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2007 J. Phys.: Condens. Matter 19 266210

(http://iopscience.iop.org/0953-8984/19/26/266210)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **19** (2007) 266210 (12pp) doi:10.1088/0953-8984/19/26/266210

# The strong thermoelectric effect in nanocarbon generated by the ballistic phonon drag of electrons

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Received 31 January 2007, in final form 16 May 2007
Published 7 June 2007
Online at stacks.iop.org/JPhysCM/19/266210

**Abstract**

The thermoelectric power and thermoelectric figure of merit for carbon nanostructure consisting of graphite-like ($sp^2$) and diamond-like ($sp^3$) regions have been investigated. The probability of electron collisions with quasi-ballistic phonons in $sp^2$ regions has been analysed for the first time. We have shown that the probability is not small. We have analysed the influence of various factors on the process of the electron–ballistic phonon drag (the phonon drag effect). The thermoelectric power and thermoelectric figure of merit under conditions of ballistic transport were found to be substantially higher than those in the cases of drag by thermalized phonons and of electron diffusion. The thermoelectric figure of merit ($ZT$) in the case of a ballistic phonon contribution to the phonon drag of electrons should be 50 times that for chaotic phonons and 500 times that in the case of the diffusion process. In that case $ZT$ should be a record ($ZT \geqslant 2$–3).

## 1. Introduction

In recent years, the effect of nanoscaling on transport phenomena in solids, in particular on thermoelectric phenomena, has become a subject of intense interest [1–5].

The interest centres at present on synthesis of new materials with the highest possible value of the thermoelectric figure of merit $Z$, which could lead to use in refrigeration or power generation [2]: $Z = S^2\sigma/\kappa$. Here $S$ is the thermoelectric power or the Seebeck coefficient, $\sigma$ is the electrical conductivity and $\kappa$ is the thermal conductivity.

The higher the $ZT$ product of a material (where $T$ is the temperature in kelvins), the more useful it may be for thermoelectric purposes. This is why one uses $ZT$ as a dimensionless quantity for characterization of thermoelectric materials.

Serious efforts were undertaken to increase $Z$ either by selecting an appropriate semiconductor for the thin layer and thickness of this layer [3, 4], or by growing a superlattice from appropriately optimized materials [5]. In the latter case, a record high value of $ZT = 2.31$ at 300 K was reached for a Bi/EuTe superlattice.

  

Particularly promising appears to be investigation of thermoelectric phenomena in carbon nanostructures. Such nanoscale structures can support coexistence of $sp^2/sp^3$ hybridized carbon. Coexistence of regions with radically different electrical and thermal properties within such short distances is indeed a unique feature of these structures. Graphite-like regions ($sp^2$) represent essentially a semimetal with a high electrical conductivity but relatively low thermal conductivity. Diamond-like regions ($sp^3$) can be identified with a wide bandgap semiconductor, actually a dielectric but with a high thermal conductivity. The corresponding transport coefficients differ by many orders of magnitude.

The paper considers the ballistic phonon drag of electrons in an $sp^2$ region a few nm in size that borders a macroscopic $sp^3$ region. We assumed that the interactions of phonons with one another should be negligible in such nanostructures with characteristic dimensions of the order of the phonon mean free path length. This means that phonons in the $sp^2$ region propagate ballistically.

It is assumed that the flux of ballistic phonons in the $sp^2$ region is driven by a temperature gradient, and that the reverse flux of phonons from the $sp^3$ region is small. We believe that the above-mentioned differences in thermal and electrical properties between the $sp^3$ and the $sp^2$ regions validate this model.

Transition from a graphite-like to a diamond-like crystal lattice can occur across a thickness of as little as that of two graphene sheets [6, 7]; therefore, scattering and reflection of long-wavelength phonons at the $sp^2/sp^3$ interface may be neglected. The wavelength of such phonons is larger than the size of the transition region separating the $sp^3$ from the $sp^2$ phase, and, therefore, a ballistic regime can be realized with long-wavelength phonons.

Thermal conduction is governed not by ballistic but rather by random processes involving short-wavelength phonons. The possible effect of short-wavelength phonons on the long-wavelength ones is taken into account by including macroscopic thermal conductivity in the denominator of the figure of merit.

The contribution of the phonon flux from $sp^3$ regions to electron drag by phonons in the $sp^2$ region is considered to be small and, thus, is disregarded.

The thermoelectric effect is driven, in a general case, by three processes, more specifically, by diffusion, electron drag by random phonons, and electron drag by ballistic phonons.

