obtain 5-10 mV and $ZT = 0.75$ (Fig. 2). In nanocomposites with the quasi-ballistic drag, in which the Wiedemann – Franz law is not fulfilled, namely, the thermal conductivity is determined by the Kapitza thermal resistance, it is possible to achieve the thermoelectric parameter 3.5 (Fig. 3).

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