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### THERMOELECTRIC PHENOMENA IN “BOTTOM – UP” APPROACH

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*Thermoelectric phenomena of Seebeck and Peltier, quality indices of thermoelectric devices and materials and thermoelectric optimization, ballistic and diffusive transport of phonons and its role in the thermal conductivity are discussed in the frame of the «bottom – up» approach of modern nanoelectronics.*

**Key words:** nanoelectronics, microelectronics, electron conductivity modes, phonon conductivity modes, Seebeck effect, Peltier effect, power factor,  $ZT$  product, thermoelectric optimization.

#### Introduction

Both previous publications [1, 2] have been devoted to modern Landauer – Datta – Lundstrom (LDL) electron and heat transport model [3 – 7] which works well at the nanoscale as well as at macroscale for 1D, 2D, and 3D resistors in ballistic, quasi-ballistic, and diffusive linear response regimes when there may be differences in both voltage and temperature across the device. Success of the LDL transport model is associated primarily with the use of the “bottom – up” approach when discussing different topics in electronics in contrary to historically traditional “top – down” approach [8 – 11].

We seek today to bring a new perspective to university and engineering education to meet the challenges and opportunities of modern nanotechnology. Sixty years ago electronics faced a similar challenge brought on by the advent of the transistor and it was met effectively: a generation of physicists and engineers ready to lead the modern electronics industry has been trained.

Today we face the need for a comparable revolution in education as well as in research. Ever since the birth of solid state physics, materials have been described in terms of average material parameters like the mobility or the optical absorption coefficient which are then used as inputs to macroscopic device models. This “top – down” approach is being widely used even for modern nanostructured materials, but we believe that it is no longer adequate to meet the challenges and opportunities of our day. An integrated approach is needed that embeds new ways of thinking, emerging from current research on nanoscience, directly into the models used for non-equilibrium problems like nanoscale transistors, energy conversion devices and bio-sensors. This new “bottom – up” approach to electronic devices and materials is being most successfully demonstrated in the

Network of Computational Nanotechnology at Purdue University, USA [12]. In this paper we discuss thermoelectric phenomena in the “bottom – up” approach partly following lecture course “Fundamentals of Nanoelectronics: Basic Concepts” given by Supriyo Datta in 2012 [13].

Conduction measurements themselves do not tell us anything about the nature of the conduction process inside the conductor. In the closed circuit, electrons always move from the negatively charged contact through conductor to the positively charged contact whatever the physical and chemical nature of the conductor. This is true for all conductors and therefore conductivity measurements do not tell us anything about the conductor itself.

On the other hand, thermoelectric phenomena as those where current is generated by the temperature difference on the conductor contacts, provide the opportunity to judge on the physical nature of the conductivity. The simplest examples are the conductors of  $n$ - and  $p$ -type. In the  $n$ -type conductors, electrons move from the hot contact through conductor to the cold one, but in the  $p$ -type conductors the direction of electron transport is opposite. Why?

It is often explained that  $p$ -conductors show the opposite effect due to the carriers (so called “holes”) having the opposite sign relative to electrons moving in the  $n$ -conductors. However, this explanation is not quite satisfactory since what actually move are electrons with a negative charge. “Holes” are at the best a conceptual convenience and experimental effects observed in the laboratory should not depend on the subjective conveniences.

Differences between  $n$ - and  $p$ -conductors are best explained in the “bottom – up” approach [13 – 17]. In  $n$ -conductors the density-of-states  $D(E)$  increases with increasing energy  $E$ , while in the  $p$ -conductors it decreases with increasing  $E$ . In the  $n$ -type conductors the electrochemical potential  $E_F$  is located near the bottom of a band of energies, while in the  $p$ -type conductors it is located near the top. In the last case the flow of electrons happens near the top of a band of energies and it is just convenient to keep track of the empty states above  $E_F$  rather than the filled states below  $E_F$ . These empty states are called holes and since they represent the absence of an electron they behave like positively charged entities.

Differences between  $n$ - and  $p$ -conductors do not require new principles or assumptions beyond what we have already discussed [1, 2], namely: electric current is driven by the difference between Fermi functions on contacts of the conductor  $f_1(E) - f_2(E)$ .

Another important physical phenomenon is known, called the Hall effect, which changes sign for the  $n$ - and  $p$ -types conductors and the Hall effect too is commonly blamed for negatively charged electrons and positively charged “holes”. The Hall effect, however, has a totally different origin related to the negative mass associated with  $E(p)$  relations in  $p$ -conductors that points downwards [18]. By contrast the thermoelectric phenomena do not require a conductor to even have a  $E(p)$  relation. Even small molecules show sensible thermoelectric effects [19 – 21]. Molecular junctions hold significant promise for efficient and high-power-output thermoelectric energy conversion.