The thermoelectric coefficient in the case of electron drag by phonons is known [8] to be always larger than that for the process driven by diffusion. The mean electron displacement by the phonon wind is larger with ballistic than with random phonons. It appears therefore only natural to expect that the thermoelectric coefficient corresponding to the electron drag by ballistic phonons should be the largest.

This means that the above structure made up of a nanosized $sp^2$ region surrounded by macroscopic $sp^3$ regions should have a high thermoelectric power factor (thermopower) because of the phonon drag of electrons, even at room temperature.

Randomly propagating phonon drag of electrons in metals has been known of for a long time [8]. We are reporting here on the effect of quasi-ballistic phonon (QBP) drag of electrons; by QBPs one understands phonons that interact only weakly with one another and the lattice, in other words, that do not thermalize in the time required for their interaction with electrons. We shall consider electron interaction with QBPs which is generated in carbon nanostructures by a temperature difference, and calculate the thermoelectric power. We are going to show that the QBP contribution to the phonon drag effect gives rise to a strong ($10^2$ times) increase of the thermoelectric power or the Seebeck coefficient.

There are grounds for expecting that the $ZT$ should increase correspondingly. We will show that it is indeed true and that the value $ZT \gg 1$ can be reached when the effect of ballistic phonon drag of electrons is realized. This result is of general interest

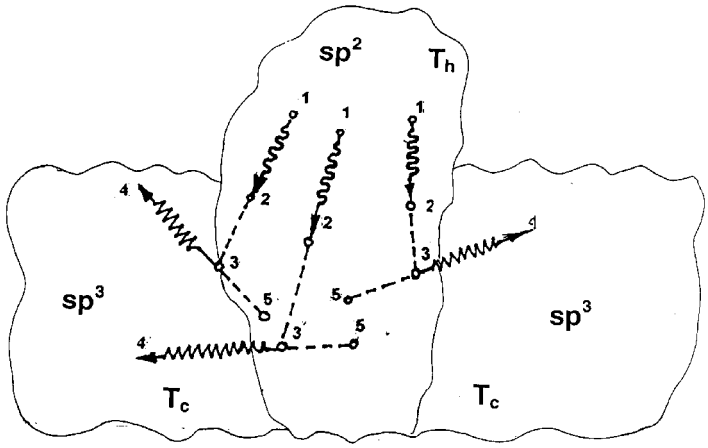


**Figure 1.** Schematic diagram of the ballistic phonon drag of electrons. 1—hottest part of $sp^2$ region. Distance 1–2 is the mean free path of a phonon of energy $\hbar\omega_q$ before collision with an electron at point 2. 2—electron of energy $\varepsilon_k$ absorbs a phonon; 2–3: displacement of the electron of energy $\varepsilon_{k+q}$ upon absorption of the phonon; 3—electron of energy $\varepsilon_{k+q}$ emits a phonon of energy $\hbar\omega_q$; 3–4 is displacement of the emitted phonon. The emitted phonons have displaced to the cold $sp^3$ region 4. Emitted phonons propagate randomly. 3–5: displacement of electron of energy $\varepsilon_k$ following emission of the phonon; 2–5: electron displacement by the ballistic phonon drag effect.

because it offers a new look at the potential of nanocarbon structures for thermoelectric power generation.

The key issue in the analysis of the drag effect in a nanostructure is the interaction of ballistic phonons with electrons.

We shall assume that if there is a temperature difference in a nanostructure, the generated phonon flow has a wavelength distribution coinciding with that of the black body radiation. As this has been recently demonstrated, this assumption is valid [9].

We are going to discuss, step by step, a qualitative model for the phonon drag of electrons having an energy distribution coinciding with that of black body radiation, calculate the probability of collision of such phonons with electrons, and estimate the thermoelectric figure of merit. We shall always consider transformation of heat to electricity.

## 2. Qualitative model

Consider a carbon structure (figure 1) consisting of nanoregions of two types, with carbon atoms in one of them (region 1) being $sp^2$ and in the other (region 4), $sp^3$ hybridized, i.e., a structure made up of graphite- and diamond-like regions. We assume a situation in which the surface of the $sp^2$ regions is heated to a high temperature $T_h$, while the diamond-like $sp^3$ regions retain a relatively low temperature $T_c$. Diamond-like regions act as specific coolers, i.e., they remove heat from the graphite-like ones. A temperature difference forms between the $sp^2$ and $sp^3$ regions, with a phonon flow setting in.

