

# Theory of thermoelectric cooling in semiconductor structures

Yu. G. Gurevich and G.N. Logvinov

*Departamento de Física, CINVESTAV del I.P.N., Apartado Postal 14-740, 07000, D.F., México, México.*

*SEPI-ESIME Culhuacán, Instituto Politécnico Nacional, Av. Santa Ana 1000, Col. San Francisco Culhuacán, 04430, D.F., México, México.*

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A new approach is suggested to explain the Peltier effect. This approach is based on the idea of the occurrence of induced thermal diffusion fluxes in any non-uniform medium through which a d.c. electric current flows, in particular in a structure composed of two different uniform semiconductors. These induced thermal diffusion fluxes arise to compensate for the change in thermal fluxes carried out by an electric current (drift thermal fluxes) during their driving through the junction in accordance with the general Le Châtelier-Braun principle. The occurrence of these thermal diffusion fluxes leads to temperature non-uniformity in the structure and, as a result, to the junction's cooling or heating. The general heat balance equations are obtained. It is shown that only two sources of heat exist: the Joule source of heat, and the Thomson source of heat. They have commensurable magnitudes in the problem considered. There is no Peltier's source of heating or cooling present. The new equation for the Thomson heat is obtained and its physical interpretation is made. New boundary conditions for the heat balance equation are derived. The analysis of these boundary conditions shows that the Peltier sources of heat are also absent at the junctions. It is shown that, in the general case, the thermoelectric cooling represents the superposition of two effects, the isothermal Peltier effect and the adiabatic Peltier effect. Both essentially depend on the junction surface thermal conductivity. The isothermal Peltier effect disappears in the limiting case of a very small surface thermal conductivity while the adiabatic Peltier effect disappears in the limiting case of a very large surface thermal conductivity. The dependence of thermoelectric cooling on the geometrical dimensions of the structure is discussed. It is shown that the thermoelectric cooling (heating) is a thermodynamically reversible process in the linear approximation of the electric current applied.

*Keywords:* Thermoelectricity; thermoelectric cooling; Peltier effect.

Un nuevo enfoque es sugerido para explicar el efecto Peltier. Este enfoque está basado en la idea de la aparición de flujos de difusión térmicos inducidos en cualquier medio no uniforme a través del cual circula una corriente de d.c., en particular en una estructura compuesta de dos semiconductores uniformemente diferentes. Estos flujos de difusión térmicos inducidos aparecen para compensar el cambio de los flujos térmicos llevados por una corriente eléctrica (flujos térmicos de deriva) durante su conducción a través de la unión de acuerdo con el principio general de Le Chatelier-Braun. La aparición de estos flujos de difusión térmicos resulta en la no uniformidad de temperatura en la estructura y, por consiguiente, el enfriamiento o calentamiento de la unión. La ecuación general de balance de energía es obtenida. Se muestra que solamente existen dos fuentes de calor. Existe la fuente de calor de Joule y la fuente de calor de Thompson. Ambos son proporcionales al valor de sus magnitudes en el problema considerado. Cualquier fuente de calentamiento o enfriamiento de Peltier está ausente. Es obtenida la nueva ecuación para el calor de Thompson y es llevada fuera de sus interpretaciones físicas de esta. Las nuevas condiciones de frontera para la ecuación de balance de calor son obtenidas. El análisis de estas condiciones frontera muestra que las fuentes de calor de Peltier están también ausentes en la unión. Es mostrado que, en el caso general, el enfriamiento termoeléctrico representa la superposición de dos efectos, el efecto Peltier isotérmico y el efecto Peltier adiabático. Ambos son esencialmente dependientes de la conductividad térmica superficial de la unión. El efecto Peltier isotérmico desaparece en el limitante caso de una muy pequeña conductividad térmica superficial mientras que el efecto Peltier adiabático desaparece en el limitado caso de una muy grande conductividad térmica superficial. La dependencia del enfriamiento termoeléctrico sobre las dimensiones geométricas de la estructura es discutida. Se muestra que el enfriamiento termoeléctrico (calentamiento) es un proceso termodinámico reversible en aproximación lineal con la corriente eléctrica aplicada.

*Descriptores:* Termoelectricidad; enfriamiento termoeléctrico; efecto Peltier.

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## 1. Introduction

Nowadays thermoelectric cooling is associated exclusively with the Peltier effect, which was discovered in 1834 by Peltier [1]. From the earliest papers on thermoelectrics right up to the latest publications, this effect has been defined as an absorption of heat or its evolution (in addition to the Joule heat) on the junction of two conductors through which a d.c. electric current runs (see, for example, Refs. 2 to 8). The absorption of this heat or its evolution depends on the direction of the electric current, and per unit time it is equal to

$$Q_{\Pi} = (\Pi_1 - \Pi_2) J, \quad (1)$$

where  $\Pi_{1,2}$  are the Peltier coefficients of the conducting materials, and  $J$  is the electric current.

In some papers (see, for example, Refs. 2 and 6) it is emphasized that the Peltier effect manifests itself in the thermally-uniform systems, *i.e.* when the temperature gradient is absent.

Thus, authors of [6] describing the Peltier effect write the following: “*If an electric current is driven in a bimetallic circuit maintained at uniform temperature, heat is produced at*

one junction and absorbed at the other (Fig. 1). This is because an isothermal electric current in a metal is accompanied by a thermal current  $\vec{j}^q = \Pi \vec{j}$ , where  $\vec{j}$  is the electric current density. Because the electric current is constant in the closed circuit and the Peltier coefficients differ from metal to metal, the thermal currents in the two metals are not equal, and the difference must be produced at one junction and supplied to the other to keep the temperature uniform”.

As a rule, the physical discussion of the Peltier effect is concluded thus, and the main attention is concentrated on the applications of this effect. Actually there are many of them, for several reasons. Semiconductor thermoelectric coolers (also known as Peltier coolers) offer several advantages over conventional systems. They are entirely solid-state devices, with no moving parts. Thermoelectric coolers do not produce noise or vibrations. They have a small size and weight. Parameters of thermoelectric coolers do not depend on their space orientation. Thermoelectric coolers are highly reliable; their lifetimes are more than 20 years. At the same time they do not need technical servicing. Electrons and holes are the coolants in these devices, so these kinds of refrigerators do not use ozone-depleting chlorofluorocarbons, potentially offering a more environmentally responsible alternative to conventional refrigeration. They can be extremely compact, much more so than compressor-based systems. Thermoelectric devices consume d.c. electric current, and a change in the direction of the electric current switches this device from the cooling mode to the heating mode or vice-versa. Precise temperature control ( $< \pm 0.1^\circ\text{C}$ ) can be achieved with Peltier coolers. Having such advantages, thermoelectric coolers find a lot of applications in such areas as consumer products (recreational vehicle refrigerators, automobile seat coolers, portable picnic coolers, motorcycle helmet refrigerators, residential water coolers/purifiers); laboratory and scientific equipment (coolers of infrared detectors, laser diode coolers, integrated circuit coolers, heat density measuring); industrial (PC computer microprocessors, fine temperature control); medical instruments (pharmaceutical refrigerators-portable and stationary, blood analysis, insulin coolers); restaurants, hotels, bars (hotel room refrigerators, noiseless air-conditioners, ice-makers). This list is not complete and can go on and on.

At the same time it is necessary to point out disadvantages of thermoelectric coolers. First of all they have a low efficiency compared to conventional refrigerators. Present thermoelectric devices operate at about 10% of Carnot efficiency, whereas the efficiency of a compressor-based refrigerator is about 30% of Carnot efficiency. Thus, nowadays the thermoelectric coolers are put expediently to use in applications where their unique advantages outweigh their low efficiency. Although some large-scale applications have been considered, Peltier coolers are generally used in applications where small size is needed and the cooling demands are not too great, such as for cooling electronic components (see, for example, Refs. 9 and 10).

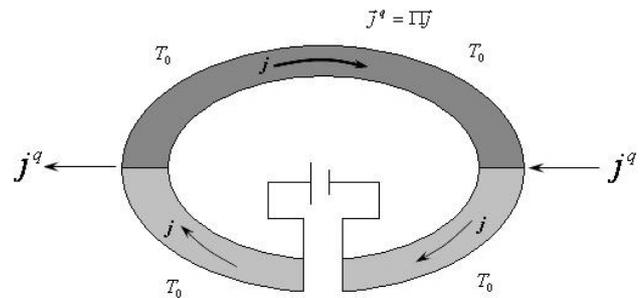


FIGURE 1. Effect Peltier [6].