To explain differences between  $n$ - and  $p$ -conductors in the “bottom – up” approach, let us

remind well known now expression for current through an elastic resistor (32) in [14]:

$$I = \frac{1}{q} \int_{-\infty}^{+\infty} dE G(E) (f_1(E) - f_2(E)), \quad (1)$$

where  $G(E)$  is the conductivity. If previously [14] the difference between the Fermi functions was generated by the difference between the electrochemical potentials at the same temperature of the contacts, the difference as well can be generated by the difference in temperature of contacts since the Fermi functions depend on both  $E_F$  and  $T$ , namely:

$$f_1(E) = 1 / (e^{(E-E_{F1})/kT_1} + 1) \quad (2a)$$

and

$$f_2(E) = 1 / (e^{(E-E_{F2})/kT_2} + 1). \quad (2b)$$

Why with the temperature difference between contacts the direction of current is opposite in  $n$ - and  $p$ -type conductors? The reason lies in the behavior of the difference of the Fermi functions of hot and cold contacts (Fig. 1).

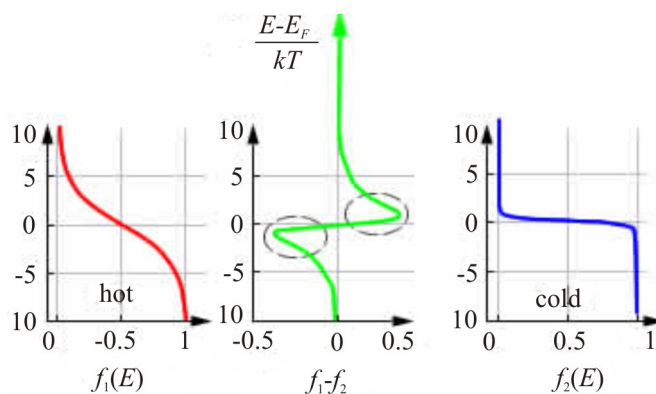


Fig. 1. Two contacts, hot and cold, with the same value of  $E_F$ : the difference of the Fermi functions is positive for  $E > E_F$  and negative for  $E < E_F$ .

In the  $n$ -type channel conductivity  $G(E)$  is the increasing function of energy, so that the states with  $E > E_F$  dominate in the total current, the electrons move from the left contact to the right one, from hot to cold (Fig. 2).

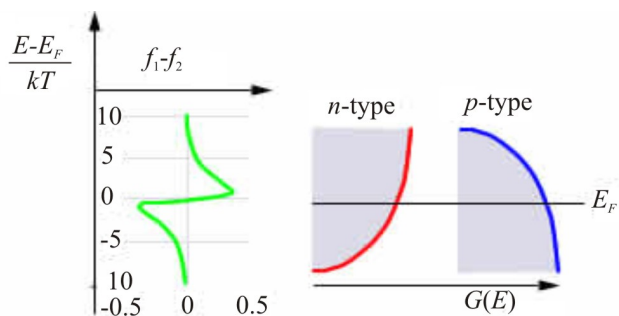


Fig. 2. For the  $n$ -conductor the current for  $E > E_F$  dominates the current for  $E < E_F$ , while for  $p$ -conductors situation is opposite – the current for  $E < E_F$  dominates the current for  $E > E_F$ .

Situation is opposite in the  $p$ -channels. Conductivity  $G(E)$  is the decreasing function of energy, so that the states with  $E < E_F$  dominate in the total current, the electrons move from the right contact to the left one, from cold to hot (Fig. 2).

Consequently, electrons flow from hot to cold across the  $n$ -type resistor, but from cold to hot in a  $p$ -type channel. Exactly this explanation of the different behavior of  $n$ - and  $p$ -thermics in the "bottom – up" approach is used in the LDL transport model [22, 23].

### Seebeck coefficient

To calculate the current due to the difference in the temperature of contacts, one can use eqn (1) directly, without introducing any simplifications. However, in the case of small differences in the temperature of contacts, as has been already demonstrated in the case of the small difference between the electrochemical potentials in [1, 7, 14, 15], which corresponds to the low bias or linear response regime, you can use the decomposition of the difference of the Fermi functions in (1) in the Taylor series and limit itself by the linear term. Then we can write

$$I = G(V_1 - V_2) + G_s(T_1 - T_2). \quad (3)$$

This shows that the electrons move from the hot contact through the  $n$ -conductor to the cold contact, and in the  $p$ -conductors the direction of transport is opposite. Let us rewrite (3) as

$$\Delta V = \frac{I}{G} + \left( -\frac{G_s}{G} \right) \Delta T, \quad (4)$$

where  $V_1$  and  $V_2$  are defined as  $E_{F_1}/q$  and  $E_{F_2}/q$ , and the conductance  $G$  is given by [1]

$$G = \int_{-\infty}^{+\infty} dE G(E) \left( \frac{\partial f_0}{\partial E_F} \right) = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) G(E), \quad (5)$$

whereas the Seebeck conductivity

$$G_s = \frac{1}{q} \int_{-\infty}^{+\infty} dE G(E) \left( \frac{\partial f_0}{\partial T} \right) = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{E - E_{F_0}}{qT} G(E). \quad (6)$$