In figure 1, distance 1–2 corresponds to the mean free path of phonons of energy $\hbar\omega_q$ until collision with an electron of energy $\varepsilon_k$ at point 2. At this point, the electron absorbs a phonon. On moving the distance 2–3 in the phonon drift direction, the electron with energy $\varepsilon_{k+q}$ emits a phonon of energy $\hbar\omega_q$. The displacement 3–4 identifies transport of the emitted phonon to the cold $sp^3$ region 4, which is in thermal contact with the massive substrate. In the model under study, the temperature of the substrate and, hence, that of the $sp^3$ regions is assumed constant.

That such a formulation of the problem is valid is substantiated by the thermal conductivity ratio of the $sp^2$ and $sp^3$ regions: $\kappa_{sp^3}/\kappa_{sp^2} \gg 1$, which ensures adequate heat removal from diamond-like regions to the substrate. In the case of macroscopic $sp^2$ and $sp^3$ regions, i.e., of the diamond and graphite, this ratio is 20 [10].

Phonons are emitted in random directions. On emitting a phonon at point 3, the electron moves to region 5. Obviously, 2–5 is the distance through which a ballistic phonon drags the electron. Thus, a phonon flow drags the electron gas in the graphite-like region and, in doing this, generates a thermoelectric field.

The purpose of the present study is to calculate the efficiency of the drag process and the thermoelectric power associated with the drag effect. We shall calculate the probability for a QBP to collide with an electron, find the temperature dependence of the phonon relaxation time, and show that the thermoelectric power of a graphite-like nanocluster exceeds by orders of magnitude the known values of the thermoelectric power for graphite, which are ≈10–20 $\mu$V K$^{-1}$ for the region above room temperature.

The actual structure and design of the thermoelectric generator can be realized in various ways.

## 3. Estimation of the parameters of the problem

Estimate first the phonon mean free path $l$ in the $sp^2$ region [11]. The estimate will be made for temperatures $T_h \approx 500$ K, where the lattice vibration amplitude $\xi$ becomes comparable to the lattice constant $a$. As a rough approximation, one may use the classical relation $M\omega^2\xi^2 \approx k_B T$ for the vibration energy of a carbon atom of mass $M = 12$ amu, where $k_B$ is the Boltzmann constant. Accepting $\omega \approx c/a$ as a characteristic frequency, where $c \approx 5 \times 10^4$ m s$^{-1}$ is the sound velocity in the $sp^2$ region, we arrive at

$$l \approx \frac{Mc^2 a}{k_B T} \geqslant 10 \text{ nm}. \tag{1}$$

This means that in an $sp^2$ region of size $d \leqslant l$ the major contribution to the phonon drag effect comes from QBPs. The main contribution to the drag is known to be due to long-wavelength phonons [8]. It is through absorption of longitudinal acoustic phonons that electron–phonon interaction occurs at temperatures above 10 K [11].

This ballistic propagation mode of phonons without collision with one another ($l \approx d$) permits one to calculate the phonon flux as black body radiation intensity (for phonons):

$$r = \frac{4\pi\hbar c^2}{\lambda^5}\left[\exp\left(\frac{2\pi\hbar c}{\lambda k_B T}\right) - 1\right]^{-1} \tag{2}$$

where $\lambda$ is the wavelength and $\hbar$ is the Planck constant.

Let us now determine the conditions in which electrons reside ($m$ is the electronic mass). In the $sp^2$ region, the electron gas is degenerate, with the degeneracy temperature

$$\frac{\hbar^2}{k_B m a^2} \approx 10^5 \text{ K} \gg T_h. \tag{3}$$

It appears appropriate to point out here that energy quantization in the $sp^2$ region may be neglected for both electrons and phonons, even if the drag occurs to the largest distance $\lambda \approx \xi \approx d$.

Indeed, for phonons this condition can be written as (see section 23 in [12])

$$\frac{e^2 E^2 d}{m_{Ph} c^2 4\pi^2} \geqslant \frac{2\pi c\hbar}{d} \tag{4}$$

and a similar condition for electrons (section 22 in [12])

$$\frac{e^2E^2d^2}{m_{\mathrm{Ph}}c^2 4\pi^2} \geqslant \frac{\hbar^2\pi^2}{2md^2}. \tag{5}$$

Invoking now the uncertainty relation $m_{\mathrm{ph}} \geqslant \hbar/cd$ to exclude the phonon mass, we find that size quantization effects do not apply to phonons if

$$d \geqslant \sqrt{2\pi\frac{\hbar c}{eE}} \geqslant 2\ \mathrm{nm} \tag{6}$$

and to electrons if

$$d \geqslant \left(\frac{4\pi^4\hbar^3 c}{me^2E^2}\right)^{1/5} \geqslant 2\ \mathrm{nm}. \tag{7}$$

We believe that phonon reflection at the $sp^2/sp^3$ interface should not change significantly the above qualitative pattern of the phenomenon. This assumption finds justification in the lattice similarity between these regions. In these conditions, phonons have a velocity component directed opposite to the temperature gradient (figure 1).