Summing up, one could say that the traditional explanation of the Peltier effect presupposes the following:

1. An isothermal state of the structure (bimetallic circuit), through which an electric current flows, and consequently the absence of thermal fluxes, which are proportional to  $\kappa \nabla T$  ( $\kappa$  is the thermal conductivity,  $T$  is the temperature). The only thermal fluxes are those accompanying the electric current.
2. If need for the thermal interaction between this structure and the external heat reservoirs to maintain this isothermal state (the presence of the Peltier heat source and the Peltier heat sink). To keep up the isothermal state, in this case, it is necessary to take into account the external sources of heat.

An important question arises regarding these considerations: What do authors imply by the concepts of thermoelectric “cooling” or “heating” in the traditional theories? Presence of the heat fluxes from the external reservoirs into the structure and vice versa from the structure to the external reservoirs do not describe heating or cooling processes under the condition of the structure’s isothermality.

Another question is: can the Peltier effect occur in the thermoelectric circuit without a thermal interaction with the surroundings at the junctions, *i.e.* can the Peltier effect occur as a physical phenomenon in a structure adiabatically insulated?

The answer given by cited works’ to the second question is negative. At the same time we consider the Peltier effect in the adiabatic structure possible if we refuse the traditional interpretation of the Peltier effect.

From our point of view the origin of the Peltier effect is not associated with the external Peltier heat sources or the Peltier heat sinks. This effect can also exist in the adiabatically insulated thermoelectric structure. It is necessary to understand the concepts of “cooling” or “heating” of the junctions as the decrease or increase in the junction’s temperature compared to the equilibrium temperature when the electric current is absent. Of course, this statement contradicts the isothermal conditions, whence the natural question immediately arises: Why does the temperature distribution appear in the structure in the absence of external heat sources when the electric current runs through the structure of two media? The

answer to this question and the calculation of the mentioned temperature distribution is the main goal of this paper.

### 2. The Le Châtelier-Braun Principle and the induced thermal diffusion fluxes

Let us consider the simplest structure composed of two uniform semiconductors through which the electric current flows in the direction  $ox$  (Fig. 2). We suppose that the electric contacts  $x = -d_1$  and  $x = d_2$  are kept at the equilibrium temperature  $T_0$ , the lateral surfaces are insulated adiabatically, and the structure's cross-sectional area is equal to the unit measurement everywhere. For simplicity, we shall assume from the beginning that a heat resistance of the junction located at  $x = 0$  can be neglected (this assumption will be removed later on). This assumption implies temperature continuity at the interface  $x = 0$ ,

$$T_1(x = 0) = T_2(x = 0), \tag{2}$$

where  $T_{1,2}(x)$  are the temperature distributions in the first and second samples of the structure.

Usually the thermal flux  $\Pi \vec{j}$  is named the Peltier heat flux [3]. For the theory stated, it is more convenient to name this heat flux a "drift heat flux" since it is associated with the charge drift transport in the external electric field.

According to the Le Châtelier-Braun principle in the irreversible thermodynamics [11] "some internal fluxes appear in the system in the stationary state when an external influence affects this system, and these internal fluxes weaken the results of this influence". Applying this principle to our problem, one can say that the discontinuity in the drift fluxes at the junction  $x = 0$  that appears due to the different Peltier coefficients ( $\Pi_1 \neq \Pi_2$ ) must lead to other thermal fluxes tending to decrease this discontinuity [12]. These thermal fluxes can only be thermal diffusion fluxes, since the other drift heat fluxes are absent. Thus, the temperature heterogeneity arises inevitably in the structure in the presence of an electric current. Due to this temperature distribution, the temperature of the junction can be lower (thermoelectric cooling) or higher (thermoelectric heating) than the equilibrium temperature.

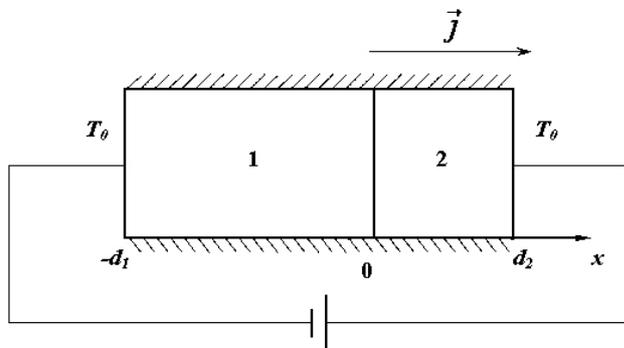


FIGURE 2. Sketch of the semiconductor structure through which a d.c. electric current passes.

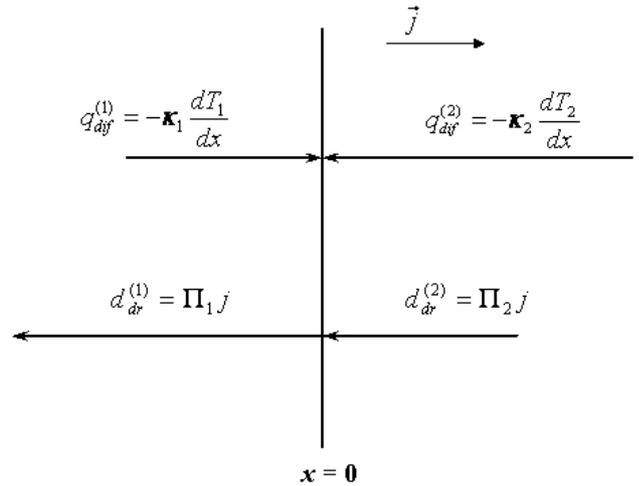


FIGURE 3. Drift and induced thermal fluxes when  $|\Pi_2| < |\Pi_1|$ .

We do not take an interest in the magnitude of the Peltier effect in this paper. For this reason we consider the simplest structure presented in Fig. 2, assuming that it is composed of two  $n$ -type semiconductors. The drift heat fluxes  $\vec{q}_{dr}^{1,2} = \Pi_{1,2} \vec{j}$  flow in this structure in the direction opposite to the electric current direction, as it is pointed in Figs.3, 5 since  $\Pi_{1,2} < 0$  in the  $n$ -type materials [5].

Let us suppose that  $|\Pi_2| < |\Pi_1|$  for definiteness. In this case the drift thermal flux increases when coming from sample 2 into sample 1 (Fig. 3). According to the Le Châtelier-Braun principle, some thermal diffusion flux  $\vec{q}_{dif}^{(1)} = -\kappa_1 dT_1/dx$  ( $\kappa_1$  is the thermal conductivity of the first sample) should arise in the first sample, tending to compensate for this increase. It is clear that the direction of this flux should be opposite to the direction of the drift flux  $\vec{q}_{dr}^{(1)} = \Pi_1 \vec{j}$ . We name these arising thermal diffusion fluxes the "induced thermal diffusion fluxes".

In turn, this means that the temperature of the junction from the side of the first sample decreases in comparison with the temperature on the surface  $x = -d_1$ . The condition of the temperature continuity (2) requires the decrease in temperature in the junction from the side of the second sample too, as compared with the temperature on the surface  $x = d_2$ . As a result, the induced thermal diffusion flux  $\vec{q}_{dif}^{(2)} = -\kappa_2 (dT_2/x)$  arises in the second sample too, where  $\kappa_2$  is the thermal conductivity of the second sample. Let us notice that this thermal flux direction coincides now with the direction of a drift heat flux  $\vec{q}_{dr}^{(2)} = \Pi_2 \vec{j}$  in this sample (Fig.3), tending to decrease the discontinuity in drift heat fluxes.

The corresponding temperature distributions in the structure are qualitatively represented in Fig. 4. It is obvious that at  $|\Pi_2| < |\Pi_1|$  and the chosen electric current direction, the junction temperature  $T(x = 0)$  decreases as compared with the equilibrium temperature  $T_0$ . The lowering of the temperature caused by the appearance of the induced thermal diffusion fluxes is the essence of the Peltier thermoelectric cooling.