The Seebeck coefficient  $S$  is defined as the ratio of these two conductivities:

$$S = -G_s/G. \quad (7)$$

Equation (6) mathematically expresses the fact that the states with energy higher and lower of the electrochemical potential, contribute to the thermoelectric Seebeck coefficient  $S$  with different signs. From this equation it is clear that selecting the material with the best Seebeck coefficient one should choose such a material in which all the state density is concentrated on one side of the electrochemical potential  $E_{F_0}$ , since even the small fraction of the states on the other side of  $E_{F_0}$  only brings the Seebeck coefficient down.

Relations (3) and (4) may be illustrated by the two circuits (Fig. 3): short circuit with current

$$I_{sc} = G_S(T_1 - T_2) \quad (8)$$

and open circuit, which is usually used in thermoelectric power measurements giving voltage

$$V_{oc} = -\frac{I_{sc}}{G} = -\frac{G_S}{G}(T_1 - T_2). \quad (9)$$

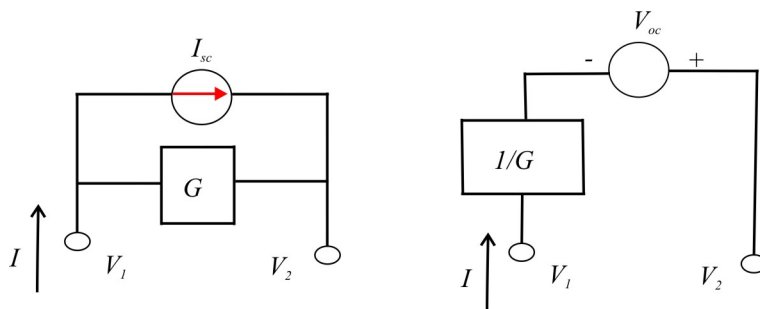


Fig. 3. Short circuit (sc) and open circuit (oc) illustrating the eqns (3) and (4).  
For the direction of current (the same as the direction of electron flow)  
and for the voltage sign the natural conditions are used, which are opposite  
to the ones traditionally used.

For example, for the  $n$ -conductors the Seebeck conductivity is positive, thus the voltage  $V_{oc}$  is negative if  $T_1 > T_2$ . This means that contact with the higher temperature is charged negatively (positive in the conventional sense). According to agreement, the Seebeck coefficient

$$S \equiv \frac{V_{oc}}{T_1 - T_2} = -\frac{G_S}{G}. \quad (10)$$

### Quality indices of thermoelectric devices and materials

In practical applications the thermoelectric effect is interesting in a sense that the heat excess can be converted into electricity [24]. Maximum of power  $P$  is generated when the loaded resistance  $R_L = 1/G$ , namely:

$$P_{max} = V_{oc}^2 G / 4 = S^2 G (T_1 - T_2)^2 / 4, \quad (11)$$

where  $S^2 G$  is known as the power factor and is one of the standard figures of merit for thermics.

The ratio of the maximum generated power to the power that is supplied by the external source is a good measure of the efficiency of the thermoelectric material in converting heat to electricity and is called the coefficient of performance

$$\eta \equiv \frac{P_{max}}{G_k (T_1 - T_2)} = \frac{S^2 G T_1 - T_2}{G_k 4T}, \quad (12)$$

where  $G_K$  – the thermoconductivity of the material, and  $T$  is the mean temperature  $(T_1 + T_2)/2$ . The standard figure of merit for thermics, called its  $ZT$  product is proportional to the ratio of  $S^2G$  to  $G_K$ :

$$ZT \equiv \frac{S^2GT}{G_K} = \frac{S^2\sigma T}{k}, \quad (13)$$

where the specific thermal conductivity  $k$  is related to the thermal conductivity  $G_K$  of the conductor material

$$G_K = k \cdot A / L \quad (14)$$

as the electric conductivity is related to the specific conductivity of the conductor of length  $L$  with cross-sectional area  $A$ . Fourier law for the thermoconduction, the analog of the  $\Omega$  law for the electrical conductivity, when applied to nanoresistors, needs the same correction ( $L \Rightarrow L + \lambda$ ) as the  $\Omega$  law [7, 14].

The electrical conductivity arises solely from electrons. The thermal conductivity includes also a contribution of phonons. Usually it is the phonon component that dominates the thermal conductivity. It will be discussed a bit later. For now we shall discuss the heat carried by electrons only.

### Heat current

So far, we have discussed the thermoelectric conductivity of a material with any arbitrary conductance  $G(E)$ . Model of the elastic resistor [14, 15] is attractive in a sense that modes at different energies all conduct in parallel, so that we can consider the conductivity at a certain value of the energy, and then just sum up over the entire spectrum of energies. Consider a small energy range between  $E$  and  $E + dE$  located either above the value of the electrochemical potential  $E_{F_0}$  ( $n$ -type modes) or below ( $p$ -type modes) (Fig. 4). As it was mentioned above, the contributions of these two different types of modes into Seebeck effect are opposite in sign.