## 4. Calculation of the probability of electron collision with a ballistic phonon

Let us turn now to estimating the probability for a degenerate electron gas to interact with ballistic phonons (figure 1). As already pointed out in describing the model (see [13] or [14]), an electron with energy $\varepsilon_k$ absorbs a long-wavelength phonon of energy $\hbar\omega_q$ to become an electron of energy $\varepsilon_{k+q}$, after which this electron is displaced (dragged) and emits subsequently a phonon of energy $\hbar\omega_q$. If phonons are thermalized (at the Debye temperature $\theta$), the resultant electron displacement can be determined by subtracting from the displacement of the electron that has absorbed a phonon the displacement of the same electron after it has emitted the phonon, so that eventually the thermoelectric power scales as $\theta/T$.

The situation is different when electrons are dragged by ballistic phonons. All the absorbed phonons were propagating in the same direction, more specifically, against the temperature gradient, while the phonons emitted by electrons are isotropic. One may therefore assume that, on average, emission of phonons does not affect phonon drag due to the ballistic phonon flow.

This simplifies the calculation of the parameters of the drag of electrons by phonons; indeed, one has only to find the probability of phonon scattering from electrons.

The scattering probability per unit time can be calculated by the standard quantum mechanical procedure. This procedure is explained in [13] in the form most appropriate for the problem of interest to us here. For the case of phonon absorption we have

$$W_q = \frac{2\pi}{\hbar}\left|\left\langle\vec{k}+\vec{q};\, N_q - 1\right|\hat{H}_{\mathrm{in}}\left|\vec{k};\, N_q\right\rangle\right|^2\delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q). \tag{8}$$

Besides the widely used and already explained notation, we meet here $\hat{H}_{\mathrm{in}}$, a Hamiltonian of electron interaction with longitudinal acoustic phonons, and $N_q$, the number of phonons with wavevector $\vec{q}$.

The matrix element in equation (8) was calculated in [13] in the deformation potential approximation

$$W_q = W(q)N_q\delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q) \tag{9}$$

where

$$W(q) = \frac{4\pi}{9N}\frac{C^2q^2}{M\omega_q}. \tag{10}$$

We have introduced here $N = d^3/a^3$, the number of atoms in the $sp^2$ region, and $C$, a quantity with the dimension of energy which characterizes the intensity of electron interaction with a phonon. To avoid overestimation of the interaction probability, one should take the smallest possible value for $C$. The corresponding change of potential energy of an electron in the cell corresponds to its displacement by the lattice constant $a \cong 1$ Å, i.e.,

$$C \leqslant \frac{k_e e^2}{a} \approx \frac{\hbar^2}{2ma^2} \tag{11}$$

(here $k_e$ is the electric constant, and $e$ is the electronic charge) and $C \cong$ 1–10 eV.

The latter approximate equality in equation (11) is the consequence of the potential energy of an electron being approximately equal to its kinetic energy. It is known also (see [11] and [14]) that the drag is largely determined by phonons with energies of the order of the energies of the electrons which absorb them. Therefore, $\varepsilon_k \approx \hbar\omega_k$. This yields the lower estimate of the delta function

$$\delta(\varepsilon_{k+q} - \varepsilon_k - \hbar\omega_q) \approx \frac{1}{\hbar\omega_q}. \tag{12}$$

Invoking the relation $\omega_q = cq$, which appears fairly obvious for acoustic phonons, we can now recast conveniently the transition probability per unit time in the form

$$W_q \approx \frac{4\pi a^3}{d^3}\left(\frac{\hbar^2}{2ma^2}\right)^2 \frac{1}{Mc^2\hbar} N_q. \tag{13}$$

Estimate now the number of phonons $N_q$. The main idea underlying this study suggests that the flux of these phonons, i.e., phonons with the wavelength lying in the interval from $\lambda$ to $\lambda + \mathrm{d}\lambda$, should be equal to the black body radiation intensity

$$\frac{r\,\mathrm{d}\lambda}{\hbar\omega_q}. \tag{14}$$

This is the number of phonons with wavelength $\lambda$ that pass through unit area per unit time. The area of the $sp^2$ region is of the order of $d^2$, and the time a phonon takes to cross this region is of the order of $d/c$.