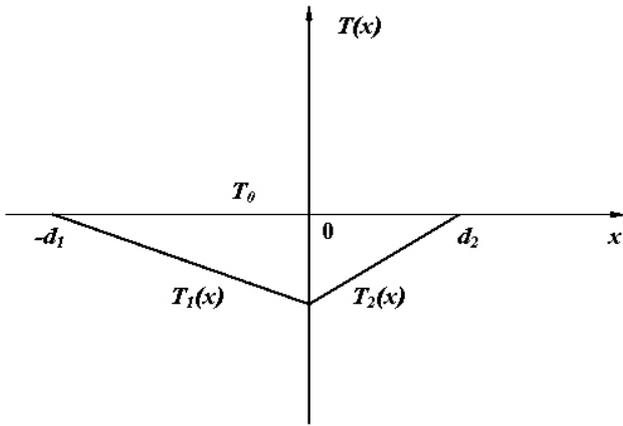


FIGURE 4. Temperature distributions in the structure when  $|\Pi_2| < |\Pi_1|$

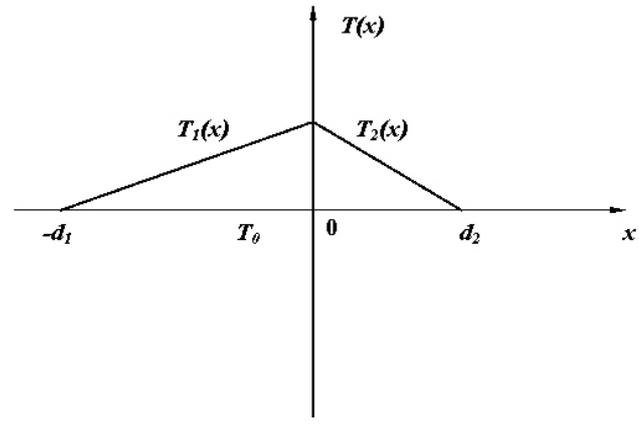


FIGURE 6. Temperature distributions in the structure when  $|\Pi_2| > |\Pi_1|$ .

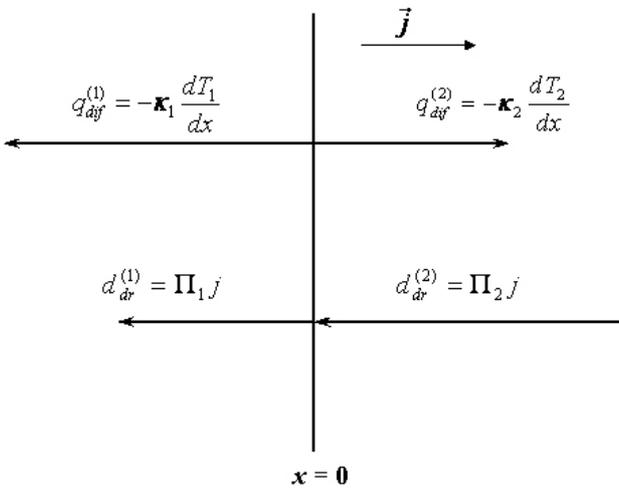


FIGURE 5. Drift and induced thermal fluxes when  $|\Pi_2| > |\Pi_1|$ .

If the condition  $|\Pi_2| > |\Pi_1|$  takes place, and the electric current has the same direction, the drift heat flux decreases when passing through the junction. In this case the induced thermal diffusion flux arises in the first sample again, but its direction changes to the opposite, compared with the previous case (Fig. 5). Now this flux tends to increase the drift thermal flux  $q_{dr}^{(1)} = \Pi_1 j$ , which has decreased compared with  $q_{dr}^{(2)} = \Pi_2 j$ .

Further reasoning is similar to that used in the analysis of the previous situation, and it leads to the temperature distributions in the structure presented in Fig.6. In this case the junction temperature increases in comparison with the equilibrium temperature  $T_0$ , and this situation corresponds to the Peltier thermoelectric heating.

Thus, we have to understand the Peltier effect as the lowering or raising of the junction temperature (depending on the current direction) due to the appearance of the induced thermal diffusion fluxes in the structure, but not as an evolution or absorption of the additional heat on the junction.

The quantitative calculation of the thermoelectric cooling or thermoelectric heating requires a solution to the heat transfer equation with corresponding boundary conditions. The following section is devoted to this calculation.

### 3. Energy and heat balance equations

Let us now reject the assumption about the absence of the thermal resistance on the junction  $x = 0$ . Instead, we shall describe this junction by the coefficient of the surface thermal conductivity  $\eta$  [13-15], which can take arbitrary values. Later we shall show that the junction is described not only by the surface thermal conductivity but by some other surface parameters.

The required temperature distribution in the structure can be obtained from the energy balance equation. In a steady state, it is given by [3]:

$$\nabla \cdot \vec{w} = 0, \tag{3}$$

where  $\vec{w} = \vec{q} + \vec{\varphi} \vec{j}$  is the energy flux of charge carriers (electrons or holes),  $\vec{q} = -\kappa \nabla T + \Pi \vec{j}$  is a total heat flux of these carriers,  $\vec{\varphi} = \varphi - \mu/e$  is the electrochemical potential,  $\varphi$  is the electric potential,  $\mu$  is the chemical potential, and  $-e$  is the electron charge.

Now Eq. (3) can be rewritten in the form

$$\nabla \cdot \vec{q} + \vec{j} \nabla \varphi = 0. \tag{4}$$

Here we have made the assumption that nonequilibrium carriers are absent in the structure [16], i.e.  $\nabla \cdot \vec{j} = 0$ . Let us note that it is necessary to take into account the nonequilibrium carriers in the  $p-n$  structures [17-18].

Using the equation for the electric current  $\vec{j} = -\sigma(\nabla \varphi + \alpha \nabla T)$  [19] to eliminate the electrochemical potential  $\vec{\varphi}$  ( $\sigma$  is electric conductivity,  $\alpha$  is the Seebeck

coefficient), we arrive at the heat balance equation

$$\nabla \cdot \vec{q} = \frac{j^2}{\sigma} + \alpha \vec{j} \nabla T. \quad (5)$$

It is easy to see, from the shape of this equation, that there are only two sources of heat: one of them is the Joule heat, and the other source of heat can be named the Thomson heat due to its proportionality to the product of  $\vec{j}$  and  $\nabla T$  [20].

Since the temperature gradient has appeared due to the Peltier effect we can say that the Thomson effect occurs as a consequence of the Peltier effect in the thermoelectric cooling (heating) phenomenon.

Let us note that according to our definition following from the heat balance equation (5), the Thomson coefficient is equal to the Seebeck coefficient  $\alpha$ . From this definition it follows that the Thomson heat occurs even in the case when the Seebeck coefficient does not depend on temperature. Moreover, it is possible to claim that thermoelectrics contains only one fundamental parameter, which is the Seebeck coefficient.

Thus, there is only one thermoelectric relationship which was named the second thermoelectric relationship,  $\Pi = \alpha T$  [2,3]. As was shown in Ref. 3, it follows from the Onsager's principle of kinetic coefficients symmetry. The first thermoelectric relationship actually determines the Thomson coefficient  $\tau$ . As follows from (5), it can be reduced to the trivial equality  $\tau = \alpha$ .

The Thomson coefficient was determined by the equation  $\tau = \partial \Pi / \partial T - \alpha$  in the previous publications. The authors of these works formed the term  $\vec{j} \frac{\partial \Pi}{\partial T} | \vec{r} \nabla T$  by joining  $\nabla \cdot \vec{q}$  with the term  $\alpha \vec{j} \nabla T$  presented on the right side of Eq. (5).

This is wrong, because  $\alpha \vec{j} \nabla T$  is the source of heat while  $\vec{j} (\partial \Pi / \partial T) | \vec{r} \nabla T$  is part of the thermal flux change. It is wrong from the formal point of view. We cannot state that the left hand side of Eq.(5) is still the complete divergence of the thermal flux vector  $\vec{q} = -\kappa \nabla T + \Pi \vec{j}$  when the term  $\vec{j} (\partial \Pi / \partial T) | \vec{r} \nabla T$  is transported to the right hand side of Eq.(5), or that it is the divergence of another vector in this case.

Now the sense of the Thomson heat is very transparent. It is the charge carriers heating or cooling in the thermoelectric field  $\vec{E}_{te} = \alpha \nabla T$ . In a certain sense, it can be named the Joule effect associated with the thermoelectric field. The Joule heating takes place in the electric field. It is important to note that the Joule effect leads to heating in any case, while the Thomson effect may lead to either heating or cooling depending on the relative directions of the electric current and the temperature gradient. The further development of these ideas can be found in Ref. 20.

Equation (5) demonstrates that the Peltier source of heat is absent everywhere in the structure volume, which was noted before in this paper. For this reason, the statement about the Peltier's heat absorption or generation loses its physical sense in the bulk of the structure (the analysis of this situation at the junction is presented below).