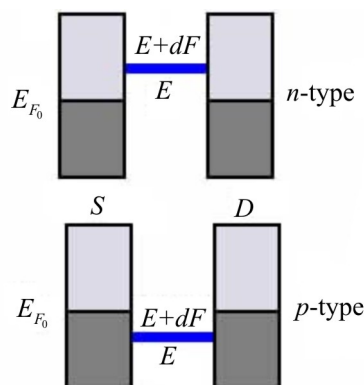


Fig. 4. The simplest single-mode conductance  $G(E)$  with the conductance mode between energies  $E$  and  $E + dE$  ( $dE \ll kT$ ) above ( $n$ -type mode) and lower ( $p$ -type mode) of the electrochemical potential.

When there is a current in the elastic resistor the Joule heat  $I^2R$  is dissipated at the contacts of the conductor with the source  $S$  and drain  $D$  [14, 15]. In channels of the  $n$ - and  $p$ -type in Fig. 4

heat is not released at the contacts, since there is no current in the channels (there is the same electrochemical potential at the  $S$  and  $D$ ). Let us now consider the situation in Fig. 5 with different electrochemical potentials at the  $S$  and  $D$ , which corresponds, for example, to the contact between two different metals. Every time when an electron is transferred from  $S$  to  $D$  through the  $n$ -type mode the source is cooled, and the drain is heated, and it is in contrary for the  $p$ -type mode – the source is heated, and the drain is cooled (Peltier effect), but each time the cumulative effect is  $E_{F_1} - E_{F_2} = qV$  with the Joule heating.

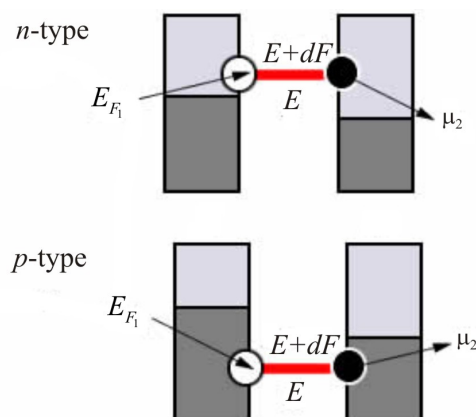


Fig. 5. Contact of two metals with different electrochemical potentials (Peltier effect).

The charge current  $I$  is given by eqn (1). Keeping in mind that in the window  $E_{F_1} - E_{F_2}$  an electron loses energy  $E - E_{F_1}$  on  $S$  and gains the energy  $E - E_{F_2}$  on  $D$ , we can write the thermoelectric energy contributions separately for the  $S$  and  $D$ , namely:

$$I_{Q_1} = \frac{1}{q} \int_{-\infty}^{+\infty} dE \frac{E - E_{F_1}}{q} G(E) (f_1(E) - f_2(E)) \quad (15)$$

and

$$I_{Q_2} = \frac{1}{q} \int_{-\infty}^{+\infty} dE \frac{E_{F_2} - E}{q} G(E) (f_1(E) - f_2(E)). \quad (16)$$

Energy extracted from an external source

$$I_{ext} = \frac{E_{F_1} - E_{F_2}}{q} I = VI, \quad (17)$$

thus the energy conservation law is satisfied:

$$I_{Q_1} + I_{Q_2} + I_{ext} = 0. \quad (18)$$

### Linear response

Lets linearize eqs (15) and (16) in the same way as we have obtained eqn (3) from eqn (1) and will get

$$I_Q = G_P(V_1 - V_2) + G_Q(T_1 - T_2), \quad (19)$$

where

$$G_P = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{E - E_{F_0}}{q} G(E) \quad (20)$$

and

$$G_Q = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{(E - E_{F_0})^2}{q^2 T} G(E) \quad (21)$$

are the standard expressions for the thermoelectric coefficients, which are usually obtained by using of such sophisticated approaches as the Boltzmann transport equation technique [5] or Kubo formalism [6]. We are still talking about electronic contributions to the thermoelectric coefficients.

It should be remembered that the value  $G_Q$  is not the thermoconductivity  $G_K$  of the conductor material commonly used in the standard figure of merit  $ZT$  (13). One reason for this, as already mentioned, is that in the thermoconductivity  $G_K$  there is the phonon contribution, which has not yet been taken into account. But there is one more, very different reason.