Because phonons involved in the drag have different wavelengths, to obtain the total transition probability $W$ per unit time we have to integrate equation (14) over all wavelengths of phonons with energies of the order of Fermi energy or less, i.e., of phonons responsible for the drag. Their wavelength is larger than $2\pi\hbar c/\varepsilon_F$. The Fermi energy for carbon structures is of the order of 1 eV, and the corresponding wavelength $\approx 10^{-12}$ m, which is much less than the lattice constant $a$. We may recall that it was the size $a$ that entered the estimate of electron interaction with phonons (11). Phonons with wavelength $\lambda \approx a$ should yield the major contribution to the total transition probability. Therefore, integration of the flux (14), in conjunction with equation (2), with a desired accuracy should be started not from the wavelength $2\pi\hbar c/\varepsilon_F$ but rather from $\lambda = 0$. This integration

$$\int_0^\infty \frac{r\,\mathrm{d}\lambda}{\hbar\omega_q} = \int_0^\infty \frac{1}{\hbar}\frac{4\pi^2\hbar c^2}{2\hbar c/\lambda}\frac{\mathrm{d}\lambda}{\lambda^5}\frac{1}{\exp(2\pi\hbar c/k_B T\lambda) - 1} \tag{15}$$

yields the probability for ballistic phonons to be absorbed by electrons of the degenerate gas per unit time:

$$W = \frac{4\pi a^3}{d^3}\left(\frac{\hbar^2}{2ma^2}\right)^2 \frac{1}{Mc^2}\frac{2\pi c}{\hbar}\left(\frac{k_B T}{2\pi\hbar c}\right)^3 \Gamma(3)\zeta(3)\frac{d}{c}d^2. \tag{16}$$

Here $\Gamma(3) = 2$ is the gamma function, and $\zeta(3) \approx 1.2$ is the Riemann zeta function. One can readily verify that $W > 10^{12}\ \mathrm{s}^{-1}$.

Notice that consideration of the interaction of phonons with weakly bonded $\pi$ electrons in graphite [9] yielded a similar result.

The probability for colliding with an electron in the time it takes a phonon to cross an $sp^2$ region, $d/c$, turns out to be more than 40%, which is quite high. This is why the thermoelectric power turns out to be high.

## 5. Thermoelectric power generated by ballistic phonon drag of electrons

The thermoelectric power $S$ in the region of random phonon motion is well known:

$$S = \alpha \frac{k_B}{e}; \qquad \alpha = \left( A_{dif} \frac{k_B T}{\varepsilon_F} + A_{dr} \frac{\theta}{T} \right) \tag{17}$$

(see [11] or [14]). The numerical coefficients $A_{dif}$ and $A_{dr}$ are of the order of 0.1–10. The first term in equation (17) describes diffusion processes, and the second, the drag by randomly propagating phonons.

Compare the contributions due to these processes.

It is known [11, 14] that the Debye temperature, which, by definition, is expressed through the maximum phonon frequency $\omega_m$ in a random process, is related to the Fermi energy ($p_F$ is the Fermi momentum, and $\upsilon_F$ is the Fermi electron velocity) as

$$k_B \theta = \hbar \omega_m \approx \frac{\hbar c}{a} \approx p_F c \approx p_F \upsilon_F \left( \frac{m}{M} \right)^{1/2} \approx \varepsilon_F \left( \frac{m}{M} \right)^{1/2}. \tag{18}$$

Substituting this estimate in equation (17) yields

$$\alpha_{ch} = \left( A_{dif} \frac{T}{\theta} \sqrt{\frac{m}{M}} + A_{dr} \frac{\theta}{T} \right). \tag{19}$$

Hence it follows that for temperatures $T = (2\text{–}5)10^2$ K the drag process is dominant throughout the temperature range covered: $A_{dr} \gg A_{dif}(m/M)^{1/2}$, and $\theta/T \approx T/\theta$.

Thus, it is the phonon drag of electrons rather than electron diffusion that dominates thermoelectric power in the phonon thermalization region.

In the ballistic phonon propagation region, only phonon drag of electrons persists. As already mentioned, the electron absorbs a phonon with a momentum directed against the temperature gradient.