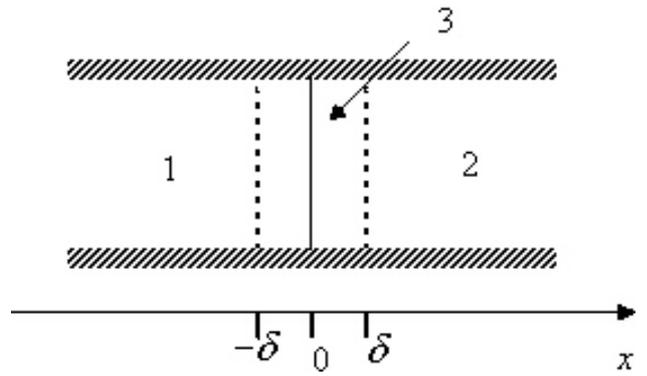


FIGURE 7. Boundary between two samples composing the structure.

#### 4. Boundary conditions for the heat balance equation

Let us obtain the boundary conditions for Eq. (5). Since Eq. (5) is an equation of the second order in relation to unknown temperatures  $T_1(x)$  and  $T_2(x)$  for two-structure samples, it is necessary to obtain four boundary conditions. Two of them correspond to the assumptions that were made in Sec. 2:

$$T_1(x = -d_1) = T_0, \quad (6)$$

$$T_2(x = d_2) = T_0. \quad (7)$$

To obtain the two remaining boundary conditions, let us rewrite Eq. (5) for the one-dimensional case ( $\rho = \sigma^{-1}$ ):

$$\frac{dq}{dx} = \rho j^2 + \alpha j \frac{dT}{dx} \quad (8)$$

or

$$-\frac{d}{dx} \left( \kappa \frac{dT}{dx} \right) + \frac{d\Pi}{dx} \vec{j} = \rho j^2 + \alpha j \frac{dT}{dx}. \quad (9)$$

Actually, the boundary between two media of the structure is the transition layer (medium 3) of the thickness  $2\delta$  (Fig.7), where the parameters of sample 1 continuously turn into the parameters of sample 2 [13]. One can consider the thickness of this layer to be zero if one is not interested in the microscopic processes in the layer. In this case, the scattering mechanisms in this layer become surface scattering mechanisms. The experimental proofs of these surface scattering mechanisms [21, 22] make it possible to suggest the occurrence of the surface kinetic coefficients, which are different from the bulk ones. It is necessary to take into account that these surface kinetic coefficients can change under a change in surface thickness change, and can take on singularities in the limiting case  $\delta \rightarrow 0$  [13].

Since our purpose is to obtain the boundary conditions and not to obtain their microscopic values (a microscopic theory of the surface relaxation processes does not exist), we shall obtain the average surface kinetic coefficients instead of the surface kinetic coefficients depending on the coordinates of the transition layer  $2\delta$ . At the same time, we shall take

into account that they can change under the charge in surface thickness.

To obtain the boundary conditions at the interface  $x = 0$ , let us use the approach developed in Refs. 23 and 15. The main idea of this approach is to find a correlation between heat fluxes at the boundary between media 1 and 3 in the plane  $x = -\delta$  and at the boundary between media 3 and 2 in the plane  $x = \delta$ . The further limiting transition  $\delta \rightarrow 0$  leads to the model of the plane junction and to the concept of the surface heat flux.

First of all let us integrate Eq. (9) by the coordinate  $x$  in the limits from  $-\delta$  to  $\xi$ , where  $\xi$  is an arbitrary point from the region  $-\delta < \xi < \delta$ :

$$\begin{aligned}
 & - \left( \kappa(\xi) \frac{dT}{dx} \Big|_{x=\xi} - \kappa(-\delta) \frac{dT}{dx} \Big|_{x=-\delta} \right) \\
 & + j (\Pi(\xi) - \Pi(-\delta)) = j^2 \int_{-\delta}^{\xi} \rho(x) dx \\
 & + j \int_{-\delta}^{\xi} \alpha(x) \frac{dT(x)}{dx} dx. \tag{10}
 \end{aligned}$$

Now let us divide Eq. (10) by  $\kappa(\xi)$  and integrate the obtained result by  $\xi$  in the limits from  $-\delta$  to  $\delta$ :

$$\begin{aligned}
 & - (T(\delta) - T(-\delta)) + \kappa(-\delta) \frac{dT}{dx} \Big|_{x=-\delta} \cdot \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \\
 & + j \left( \int_{-\delta}^{\delta} \frac{\Pi(\xi)}{\kappa(\xi)} d\xi - \Pi(-\delta) \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \right) = j^2 \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \\
 & \times \int_{-\delta}^{\xi} \rho(x) dx + j \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{-\delta}^{\xi} \alpha(x) \frac{dT(x)}{dx} dx \tag{11}
 \end{aligned}$$

Dividing Eq.(11) by

$$\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}$$

and taking the limit  $\delta \rightarrow 0$  we obtain:

$$\begin{aligned}
 & \eta (T_1(0) - T_2(0)) + j_x \Pi_s - \left[ -(\kappa_1 \frac{dT_1}{dx}) \Big|_{x=0} + j_x \Pi_1 \Big|_{x=0} \right] \\
 & = j^2 \rho_{s1} + j \alpha_{s1} (T_2(0) - T_1(0)), \tag{12}
 \end{aligned}$$

where

$$\eta = \lim_{\delta \rightarrow 0} \frac{1}{\delta \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}}, \tag{13}$$

$$\Pi_s = \lim_{\delta \rightarrow 0} \frac{\int_{-\delta}^{\delta} \frac{\Pi(\xi)}{\kappa(\xi)} d\xi}{\delta \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}}, \tag{14}$$

$$\rho_{s1} = \lim_{\delta \rightarrow 0} \left( \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{-\delta}^{\xi} \rho(x) dx}{\delta \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \right), \tag{15}$$

and

$$\alpha_{s1} = \lim_{\delta \rightarrow 0} \left( \frac{\frac{1}{2\delta} \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{-\delta}^{\xi} \alpha(x) dx}{\delta \int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \right). \tag{16}$$

Equation (12) is the third boundary condition. The coefficients (13)-(14) are the surface thermal conductivity and the surface Peltier coefficients. The coefficients (15) and (16) are the surface electric resistance and the surface Seebeck coefficients at the junction side  $x = 0$ .

To understand the physical sense of the boundary condition (12), let us rewrite it in the following form:

$$q_s - q_1(x=0) = \tau_{1s}. \tag{17}$$

Here  $q_s = \eta (T_1(0) - T_2(0)) + j_x \bar{\Pi}$  is the heat flux through the boundary  $x = 0$ ,

$$q_1(x=0) = -(\kappa_1 \frac{\partial T_1}{\partial x}) \Big|_{x=0} + j_x \Pi_1 \Big|_{x=0}$$

is the heat flux in the first medium in the plane  $x = 0$ , and  $\tau_{1s} = j_x^2 \rho_{s1} + j_x \alpha_{s1} (T_2(0) - T_1(0))$  are the total surface heat sources at the boundary between medium 1 and the junction. These heat sources are the surface Joule heat and the surface Thomson heat correspondingly.

So, boundary condition (12) or (17) can be formulated in the following way: the difference between the heat flux in the surface layer and the heat flux in the first medium at the boundary of this medium and this layer is equal to the surface heat sources at this boundary.

The fourth boundary condition at the boundary between the second medium of the structure and the surface layer can be obtained by analogy with the procedure used above. It is necessary to make the same calculation but to integrate at the beginning from  $\xi$  to  $\delta$ .

As a result, we reach to the following boundary equation:

$$\begin{aligned}
 & -(\kappa_2 \frac{dT}{dx}) \Big|_{x=0} + j \Pi_2 \Big|_{x=0} - \eta (T_1(0) - T_2(0)) - j \Pi_s \\
 & = j^2 \rho_{s2} + j \alpha_{s2} (T_2(0) - T_1(0)). \tag{18}
 \end{aligned}$$

Here

$$\rho_{s2} = \lim_{\delta \rightarrow 0} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{\xi}^{\delta} \rho(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \quad (19)$$

and

$$\alpha_{s2} = \lim_{\delta \rightarrow 0} \left( \frac{1}{2\delta} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{\xi}^{\delta} \alpha(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \right) \quad (20)$$

are the surface electric resistance and the surface Seebeck coefficient at the junction's side  $x = +0$ .