Value  $G_K$  is defined as the thermal conductivity of the resistor under the open circuit conditions ( $I = 0$ )

$$G_K = \left( \frac{\partial I_Q}{\partial (T_1 - T_2)} \right)_{I=0}, \quad (22)$$

whereas the value of  $G_Q$  is the thermal conductivity of the resistor under the short circuit conditions ( $V = 0$ ;  $V_1 = V_2$ )

$$G_Q = \left( \frac{\partial I_Q}{\partial (T_1 - T_2)} \right)_{V_1=V_2}. \quad (23)$$

However, we can rewrite eqs (3) and (19) in such a way as to give us the open circuit coefficients, namely:

$$(V_1 - V_2) = \frac{1}{G} I - \frac{G_S}{G} (T_1 - T_2), \quad (24)$$

$$I_Q = \frac{G_P}{G} I + \left( G_Q - \frac{G_P G_S}{G} \right) (T_1 - T_2) \quad (25)$$

with notification, of course, as mentioned earlier, that  $V$  and  $I$  represent the voltage  $E_F/q$  and electron current, which are opposite in sign to the conventional agreement about voltage and current, where  $-G_S/G$  is the Seebeck coefficient (10), the Peltier coefficient

$$\Pi = -G_P/G \quad (26)$$



and the thermal conductivity

$$G_k = G_Q - G_p G_s / G. \quad (27)$$

Using the eqs (6) and (20), the Seebeck and Peltier coefficients in eqs (24) and (25) are related by the Kelvin relation

$$\Pi = TS, \quad (28)$$

which is the special case of the fundamental Onsager relations [27].

### Delta thermoelectrics

It is useful to look at a so called delta-function thermoelectric, which is considered to be a hypothetical material with a narrow conductance mode at energy  $\varepsilon$  with a width  $\Delta\varepsilon \ll kT$ , and calculate its thermoelectric coefficients (Fig. 6).

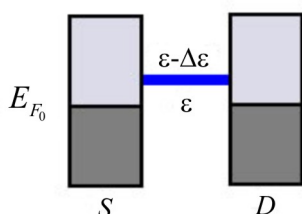


Fig. 6. Model of the delta thermoelectrics.

Let us first recall general definitions for thermoelectric coefficients obtained so far:

$$G = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) G(E), \quad G_S = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{E - E_{F_0}}{qT} G(E),$$

$$G_P = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{E - E_{F_0}}{q} G(E), \quad G_Q = \int_{-\infty}^{+\infty} dE \left( -\frac{\partial f_0}{\partial E} \right) \frac{(E - E_{F_0})^2}{q^2 T} G(E).$$

Conductivity  $G(E)$  in the integrand is different from zero in the very narrow range of energy and the factors  $(E - E_{F_0})$  are practically constant and can be pulled out of the integrals, thus giving

$$G = G(\varepsilon) \Delta\varepsilon \left( -\frac{\partial f_0}{\partial E} \right)_{E=\varepsilon}, \quad (29)$$

$$G_S = \frac{\varepsilon - E_{F_0}}{qT} G, \quad (30)$$

$$G_P = \frac{\varepsilon - E_{F_0}}{q} G, \quad (31)$$

$$G_Q = \frac{(\varepsilon - E_{F_0})^2}{q^2 T} G. \quad (32)$$

Using (24) and (25) it is now easily to obtain the thermoelectric coefficients for the delta-thermoelectrics:

$$S = -\frac{G_S}{G} = -\frac{\varepsilon - E_{F_0}}{qT}, \quad (33)$$

$$\Pi = -\frac{G_P}{G} = -\frac{\varepsilon - E_{F_0}}{q}, \quad (34)$$

$$G_K = G_0 - \frac{G_P G_S}{G} = 0. \quad (35)$$

Zero conductivity  $G_K$  for the delta thermoelectrics deserves discussion. First, however, we shall consider the physical meaning of the Seebeck (33) and Peltier (34) coefficients for the delta thermoelectrics. The Seebeck coefficient (33) is the open circuit voltage required to maintain zero current. The delta-thermoelectrics conduct only when energy  $E = \varepsilon$ . In order to have no current, the Fermi functions at this energy should be the same:  $f_1(\varepsilon) = f_2(\varepsilon)$ , which in turn gives

$$\frac{\varepsilon - E_{F_1}}{kT_1} = \frac{\varepsilon - E_{F_2}}{kT_2} = \frac{(\varepsilon - E_{F_1}) - (\varepsilon - E_{F_2})}{k(T_1 - T_2)} = -\frac{E_{F_1} - E_{F_2}}{k(T_1 - T_2)}. \quad (36)$$

Since the Seebeck coefficient at zero current is defined as

$$S = \frac{(E_{F_1} - E_{F_2})/q}{T_1 - T_2}, \quad (I = 0) \quad (37)$$

we finally get

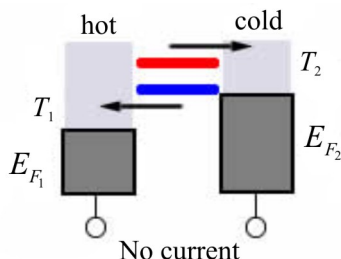
$$S = -\frac{\varepsilon - E_{F_1}}{qT_1} = -\frac{\varepsilon - E_{F_2}}{qT_2} = -\frac{\varepsilon - E_{F_0}}{qT}, \quad (38)$$

which is consistent with the earlier expression (33).