Exact calculation of the dimensionless coefficient $\alpha$ in the case of ballistic phonons would not differ from that of chaotic phonons that has already been performed in [8] if one drops the terms responsible for phonon drag by thermalized phonons in the reverse direction.

Thermalized phonons appear due to phonon–phonon scattering, which, by definition, does not exist in the ballistic phonon drag. Thus, the difference between the drag due to chaotic phonons and that produced by the ballistic ones consists in that there are phonons with wavevectors directed opposite to the main phonon stream (see figure 2).

The length of the phonon drag of electrons in the direction opposite to the temperature gradient should be subtracted from that directed along the temperature gradient (figure 2(b)). In the case of ballistic phonons, there is no drag in the direction opposite to the temperature gradient. This means that the effect of ballistic phonons on phonon drag should be substantially higher than that produced by the chaotic population.

The thermoelectric power corresponding to this process can also be estimated using the symmetry of the transport coefficients (see, e.g., [15]). By virtue of this symmetry, the

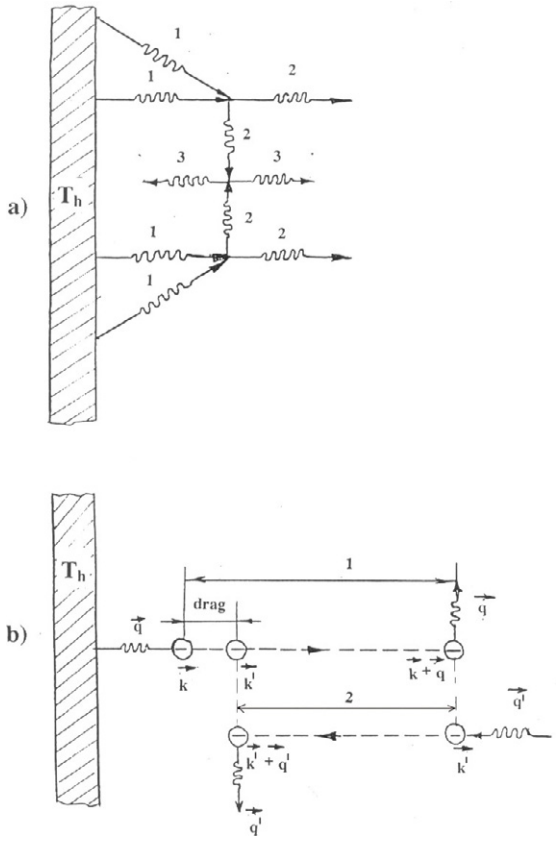


**Figure 2.** Schematic diagram of the chaotic phonon drag of electrons. $T_h$—hottest part. (a) Scheme of the process explaining generation of the phonon moving to the hottest part. 1—initial phonons from the hottest part, 2—phonons after the initial phonon's interaction, 3—phonons after interaction of secondary phonons. One of the three phonons moves to the hottest part. (b) Scheme of the chaotic phonon drag effect. 1—shift of electron (with wavevector $\vec{k}$) due to phonon (wavevector $\vec{q}$) which moves from the hottest part, 2—shift of electron ($\vec{k}'$) due to phonon ($\vec{q}'$) which moves to the hottest part, phonon drag effect ('drag') is the difference of these shifts.

thermoelectric power relates not only to the field with the temperature gradient but also to the heat released in the system with the electric field as well. Therefore, in a general case, one can write

$$\alpha = \alpha_{\text{bal}} = A_{\text{bal}} C_V / k_B N_0. \tag{20}$$

Here $A_{\text{bal}}$ is a new coefficient of the same kind as the coefficients $A_{\text{dif}}$ and $A_{\text{dr}}$ introduced earlier in equation (17), $C_V$ is the heat capacity of a unit volume of the medium releasing heat, and $N_0$ is the number of electrons absorbing this amount of heat.

Estimate now the dimensionless thermoelectric power corresponding to this process, $\alpha = \alpha_{\text{bal}}$.

In an $sp^2$ region, heat is released by the flow of quasi-ballistic phonons, i.e.,

$$C_V = \frac{16\pi^2 k_B^4 T^3}{60\hbar^3 c^3}. \tag{21}$$

This is the heat capacity of black body radiation. $N_0$ in this region of volume $d^3$ is not larger than 20–30 electrons. In actual fact, this is an overestimation used so as not to

overestimate the coefficient $\alpha_{\rm bal}$. Then

$$\alpha_{\rm bal} \approx \left(\frac{k_{\rm B}Td}{\hbar c}\right)^3. \tag{22}$$

The numerical factor in equation (22) was assumed equal to unity.