Boundary condition (18) can be written as

$$q_2(x = 0) - q_s = \tau_{2s}, \quad (21)$$

where  $q_2(x = 0) = -(\kappa_2 \frac{\partial T_2}{\partial x})|_{x=0} + j_x \Pi_2|_{x=0}$  is the heat flux in the second medium in the plane  $x = 0$ , and  $\tau_{2s} = j_x^2 \rho_{s2} + j_x \alpha_{s2} (T_2(0) - T_1(0))$  are the surface heat sources at the boundary between medium 2 and the junction. These heat sources are also the surface Joule heat and the surface Thomson heat but in the junction's plane  $x = +0$ .

The physical sense of boundary condition (18) or (21) is the same as the sense of boundary condition (12) or (17): the difference between the heat flux in the second medium and the heat flux in the surface layer at the boundary of this layer and this medium is equal to the surface heat sources at this boundary.

Thus, boundary conditions (6), (7), (12) and (18) are the complete set of equations supplementing the heat balance equation (9).

This set of boundary conditions can be changed by adding Eq. (12) to Eq. (18). As a result we obtain

$$\begin{aligned} & -(\kappa_2 \frac{\partial T_2}{\partial x})|_{x=0} + j_x \Pi_2|_{x=0} \\ & - \left( -(\kappa_1 \frac{\partial T_1}{\partial x})|_{x=0} + j_x \Pi_1|_{x=0} \right) = \rho_s j_x^2 \\ & + \alpha_s j_x (T_2(0) - T_1(0)), \end{aligned} \quad (22)$$

where

$$\begin{aligned} \rho_s = \rho_{s1} + \rho_{s2} &= \lim_{\delta \rightarrow 0} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{-\delta}^{\xi} \rho(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \\ &+ \lim_{\delta \rightarrow 0} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{\xi}^{\delta} \rho(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} = \lim_{\delta \rightarrow 0} \int_{-\delta}^{\delta} \rho(x) dx \end{aligned} \quad (23)$$

and

$$\begin{aligned} \alpha_s = \alpha_{s1} + \alpha_{s2} &= \lim_{\delta \rightarrow 0} \left( \frac{1}{2\delta} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{-\delta}^{\xi} \alpha(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \right) \\ &+ \lim_{\delta \rightarrow 0} \left( \frac{1}{2\delta} \frac{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)} \int_{\xi}^{\delta} \alpha(x) dx}{\int_{-\delta}^{\delta} \frac{d\xi}{\kappa(\xi)}} \right) \\ &= \lim_{\delta \rightarrow 0} \left( \frac{1}{2\delta} \int_{-\delta}^{\delta} \alpha(x) dx \right) \end{aligned} \quad (24)$$

are the surface electric resistance and the surface Thomson coefficient of the entire surface layer  $x = 0$ .

Boundary condition (22) can be rewritten in the following form:

$$q_2(x = 0) - q_1(x = 0) = \tau_s, \quad (25)$$

where  $\tau_s = \rho_s j_x^2 + \alpha_s j_x (T_2(0) - T_1(0))$  are the heat sources in the entire surface layer. They are the surface Joule and Thomson sources of heat.

Thus, one can use the set of boundary equations (6), (7), (12) and (22) instead of (6), (7), (12) and (18) or the set (6), (7), (18) and (22).

Now we can conclude that both the heat balance equation and the set of boundary conditions contain only the Joule and Thomson heat sources. So the Peltier's cooling or heating origin does not associate with the absorption of heat or its evolution in the bulk and in the junctions between media through which a d.c. electric current passes.

### 5. Thermoelectric cooling and heating

The heat balance equation (5) is a nonlinear equation in the running electric current  $j$ . This follows from the nonlinear terms describing the Joule and the Thomson heat. In the case of the Thomson heat, it is necessary to take into account that the temperature gradient in the problem considered is not created by any external sources. It arises only due to an electric current flow. Thus, both the Joule and the Thomson heat sources are nonlinear terms in  $j$ . As was shown in [20], these are the values of the same order. The Thomson heat even exceeds the Joule heat in the good thermoelectric materials with a figure-of-merit  $ZT$  exceeding unit. Besides, both the coefficient of thermal conductivity and the Seebeck coefficient depend on temperature, which is a function of the electric current.

At the same time, it is easy to see that the non-equilibrium temperature distributions occur even in the linear approximation with respect to the electric current. So, thermoelectric cooling or heating are linear effects in an electric current and manifested themselves "in the pure state" only at small values of current when the Joule and the Thomson heat do not

play a noticeable role. For this reason, it is convenient to consider the problem of thermoelectric cooling just in the linear approximation to the electric current  $j$ .

The heat balance equation in this approximation reduces to

$$\nabla \cdot \vec{q}_0 = 0, \tag{26}$$

where  $\vec{q}_0 = -\kappa_0 \nabla T + \alpha_0 T_0 \vec{j}$ ,  $\kappa_0$  and  $\alpha_0$  are the thermal conductivity and Seebeck coefficients at the equilibrium temperature  $T_0$

Equation (26) represents the total heat flux conservation law, which can be formulated as follows: Any change in the drift component of the heat flux is accompanied by a change in the thermal diffusion component of the same heat flux in the absence of heat bulk sources and sinks. This change occurs in such a way that the total heat flux remains invariable.

Let us write Eq. (26) in the form:

$$\nabla \cdot (\kappa_0 \nabla T) = \vec{j} T_0 \nabla \alpha_0, \tag{27}$$

One can conclude from the form of Eq. (27) that any spatial variation in the Seebeck coefficient (Peltier coefficient) leads to the appearance of thermal diffusion fluxes and, therefore, to non-equilibrium temperature distributions. So, thermoelectric cooling or heating occur in the sample points where  $\nabla \alpha_0 \neq 0$ .

The Seebeck coefficient for non-degenerate semiconductors is equal to [24]:

$$\alpha_0 = \frac{k_B}{e} \left( -\frac{\mu_0}{k_B T_0} + g_n \right), \tag{28}$$

where  $k_B$  is the Boltzmann constant,  $\mu_0$  is the chemical potential at the equilibrium temperature  $T_0$ ,  $g_n$  is the coefficient determining the momentum scattering ( $g_n = 2$  for the scattering on the acoustic phonons,  $g_n = 4$  for the scattering centers of the on the impurities,  $g_n = 3$  for the scattering on the optic phonons at temperatures higher than the Debye temperature, and  $g_n=2.5$  for the scattering on the optic phonons at temperatures below the Debye temperature).

Assuming that the type of scattering does not change throughout the sample, one can write that

$$\nabla \alpha_0 = \frac{\partial \alpha_0}{\partial \mu_0} \nabla \mu_0.$$

So, any spatial change in the chemical potential leads to the bulk Peltier effect. One of the most important cases of this spatial change is the non-uniform sample impurity doping. This case was studied in detail in Ref. 25. However, other reasons for the chemical potential uniformity can exist, if for example, there are varied band-gap semiconductors.

Usually, in practice, the non-homogeneity occurs in the thermoelectric modules composed of two different uniform semiconductors with  $n$ - and  $p$ -types of conductivity, joined by the metal plate (Fig. 8) [8].

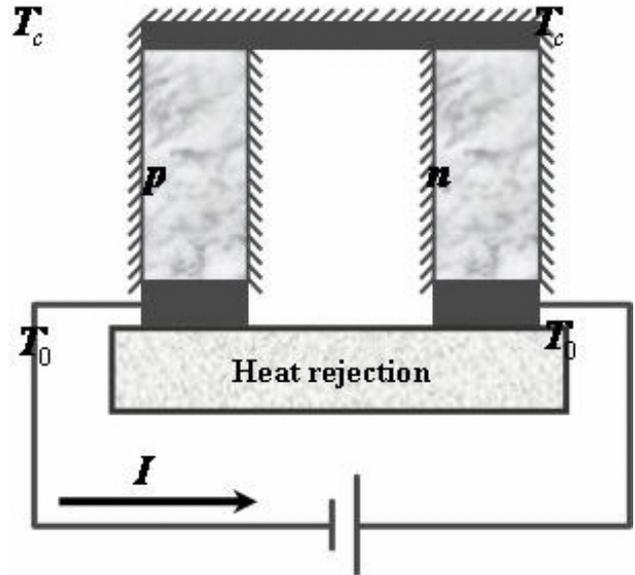


FIGURE 8. Sketch of the thermoelectric module ( $T_c$  is the temperature of the cooled junction).