Expression (34) for the Peltier coefficient of the delta-thermoelectrics also easy to understand if you remember that each electron in the delta-thermoelectrics carries heat  $\varepsilon - E_{F_0}$ , so that the ratio of the transferred heat to the charge of the electron ( $-q$ ) should be  $(\varepsilon - E_{F_0})/(-q)$ .

As a result, there is zero thermal conductivity (35), which suggests that in the delta-thermoelectrics inder open circuit conditions (no electron transfer) the heat transfer does not occur. It seems to be so. However, after all if there is no electrical current, how can there be a heat current? If the delta-thermoelectric model would be sufficient to describe the realistic thermoelectrics, then no thermoelectric would have any heat conductance.

To understand the situation, we shall complicate the model and consider the two-level thermoelectric with the temperature difference (Fig. 7). In this case, under open circuit conditions there is a voltage between the two contacts with  $E_{F_1} < E_{F_2}$ . Although the total current is zero, but the individual currents are nonzero at different levels. They are equal in magnitude but opposite in direction, so that the total current is zero.



*Fig. 7. Two-level thermoelectric with temperature differences under open circuit conditions.*

However, the heat fluxes at both levels do not compensate each other because more heat is transferred on the level with higher energy than on the level with lower energy. Thus, the zero electric current does not guarantee the zero heat transfer in the real thermoelectrics, except that it takes place only in the delta-thermoelectrics.

Since the delta-thermoelectrics has zero thermoconductivity, its  $ZT$  product (13) must be very large with the claim to be the perfect thermoelectric. As mentioned above, even with the zero heat transfer by electrons the heat transfer by phonons takes place, which do not allows  $ZT$  product getting too large. We shall discuss the role of phonons later.

### Optimizing the power factor

Now we shall discuss the factors that could maximize the power factor  $S^2G$  in expression (11) for the maximum power  $P_{max}$ . If you seek the maximum possible Seebeck coefficient, the energy  $\varepsilon$  in (33) must be chosen as far as possible from the chemical potential  $E_{F_0}$ . This, however, leads to the unacceptably low value of the conductance  $G$  (29), because the Fermi conductivity window  $(-\partial f_0/\partial E)$  decays very rapidly as energy  $E$  moves away from  $E_{F_0}$  [1, 7, 14].

From eqs (33) and (29) we have

$$S^2G = G(\varepsilon)\Delta\varepsilon\left(\frac{\varepsilon - E_{F_0}}{qT}\right)^2\left(-\frac{\partial f_0}{\partial E}\right)_{E=\varepsilon} = G(\varepsilon)\frac{\Delta\varepsilon}{kT}\left(\frac{k}{q}\right)^2 x^2 \frac{e^x}{(e^x + 1)^2}, \quad (39)$$

where  $x \equiv (\varepsilon - E_{F_0})/kT$ , and the dependence of the power factor of  $x$  is given by the function  $F(x) = x^2 e^x / (e^x + 1)^2$  with its graph shown in Fig. 8.

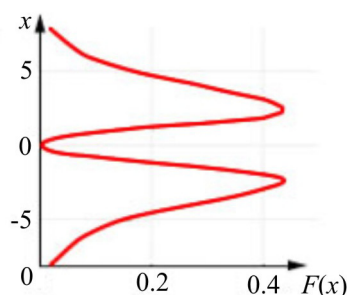


Fig. 8. Graph of the function  $F(x) = x^2 e^x / (e^x + 1)^2$ .

The function  $F(x)$  has a maximum at  $x \sim \pm 2$ , suggesting that ideally one should place the mode energy approximately  $2kT$  above or below the electrochemical potential  $E_{F_0}$ . The corresponding values of the Seebeck coefficient and the power factor is approximately equal

$$S \approx 2 \frac{k}{q}, \tag{40}$$

$$S^2 G \approx 0.5 \left( \frac{k}{q} \right)^2 G(\varepsilon) \frac{\Delta\varepsilon}{kT}. \tag{41}$$

The best thermoelectrics are characterized by the Seebeck coefficient, not much different from the value  $2(k/q) = 170 \mu\text{V/K}$ , expected according eqn (40). They are usually designed in a way that the electrochemical potential  $E_{F_0}$  is located just below the conduction band, so that the product of  $G(E)$  and  $(-\partial f_0/\partial E)$  looks like the delta-function centered at  $E = \varepsilon$  and lies just above the bottom of the conduction band as shown in Fig. 9.