Estimates yield for the thermoelectric power $\alpha \approx \alpha_{\rm bal} = 50$–$100$ ($S \cong (5$–$10)10^{-3}$ V K$^{-1}$) for temperatures $T = (2$–$5)10^2$ K.

We have arrived now at estimation of $ZT$ at $T = 300$ K for nanocarbon films with a desirable ratio of $sp^2/sp^3$ regions. At achievable values $\sigma = 300 \times 10^2$ S m$^{-1}$; $k = 2 \times 10^2$ W m $^{-1}$ K$^{-1}$ [16] we come to $ZT \cong 0.6$–$30$.

Hence the thermoelectric figure of merit in the case of a ballistic phonon contribution to the phonon drag should be a hundred times that for chaotic phonons and 500 higher than that in the case of electron diffusion.

Thus, the dimensionless thermoelectric power characterizing ballistic phonon drag of electrons turns out to be $10^2$ times higher than that for the random phonon drag of electrons, and $5 \times 10^2$ times higher than that expected for diffusion processes.

The thermoelectric figure of merit should be also larger correspondingly.

Unfortunately, experimental data on the Seebeck coefficient in nanocarbon structures are unknown to the authors; we can, however, assume that it is the drag of electrons by ballistic phonons that is responsible for the increase of the coefficient with decreasing thin layer thickness detected in [3, 4].

## 6. Analysis of the ballistic phonon drag of electrons

The above estimate of the probability of ballistic phonon absorption by electrons, equation (16), was obtained by solving the transport equation in the relaxation time approximation, i.e., assuming that before recovering their equilibrium state, electrons undergo many interactions with phonons.

This calculation is similar to the one developed for the low temperature domain and macroscopic samples. At low temperatures, the phonon mean free path is large and comparable to the size of macroscopic objects. In the present case of high temperatures, the phonon mean free path is small, but it still is larger than or of the order of the size of an $sp^2$ region in a nanostructure.

The magnitude of the probability $W$ determines the size $x$ within which phonons propagate ballistically despite scattering from electrons:

$$W\frac{x}{c} < 1. \tag{23}$$

If $x > d$, it is by the ballistic phonon drag, $\tau = \tau_{\rm bal} = W^{-1}$, that the relaxation time in the $sp^2$ region, $\tau = W^{-1}$, which determines electron displacement and, hence, the thermoelectric power, will be governed. If, however, $x < d$, the $sp^2$ region should be divided into two parts. In one of them, of size $x$, phonons may be considered ballistic, while in the other, $d - x$ in size, phonons move in random directions.

Let us analyse the expression for the probability of ballistic phonon absorption by an electron, equation (16). One may conveniently rearrange this expression to isolate the dimensional factor $c/d$ and a dimensionless one that relates to the collision process

$$E = \frac{4\pi a^3}{d^3}\left(\frac{\hbar^2}{2ma^2}\right)^2 \frac{d^2}{Mc^2}\frac{2\pi c}{\hbar}\frac{d^2}{c^2}\left(\frac{k_{\rm B}T}{2\pi\hbar c}\right)^3 \Gamma(3)\zeta(3). \tag{24}$$

Dropping inessential numerical factors, equation (24) can be recast in the form of four dimensionless parameters having a straightforward physical meaning:

$$E = V_1^3 V_2^2 V_3 V_4 \tag{25}$$

where the first dimensionless parameter

$$V_1 = \frac{k_B T}{2\pi\hbar c/a} \approx 0.1\text{–}1; \tag{26}$$

is the ratio of the imparted heat to the phonon energy. The quantity $V_1^3$ is the number of phonons incident on the electron.

The second parameter

$$V_2 = \frac{\hbar^2}{2ma^2}\frac{1}{Mc^2} \approx \frac{k_e e^2}{a}\frac{1}{Mc^2} \approx 1\text{–}0.1 \tag{27}$$

is the ratio of the electron vibrational energy to the energy of atomic vibrations in the crystal cell. The quantity $V_2$ is the matrix element of electron interaction with a phonon, and $V_2^2$ is the squared matrix element entering the interaction probability.

The third parameter (anharmonicity factor)

$$V_3 = \frac{Mc^2}{\hbar c/a} \approx 40\text{–}400 \tag{28}$$

is the ratio of atom (cell) vibration energy to phonon energy. Finally, the fourth parameter

$$V_4 = \frac{x}{a} \approx \frac{d}{a} \approx 1\text{–}10 \tag{29}$$

is the relative size of the region phonons cross ballistically.