The physical processes in these modules are usually studied within a one-dimensional model (see, for example Refs. 3, 4, 7, and 8), so that the thermoelectric module can be simulated by the same structure represented as that in Fig.2. The metal plate between two branches of the thermoelectric module does not essentially influence the thermoelectric cooling since the Seebeck coefficient is very small for metals, and we do not take it into consideration. Nevertheless, as was mentioned in Sec. 2, we consider the structure composed of  $n$ - type semiconductors for simplicity.

The heat balance equation for each structure's sample reduces in this case to the trivial equation,

$$\frac{d^2 T_{1,2}(x)}{dx^2} = 0. \tag{29}$$

Boundary conditions at the planes  $x = -d_1$  and  $x = d_2$  remain the same [see Eqs. (6) and (7)],

$$T_1(x = -d_1) = T_2(x = d_2) = T_0. \tag{30}$$

Boundary conditions (22) and (12) reduce to the following linear equations in  $j$ :

$$\kappa_1 \frac{dT_1}{dx} \Big|_{x=0} - \Pi_1 j = \kappa_2 \frac{dT_2}{dx} \Big|_{x=0} - \Pi_2 j \tag{31}$$

and

$$\eta [T_1(x = 0) - T_2(x = 0)] = -\kappa_1 \frac{dT_1}{dx} \Big|_{x=0} + \tilde{\Pi}_1 j, \tag{32}$$

where  $\tilde{\Pi}_1 = \Pi_1 - \Pi_s$ .

Here and below, up to Sec. 7, all kinetic coefficients are assumed to depend on the temperature  $T_0$ .

Boundary condition (31) describes the bulk heat flux continuity at the boundary of two media [ $q_1(x = 0) = q_2(x = 0)$ ] in the absence of heat sources and sinks at the interface  $x = 0$ . Boundary condition (32) describes the continuity of the bulk heat flux in medium 1 and the surface heat flux,  $q_1(x = 0) = q_s$ .

An equation which is similar to Eq. (32) could also be written for the second sample of the structure, nevertheless, it is unnecessary for the correct statement of the problem.

Equations(29) together with the boundary conditions (30)-(32) result in the following temperature distributions:

$$T_{1,2} = T_0 \left\{ 1 \pm \left[ \tilde{\Pi}_{1,2} \pm \frac{\eta d_{2,1}}{\kappa_{2,1}} (\Pi_1 - \Pi_2) \right] \times \frac{j(d_{1,2} \pm x)}{T_0 \kappa_{1,2} \left[ 1 + \eta \left( \frac{d_1}{\kappa_1} + \frac{d_2}{\kappa_2} \right) \right]} \right\}, \quad \left( \begin{array}{l} -d_1 \leq x \leq 0 \\ 0 \leq x \leq d_2 \end{array} \right), \quad (33)$$

here  $\tilde{\Pi}_2 = \Pi_2 - \Pi_s$ .

The second term in the square brackets of Eq. (33) determines the contribution of the Peltier effect to the temperature distribution in the structure with a finite  $\eta$ . It corresponds to the Peltier thermoelectric heating or cooling considered in the Introduction. As has been shown in Ref. 26, the value  $(\Pi_1 - \Pi_2) j$  determines the change in kinetic energy flux at the junction.

Let us note that the temperature distributions (33) strongly depend on the junction surface thermal conductivity. In addition, they include two independent parts. The second term in the square brackets of Eq. (33) corresponds to the well known Peltier effect at  $\eta \rightarrow \infty$  (the first term is absent for this condition). The contributions of this term to the total effect of thermoelectric cooling decreases for a decrease in surface thermal conductivity, while the contribution of the first term increases in this case. For the adiabatic junction ( $\eta \rightarrow 0$ ), the second term vanishes while the first term manifests itself maximally.

## 6. Isothermal and adiabatic peltier effects

The first term in the square brackets of Eq. (33) determine a new effect of cooling or heating which is not reduced to the known Peltier effect. First of all, it is determined by the difference in the bulk and surface Peltier coefficients but not by the difference in the bulk Peltier coefficients. This implies that this effect can be observed in the structure composed of two identical materials, and even in the slab in contact with external heat reservoirs [20]. This radically distinguishes it from the well-known Peltier effect. We have named this effect the "adiabatic Peltier effect" since it manifests itself in the pure form for small values of the surface thermal conductivity (adiabatic junction). The thermoelectric cooling (heating) associated with the second term in the square brackets of Eq. (33) can be named the "isothermal Peltier effect", since it manifests itself in its pure form for large values of  $\eta$  (isothermal junction). Actually, this is the Peltier effect discussed in all previous literature.

In the general case, both the isothermal and adiabatic Peltier effects occur simultaneously and are inseparable from each other except for the limiting cases of infinitely large and infinitely small surface thermal conductivity. The cor-

responding criteria, as is well seen from Eq. (33), are

$$\eta \gg \frac{d_1}{\kappa_1}, \frac{d_2}{\kappa_2}$$

and

$$\eta \ll \frac{d_1}{\kappa_1}, \frac{d_2}{\kappa_2}.$$

These criteria are known as the isothermal and adiabatic conditions of a junction separating two bounded media [27]. Let us note that the isothermal condition is implemented more easily for longer samples, while the adiabatic condition is implemented more easily for shorter samples.

Thus, the decrease in surface heat conductivity reduces the heating or cooling of the junction due to the isothermal Peltier effect. The disappearance of this effect in the case of the adiabatic insulation of the junction can be explained by the fact that the "drift" heat flux in this case is completely compensated for the induced thermal diffusion flux in each sample of the structure. This induced thermal flux takes on the maximum value due to the maximal action of the adiabatic Peltier effect at  $\eta \rightarrow 0$ . This can easily be seen from boundary condition (32).

It is clear that there is some value of  $\eta$  at which both effects may make a comparable contribution to the thermoelectric heating or cooling.

To understand the physical essence of the adiabatic Peltier effect, we shall consider the structure composed of two identical materials ( $\Pi_1 = \Pi_2 = \Pi$  and  $\kappa_1 = \kappa_2 = \kappa$ ). Let us suppose for definiteness that the geometrical sizes of this structure are the same as those shown in Fig. 2.

Now the drift heat fluxes are equal in both samples of the structure in magnitude and are directed opposite to the electric current.

Let us first suppose that the junction is isothermal. In this case, the structure represents a homogeneous semiconductor from the point of view of heat conductivity. In this semiconductor, the induced thermal diffusion fluxes are equal to zero because the temperatures on the surfaces  $x = -d_1$  and  $x = d_2$  are maintained by the external heat reservoirs at temperature  $T_0$ .

Induced thermal diffusion fluxes will occur in each sample of the structure for any non-zero surface thermal resistance. In this case, they have the equal magnitudes and are in the same direction. The thermal diffusion flux in the left sample always enters the junction, while the thermal diffusion flux in the right sample always leaves it. The induced temperature distributions arising in the structure are qualitatively represented in Fig. 9. It follows from Eq. (33) and this figure that the temperature gradient is continuous on the interface, while the temperature undergoes the discontinuity here. This discontinuity essentially depends on the magnitude of the surface thermal conductivity  $\eta$ , as follows from Eq. (33). The temperature difference  $T_1(x=0) - T_2(x=0)$  increases with a reduction in  $\eta$ , which results in an increase in the thermal fluxes in both the samples. Conversely, this difference decreases simultaneously with a decrease in the thermal fluxes

for an increase in  $\eta$ . In the limiting case of the isothermal contact ( $\eta \gg d_1/\kappa_1, d_2/\kappa_2$ ),  $T_1(x=0) = T_2(x=0) = T_0$ , and the thermal fluxes disappear in the structure. In this case, the adiabatic Peltier effect disappears too.

Let us notice that the surface heat conductivity can be represented simplistically as  $\eta = \lim_{l_s \rightarrow 0} (\kappa_s/l_s)$  [see Ref. 13], where  $l_s = 2\delta$  is the thickness of the transitive layer,  $\kappa_s$  is the thermal conductivity of this transitive layer. Generally  $\kappa_s$  can depend on  $l_s$  in that limiting transition. One can suppose that the following cases are possible:

- a)  $\kappa_s$  has a finite value at  $l_s$  tending to zero;
- b)  $\kappa_s$  tends to zero at the same speed as  $l_s$ ;
- c)  $\kappa_s$  tends to zero at a higher speed than  $l_s$ .