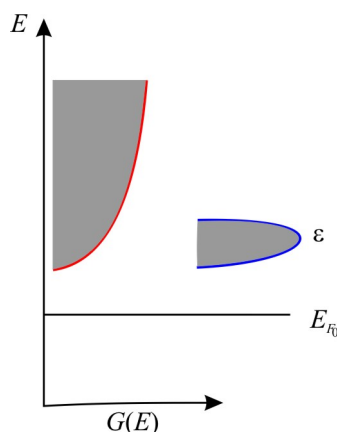


Fig. 9. To design the best thermoelectrics.

The problem, however, is that with such a design, the conductivity is not high enough, which it would be if the electrochemical potential  $E_{F_0}$  would be situated higher, which is typical for metals. However, metals are poor thermoelectrics because their Seebeck coefficients are much smaller  $k/q$ , because their electrochemical potentials are closer to the middle of the band of states, so that there are as many states lie approximately above  $E_{F_0}$  as well as below. For this

reason, the semiconductors dominate among good thermoelectrics, because they show the highest power factor. However, the power factor determines only the numerator of the  $ZT$  product (13). As already mentioned, the thermal conductivity in the denominator of eqn (13) depends strongly on the transport of heat by phonons, involving a physics that is quite different from a physics of the electron transport.

### Transport of heat by phonons

Phonon component, as is well known, along with the electronic component plays the extremely important role in the formation of the thermal properties of materials [24]. Without going into any detail of the physics of phonons [8 – 10, 28], we shall simply show how easily the model of electron transport [1, 14] can be rewritten for the phonons.

Unlike electrons, which obey Fermi statistics, the equilibrium distribution of phonons is described by the Bose function

$$n(\omega) = \frac{1}{\exp\left(\frac{\hbar\omega}{kT}\right) - 1}. \quad (42)$$

The expression obtained in [1, 14] for the electric current

$$I = \frac{q}{h} \int_{-\infty}^{+\infty} dE \left( \frac{M\lambda}{L + \lambda} \right)_{el} (f_1(E) - f_2(E)), \quad (43)$$

where the Fermi functions (2) are written for the potential difference between the electrodes  $V = (E_{F_1} - E_{F_2})/q$  and for different temperatures,  $M$  – the number of the conduction modes,  $L$  – resistor length,  $\lambda$  is the mean-free-path for electrons, can be rewritten for the phonon heat flux

$$I_Q = \frac{1}{h} \int_0^{+\infty} d(\hbar\omega) \left( \frac{M\lambda}{L + \lambda} \right)_{ph} \hbar\omega (n_1(\omega) - n_2(\omega)) \quad (44)$$

simply by replacing  $q \rightarrow \hbar\omega$ , Fermi functions (2) to the Bose functions

$$n_1(\omega) = \frac{1}{\exp(\hbar\omega / kT_1) - 1}, \quad n_2(\omega) = \frac{1}{\exp(\hbar\omega / kT_2) - 1} \quad (45)$$

and the lower limit of integration in (43) to zero.

Standard linearization [1, 14] of (44) gives

$$I_Q \approx G_K (T_1 - T_2), \quad (46)$$

where the thermal conductance due to phonons can be written as

$$G_K = \frac{k^2 T}{h} \int_0^{\infty} dx \left( \frac{M\lambda}{L + \lambda} \right)_{ph} \frac{x^2 e^x}{(e^x - 1)^2}, \quad x \equiv \frac{\hbar\omega}{kT}. \quad (47)$$

Note that just as the model of the elastic resistor for electrons does not account for effects due to the inelastic scattering between the conduction modes, our phonon model ignores effects of the so called “anharmonic interactions” which causes phonons to convert from one frequency to another [29]. In contrast to the well-studied devices based on the electron ballistic transport, it is still little known about the devices based on the ballistic transport of phonons [30 – 32].

### Ballistic transport of phonons

Ballistic phonon conductivity is usually written in the form resembling the Stefan-Boltzmann equation for photons.

From equation (47) for the ballistic conductivity ( $L \ll \lambda$ ), we have

$$[G_K]_{bl} = \frac{k^2 T}{h} \int_0^\infty dx M_{ph} \frac{x^2 e^x}{(e^x - 1)^2}. \quad (48)$$

As for the case of electrons [14], the number of modes for the phonons:

$$M_{ph} = \frac{3\pi A}{\lambda_{ph}^2}, \quad (49)$$

where three allowed directions of phonon polarization had been taken into account and

$$\lambda_{ph} = \frac{c_s}{\omega/2\pi}, \quad (50)$$

where  $c_s$  – the phonon velocity, so that

$$M_{ph} = \frac{3\omega^2 A}{4\pi c_s^2} = \frac{3k^2 T^2 A}{4\pi \hbar^2 c_s^2} x^2, \quad (51)$$

and finally from (48) we have

$$[G_K]_{bl} = \frac{3k^4 T^3}{8\pi^2 \hbar^3 c_s^2} \int_0^\infty dx \frac{x^4 e^x}{(e^x - 1)^2} = \frac{\pi^2 k^4 T^3}{10\hbar^3 c_s^2}, \quad (52)$$

where the integral on the left is  $4\pi^4/15$ . Now, from equation (46) for the heat ballistic flux we have

$$[I_Q]_{bl} = \frac{\pi^2 k^4 T^3}{10\hbar^3 c_s^2} \Delta T, \quad (53)$$

where  $\Delta T = T_1 - T_2$ , and since  $T^3 \Delta T = \Delta (T^4 / 4)$ , finally

$$[I_Q]_{bl} = \frac{\pi^2 k^4}{40\hbar^3 c_s^2} (T_1^4 - T_2^4). \quad (54)$$

The similar result for photons is known as the Stefan – Boltzmann law differing from the phonon ballistic flux (54) by the factor of 2/3, as in the case of photons the number of allowed polarization is two.