The relation of the dimensionless thermoelectric power to the rate of ballistic phonon absorption by electrons is physically obvious. The thermoelectric coefficient (22) is defined by the number of electrons which become displaced as a result of ballistic phonon absorption, and the rate of ballistic phonon absorption by electrons is characterized by the probability given by equation (16). Indeed, both these quantities are proportional to $V_1^3$, i.e., they scale as $T^3$. This pattern of behaviour is characteristic also of low temperature thermal conductivity (see chapter 6, section 7 in [14]), as well as of the acoustoelectric coefficient. It should be emphasized that the thermoelectric power in the case of electron drag by randomly propagating phonons scales as $T^{-1}$ [5, 17].

## 7. Conclusion

To sum up, we have shown that the probability of electron collisions with quasi-ballistic phonons in $sp^2$ hybridized carbon nanostructures is not small, and that it is the quasi-ballistic phonon drag of electrons with the distribution coinciding with that of black body radiation that provides the major contribution to thermoelectric power. The high efficiency of electron interaction with such phonons is accounted for by the better matching of the electron and phonon energy distributions, which distinguishes our case from the acoustoelectric effect [18–20]. Note that [20] proposes a general expression relating the drag-based thermoelectric power to the acoustoelectric effect for any phonon distribution. The above calculations combined with the formalism developed in [20] could permit computation of the acoustoelectric effect in carbon nanostructures. Experimental determination of this coefficient by the technique employed in [21] appears of interest.

As follows from calculations, the probability of electron interaction with quasi-ballistic phonons is proportional to the size of the region in which phonons propagate without collisions

with one another, thus making it possible to extend the results and methods of calculation developed for ballistic phonons at low temperatures to the high temperature domain in the case of nanostructures.

We have analysed the influence of various factors on the process of ballistic phonon drag of electrons. It turned out that the main factors are here, first, the relative size of the region of ballistic phonon propagation and, second, the ratio of lattice vibration to phonon energy, i.e., the anharmonicity factor.

We have used in the calculations the theoretical phonon mean free path $l < 10$ nm (1). Experiment revealed substantially larger mean free paths. Indeed, the experimental mean free path of ballistic phonons turned out to be larger, 2.5 mm, at a temperature $T = 1$ K. In our case, for the estimates to be valid, the mean free path can be less than 4 nm. We used in the estimates 4 nm. The probability of absorption, equation (16), scales with temperature as $T^3d^2$. This means that the mean free path has already become about 4 nm at $T \cong 500$ K. To estimate $Z$, only the probability of absorption $W$ is needed. Thus, the drag effect in the above estimates is underestimated. We want to stress once more that all our estimates were obtained with an underestimated drag probability (drag effect) and, accordingly, with underestimated parameter $Z$. The predicted effect of ballistic phonon drag of electrons and, accordingly, the corresponding increase of the $Z$ parameter compared with known mechanisms are real.

The thermoelectric power and thermoelectric figure of merit under conditions of ballistic transport were found to be substantially higher than those in the cases of the drag by thermalized phonons and that of electron diffusion. The temperature dependence of the contribution of the ballistic phonon drag of electrons to the thermoelectric power factor scales as temperature cubed, which differs radically from the well-known behaviour at high temperatures in macrostructures while coinciding with the temperature dependences observed at low temperatures [8] and characterizing the acoustoelectric effect [18, 20].

Taking into account the ballistic phonon contribution to phonon drag can be essential in other phenomena occurring in nanocarbon structures as well; in particular, it allowed us to suggest a model for the explanation of the anomalous high field electron emission in these structures [22].

## Acknowledgments

The authors are grateful to V L Gurevich who drew our attention to the ballistic phonon drag of electrons when discussing the work [2], to E L Ivchenko who pointed out the importance of estimating the quantum size effect, L P Mezhov-Deglin and R A Suris for stimulating discussions and suggestions.

The authors would like to express special thanks to D M Gruen (Argonne Lab), who was the first to direct our attention to the importance of consideration of the thermoelectric power, offered his estimates of the parameters of interest to us and suggested valuable comments during discussion of the manuscript.

This work was supported by the Russian Ministry for Education, Science and Technologies (Contract Nos 40.700.12.0117 and 40.012.11.1147) and by the Presidium of the Russian Academy of Sciences (project Quantum Nanostructures).

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