In the first case, the surface heat conductivity tends to infinity, so this situation describes the isothermal junction. The junction is determined by the finite surface heat conductivity in the second case, and this case is general. The third case corresponds to the adiabatic insulation of the junction. Finally, we can say that the dependence of both thermoelectric effects on  $\eta$  comes down to the question of the dependence of the thermal conductivity of the transitive layer  $\kappa_s$  on the thickness of this layer. This question, however, requires a separate study and is not a subject of the present work.

The adiabatic Peltier effect in the case under construction of the structure composed of identical materials ( $\Pi_1 = \Pi_2, \kappa_1 = \kappa_2$ ) can occur only at different lengths of the left and right samples. As it is well seen from Fig. 9,  $|T_1(x=0) - T_0| = |T_2(x=0) - T_0|$  at  $d_1 = d_2$ , i.e. the warming up of the right-hand area adjoining the junction is compensated for completely by the cooling of the left-hand area adjoining the junction, and the adiabatic Peltier effect is absent. Either heating of the junction or its cooling prevails at different sample lengths  $d_1 \neq d_2$ . So, the temperature  $T_1(x=0)$  decreases as compared with  $T_0$  for an increase in the left sample length. On the contrary, the temperature  $T_2(x=0)$  rises as compared with  $T_0$  for an increase in the right sample length.

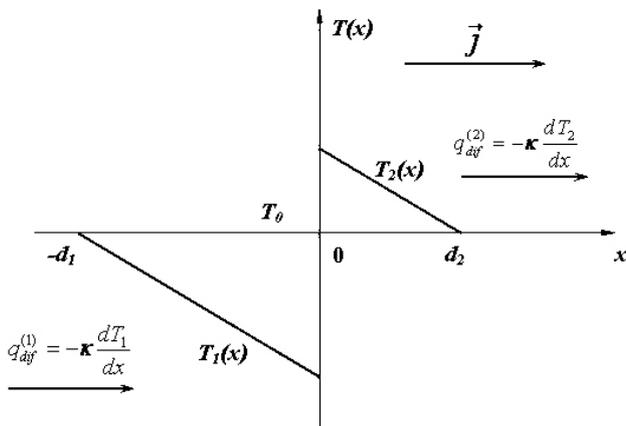


FIGURE 9. Induced thermal fluxes and the temperature distributions caused by the adiabatic Peltier effect in the structure with the same materials.

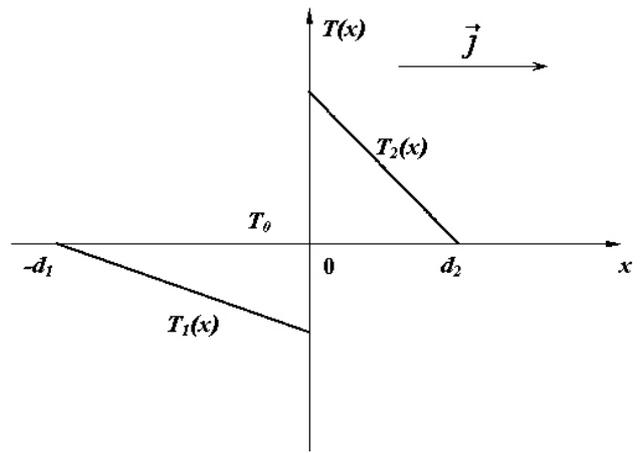


FIGURE 10. Induced thermal fluxes and temperature distributions caused by the adiabatic Peltier effect in the structure with different materials when  $|\Pi_1| < |\Pi_2|$ .

It is possible to explain this fact by noticing that the drift thermal flux  $q_{dr} = \Pi j$  does not vary with the change of the sample lengths. For this reason, the induced thermal diffusion flux does not vary either, and

$$q_{diff}^{(1,2)} = -\kappa \frac{dT_{1,2}}{dx} \propto \frac{T_{1,2}(x=0) - T_0}{d_{1,2}} = \text{Const.}$$

It is clear from this equation that an increase in  $d_{1,2}$  results in an increase the difference  $T_{1,2}(x=0) - T_0$ , i.e. the junction is cooled more intensively.

The basic reasoning regarding the physical interpretation of the adiabatic Peltier effect remains the same if the structure is made from different materials. In this case, the values of the induced thermal diffusion fluxes on the right-hand side and on the left-hand side of the junction are different. This circumstance results in a discontinuity in both the temperature and the thermal diffusion fluxes on the junction. The temperature distributions caused by the adiabatic Peltier effect are represented in Fig. 10 for the case  $|\Pi_1| < |\Pi_2|$ .

From Eq. (33) it follows that the junction heating or cooling (depending on the direction of  $\vec{j}$ ) which is associated with the isothermal Peltier cooling rises with an increase in the sample lengths  $d_1$  and  $d_2$  too.

This fact can be understood from the following reasoning: Let  $\eta$  be so large that only the isothermal Peltier effect occurs in the structure. The change in the drift fluxes  $(\Pi_1 - \Pi_2) j$  does not depend on the change in lengths and remains the same with varying values of  $d_1$  and/or  $d_2$ . As follows from the total heat flux conservation law (31), the change of the induced thermal diffusion fluxes should not vary either, so  $\kappa_1(dT_1/dx) - \kappa_2(dT_2/dx) = \text{Const.}$  The left side of this equation can be rewritten as

$$\left( \frac{\kappa_1}{d_1} + \frac{\kappa_2}{d_2} \right) [T(x=0) - T_0] = \text{Const.} \quad (34)$$

if we take into account the condition of the temperature continuity on the junction (2), where  $T(x = 0) = T_1(x = 0) = T_2(x = 0)$ .

From Eq.(34) it follows that any increase in the lengths  $d_1$  and/or  $d_2$  increases the temperature difference  $T(x = 0) - T_0$ , i.e., results in a greater heating of the junction or a deeper cooling of it.

The dependence of the maximal temperature cooling on the thermoelectric leg lengths in the cooling modules has been pointed out earlier in the experimental works [28,29].

The average temperature of the junction  $x = 0$  in the general case is determined by the action of both isothermal and adiabatic Peltier effects,

$$\begin{aligned} \bar{T} &= \frac{T_1(x = 0) + T_2(x = 0)}{2} \\ &= T_0 \left\{ 1 + \left[ \frac{1}{2} \left( \frac{\tilde{\Pi}_1 d_1}{\kappa_1} - \frac{\tilde{\Pi}_2 d_2}{\kappa_2} \right) + \frac{\eta d_1 d_2}{\kappa_1 \kappa_2} (\Pi_1 - \Pi_2) \right] \frac{j}{T_0 \left( 1 + \frac{\eta d_1}{\kappa_1} + \frac{\eta d_2}{\kappa_2} \right)} \right\} \end{aligned} \quad (35)$$

It follows from Eq.(35) that the average temperature of the junction due to the isothermal Peltier effect depends on the difference between the parameters  $\Pi_1$  and  $\Pi_2$ , as was already mentioned earlier. The contribution of the adiabatic Peltier effect to the average temperature is determined by the difference between other parameters,  $\tilde{\Pi}_1 d_1 / \kappa_1$  and  $\tilde{\Pi}_2 d_2 / \kappa_2$ . Since the parameters determining heating or cooling in both effects are different and independent, the isothermal and adiabatic Peltier effects can amplify each other or, on the contrary, suppress each other.

In the limiting case of the isothermal contact ( $\eta \gg \kappa_1 / d_1, \kappa_2 / d_2$ ), the adiabatic Peltier effect disappears, and the average temperature is determined only by the isothermal Peltier effect,

$$\bar{T}(x = 0) = T_0 \left[ 1 + \frac{\Pi_1 - \Pi_2}{T_0 (\kappa_1 / d_1 + \kappa_2 / d_2)} j \right]. \quad (36)$$

In another limiting case, when the junction is adiabatically insulated ( $\eta \ll \kappa_1 / d_1, \kappa_2 / d_2$ ), the average temperature of the junction is only determined by the adiabatic Peltier effect:

$$\bar{T}(x = 0) = T_0 \left[ 1 + \frac{1}{2T_0} \left( \frac{\tilde{\Pi}_1}{\kappa_1 / d_1} - \frac{\tilde{\Pi}_2}{\kappa_2 / d_2} \right) j \right]. \quad (37)$$

From this equation, the possibility of heating or cooling in the structure with the same materials is easily seen. When  $\Pi_1 = \Pi_2 = \Pi$  and  $\kappa_1 = \kappa_2 = \kappa$ , the average temperature is equal to

$$\bar{T}(x = 0) = T_0 \left[ 1 + \frac{\tilde{\Pi} j}{2T_0 \kappa} (d_1 - d_2) \right], \quad (38)$$

and heating or cooling is only determined by ratio of the the sample lengths. Here,  $\tilde{\Pi} = \Pi_1 - \Pi_s = \Pi_2 - \Pi_s$ .