Now let us get back to the diffusion transport of phonons.

### Thermal conductivity

Phonon thermal conductivity is determined by (47) and is connected in the usual way with its specific value

$$G_k = \frac{\kappa A}{L + \lambda}, \quad (55)$$

so that finally the specific phonon thermal conductivity

$$\kappa = \frac{k^2 T}{h} \int_0^{+\infty} dx \left( \frac{M\lambda}{A} \right)_{ph} \frac{x^2 e^x}{(e^x - 1)^2} \quad (56)$$

similar to the specific electron conduction [14]

$$\sigma = \frac{q^2}{h} \int_{-\infty}^{+\infty} dx \left( \frac{M\lambda}{A} \right)_{el} \frac{e^x}{(e^x + 1)^2}. \quad (57)$$

Broadening function in the electron transport coefficients (eqn (84) in [1])

$$F_T(x) \equiv \frac{e^x}{(e^x + 1)^2} \quad (58)$$

differs from the similar function in the phonon transport coefficients

$$F_T^{ph}(x) \equiv \frac{3}{\pi^2} \frac{x^2 e^x}{(e^x - 1)^2}, \quad (59)$$

however, there is the similarity between them as shown on Fig. 2 of [1]. So, at least qualitatively, the electrical conductivity and thermal conductivity can be described similarly.

Thus, if the specific electrical conductivity for 3D-conductor is given by eqn (68) of [14]

$$\sigma = \frac{q^2}{h} \left( \frac{M\lambda}{A} \right), \quad (60)$$

where the coefficient  $q^2/h \approx 38 \mu\text{S}$  is the inverse value of the fundamental Klitzing constant (eqn (106) in [14]), then the specific thermal conductivity is given by

$$\kappa_{ph} = \frac{\pi^2}{3} \frac{k^2 T}{h} \left( \frac{M\lambda}{A} \right)_{ph}, \quad (61)$$

where the coefficient  $(\pi^2/3)(k^2T/h) \approx 325$  pW/K with the factor  $\pi^2/3$ , opposite to that value, which is necessary to normalize the broadening function for phonons, and the number of modes per unit cross-sectional area of the conductor  $M/A$  and the mean-free-pass  $\lambda$  are estimated in the frequency gap  $h\omega$ , equal to approximately a few  $kT$ . The polarization  $g$ -factor  $g = 3$  is assumed be included in the value of the number of modes  $M$ .

For thermoelectrics with the Seebeck coefficient  $S \sim 2(k/q)$  and the dominating phonon component of the specific thermal conductivity (61) for the  $ZT$  product we can write

$$ZT \approx 4 \frac{k^2T}{q^2} \frac{\sigma}{k+k_{ph}} \approx 4 \frac{k^2T}{q^2} \frac{\sigma}{k_{ph}} \quad (62)$$

or either way, using (60) and (61),

$$ZT \approx \frac{M\lambda / A}{(M\lambda / A)_{ph}}, \quad (63)$$

where factor  $12/\pi^2 \sim 1$  was omitted. This useful expression testifies that once thermoelectric is optimized with respect to Seebeck coefficient  $S$  the corresponding  $ZT$  product approximately shows the ratio of  $M\lambda/A$  for electrons and phonons.

## Conclusions

In an effort to increase the Seebeck coefficient  $S$  we thus lower the ratio  $M/A$  for electrons. On the other hand, the ratio of  $M/A$  for the phonons are often much more, namely,  $\sim 1 \text{ nm}^{-2}$ , so that their ratio in eqn (63) is about  $\sim 0.1$  or even less. However, the electron mean-free-path is longer, thus in the best thermoelectrics  $ZT \sim 1$ . It now appears that the most promising way to improve  $ZT$  is to suppress the mean-free-path of the phonons, without affecting the behavior of electrons (so called PGEC / Phonon-Glass-Electron Crystals [33, 34]).

For a long time we can not go beyond the  $ZT \sim 1 - 3$ . Experts argue that thermoelectrics with  $ZT \sim 4 - 10$  would provide substantial progress in solving practical problems. Perspectives opened with the graphene research are briefly discussed in [35]. Hopes are still placed for nanostructured materials. Only experimental investigations will show is this perspective or not.

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