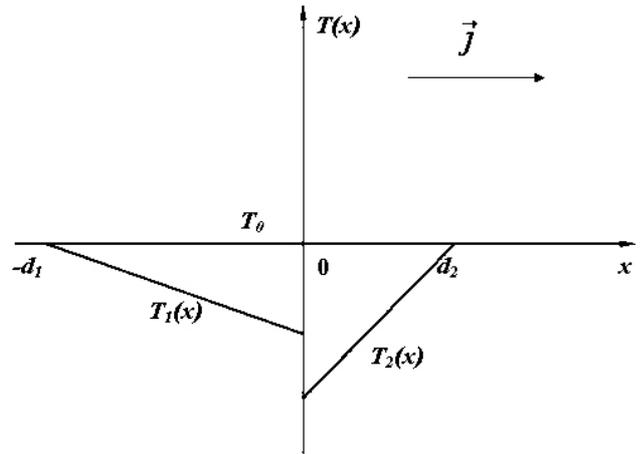


FIGURE 11. Temperature distributions which is caused by the adiabatic Peltier effect in the p-n structure.

Let us notice that all the equations obtained above remain true for the structures composed of semiconductors with the  $p$ -type conductivity. It is only necessary to take into account that  $\Pi_{1,2} > 0$  in this case.

The Peltier effect occur at the junction of semiconductors with the electron and hole conductivities too. However, the thermoelectric processes in this case essentially depend on the recombination rates in areas adjoining to the junction (see Refs. 16 to 18, and 26). In the case of an infinitely strong recombination, all the equations of this paper are correct. The essential difference between this case and the previous ones is that now the material with the n-type conductivity is characterized by the Peltier coefficient  $\Pi_n < 0$ , while the material with the p-type conductivity is characterized by the Peltier coefficient  $\Pi_p > 0$ . In this case both areas adjoining to the junction will be heated or cooled (depending on the direction of the electric current) simultaneously (Fig.11), and the effect of thermoelectric cooling (heating) is more intensive.

In fact, let us assume for simplicity that

- a) the structure represented in Fig.2 is composed of  $p$ - and  $n$  materials identical in length, and with equal values of the coefficients of thermal conductivity ( $d_1 = d_2 = d, \kappa_1 = \kappa_2 = \kappa$ );
- b) the recombination rate on  $p - n$  junction is infinitely high;
- c) the Peltier coefficients of both materials are equal in absolute magnitude ( $\Pi_1 = -\Pi_2$ ).

In this case, it follows from Eqs. (36), (37) that the isothermal and adiabatic Peltier effects have same result

$$\bar{T}(x = 0) = T_0 \left( 1 - \frac{|\Pi| d}{T_0 \kappa} j \right), \quad (39)$$

where  $|\Pi| = |\Pi_1| = |\Pi_2|$ . The last equation shows that the isothermal and adiabatic Peltier effects are commensurable in the structure considered.

## 7. Reversibility of the thermoelectric cooling process

In this section, let us briefly discuss the question of the reversibility of the thermoelectric cooling process. Discussions about the thermoelectric phenomena reversibility have been conducted since Thomson [30]. As was mentioned in Ref. 3, "Thomson has applied the first and second laws of thermodynamics for analysis of the thermoelectric phenomena, considering the thermoelectric processes to be reversible. The proportionality of the Peltier and the Thomson heats to the electric current, and hence the circumstance that absorption of these heats is changed with the change in direction of the electric current and vice versa, leads to the natural supposition that processes in the Peltier effect and the Thomson effect are reversible from the thermodynamic point of view.

...At the same time it is necessary to emphasize that Thomson himself expressed doubts regarding the correctness of applying the thermodynamics of reversible processes to the analysis of thermoelectric phenomena. His argument was that the electric current running is irreversible and associates with the irreversible evaluation of the Joule heat which is quadratically dependent on the current.

The proportionality of the Peltier effect to an electric current and, hence, the change of the cooling to heating or vice versa with the change in direction of an electric current, makes the assumption that the Peltier effect is a reversible thermodynamic process quite natural. On the other hand, it is difficult to consider a process reversible if it contains an irreversible process the heat conductivity.

...Thomson's theory was the object of sharp criticism from Boltzmann. He pointed out that the irreversibility associated with the Joule heat can be neglected for small electric currents, while the irreversibility associated with thermal conductivity is quite significant. This process, like the Thomson effect is proportional to the temperature gradient and cannot be counted as negligibly small.

We have our own point of view regarding this problem. It does not coincide with the point of view stated in Refs. 31 and 32.

As was shown in this paper, the Peltier heat sources are absent and the thermoelectric cooling (heating) effect is caused by the induced thermal diffusion fluxes. These thermal diffusion fluxes occur already in the linear approximation by the electric current. The corresponding temperature gradients are proportional to the electric current. At the same time, any irreversible source of heat is absent in this approximation. Under this condition the entropy flux does not change, and this circumstance points to the reversibility of thermoelectric cooling.

To be sure of it, let us write the entropy balance equation. Based on Eq. (5), it is easy to obtain

$$\nabla \cdot \vec{s} = \frac{\rho j^2}{T} + \frac{\kappa (\nabla T)^2}{T^2}, \quad (40)$$

where  $\vec{s} = \vec{q}/T$  is the entropy flux.

Let us note that there are only two sources of the entropy associated with the Joule heat and the irreversible thermal conductivity process. The Thomson heat does not deposit to the entropy growth. Formally, it is connected with the modified definition of the Thomson heat [see Eq.(5)]. Certainly there is a deeper physical reason for this circumstance requiring its additional study.

In the linear approximation (the condition of the thermoelectric cooling occurrence in the pure state), Eq.(40) reduces to

$$\nabla \cdot \vec{s}_0 = 0, \quad (41)$$

where  $\vec{s}_0 = (\vec{q}_0/T_0)$  is the linear entropy flux.

The entropy flux in this approximation does not change, and that proves the statement about the reversibility of thermoelectric cooling (heating).

From our point of view, this entropy constancy is associated with the simultaneous presence of two thermal fluxes in the cooling (heating) process, namely with the drift thermal flux and the thermal diffusion flux. The entropy change from part of one thermal flux is completely compensated by the entropy change from part of the other thermal flux. As a result, the total entropy change in the cooling or heating process is equal to zero. This statement can be considered to be a strict formulation of the Le Châtelier-Braun principle for the thermoelectric processes of cooling or heating.

The process of thermoelectric cooling or heating becomes irreversible if we take into account the nonlinear sources of entropy.

## 8. Conclusions

Two thermoelectric effects, the isothermal and adiabatic Peltier effects, always occur simultaneously when an electric current flows through a non-uniform medium such as a non-uniformly doped semiconductor slab with the boundaries having finite surface thermal conductivity, varied band-gap semiconductors, semiconductor structure composed from two materials and so on. Its total action determines the heating or cooling of this junction at the finite surface heat conductivity. Heating or cooling due to these effects is explained by the appearance of induced thermal diffusion fluxes but not by the evolution or absorption of heat on the junction. These induced thermal diffusion fluxes appear in accordance with the general Le Châtelier-Braun thermodynamic principle applied to the electric and heat transfer processes in a heterogeneous medium.

The adiabatic Peltier effect is a new thermoelectric effect in isotropic media and can supplement the set of well-known thermoelectric effects such as the Seebeck, Peltier, and Thomson effects.

The Peltier effect is frequently considered to be opposite to the Seebeck effect, and vice versa. The reason for this is that an electric current generates a non-uniform spatial temperature distribution in the case of the Peltier effect, while a given non-uniform temperature distribution creates an elec-

tric current in a closed thermoelectric circuit in the case of the Seebeck effect.

From our point of view the physical basis of this correspondence lies in the Le Châtelier-Braun principle. Indeed, the appearance of the temperature heterogeneity in the Peltier effect is caused by the appearance of an induced compensating thermal diffusion flux. A thermal diffusion flux is given in the Seebeck effect *a priori*. According to the Le Châtelier-Braun principle, some compensating thermal flux must appear in a thermoelectric circuit in this case also. Only the

drift thermal flux accompanied by the electric current can appear to be tending to compensate for the thermal diffusion flux.

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