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On the distribution of charge carriers in branches thermoelectric cooler

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The simulation of energy conversion in the branches of a thermoelectric cooler is carried out. The influence of various distributions of the active impurity along the branch of the thermoelement on its efficiency in the mode of maximum temperature drop is considered. The calculation is carried out within the framework of a two-band standard model of the band structure of a semiconductor for non-degenerate charge carriers. The Thomson effect was not taken into account.

Keywords:thermoelectric cooler, distributed Peltier effect, two-zone model, non-degenerate charge carriers, thermoelectric efficiency.

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Introduction

The main requirements for thermoelectrics — is the higher possible value of the thermoelectric efficiency parameter $Z = \alpha^2/\rho\chi$. Therefore, all the efforts of specialists are aimed at increasing the parameter Z. It has been understood for a long time that it is necessary to create an optimal concentration in thermoelectric materials. Optimization of the parameter Z for a one-band semiconductor was carried out in the study [1] and in fact was reduced to maximizing the power factor $\alpha^2\sigma$. Since practically used thermoelectrics are doped semiconductors of the n- or p-type, usually carriers of only one sign are taken into account during optimization, which are the main ones. There are at least two ways to increase efficiency by doping: this is the optimization of the efficiency parameter in the operating temperature range [2] and the use of the distributed Peltier effect [3]. In these and other studies devoted to the optimization of charge carriers, charge carriers of only one sign are taken into account. It is usually assumed that their concentration can be changed by doping with appropriate impurities in a very wide range, without taking into account their own charge carriers. At the same time, there is a desire to fully compensate for the Joule heat using the distributed Peltier effect [3,4]. As shown in study [3], in the optimized branch with full compensation of Joule heat the electrical conductivity on a cold end of the branch is 4 times higher than on a hot end, while differential thermal EMF module is 4 times lower. In the study [5] to maintain the optimal value of Z in PbTe, only electrons whose density is determined by the concentration of the dopant are used. By changing the composition of the material along the length of the branch of the thermoelectric element, it is recommended to maintain [6] an efficiency indicator close to the maximum at each point of the branch at a given temperature difference. In review [7] it is noted that determination of optimum profile of impurity heterogeneity is a complicated mathematical problem, several techniques of calculation of the temperature profile of thermoelement branch are specified and technologies of heterogeneities formation are discussed.

Actual low-temperature thermoelectrics with high efficiency do not have a wide forbidden band, therefore the intrinsic charge carriers [s]hould also be considered. In this paper, on the basis of a two-band thermoelectric model using classical statistics, an attempt is made to calculate the contribution of the distributed Peltier effect to the efficiency of the thermoelectric element branch based on a two-band model for various types of impurity distribution. Due to the fact that in this paper a comparative problem of the actions of the distributed Peltier effect was posed, the Thomson effect was not considered in solving the boundary value problem.

1. General calculation scheme

When optimizing the parameter of thermoelectric efficiency by changing the concentration of charge carriers, the main increase occurs mainly due to changes in differential thermal EMF and electrical conductivity. From the condition [1]

$$\Delta(\alpha^2\sigma) > 0 \tag{1}$$

it follows that the relative increment of electrical conductivity should be more than twice the relative decrease in thermal EMF:

$$\Delta\sigma/\sigma > -2\Delta\alpha/\alpha. \tag{2}$$

Considering that

$$n = N_c \exp\eta \tag{3}$$

the Pisarenko formula

$$\alpha = -(k/e)(r + 2 - \eta), \tag{4}$$

can also be estimated to limit the area of the reduced chemical potential, where an increase in thermoelectric efficiency is possible

$$\eta < r. \tag{5}$$

Thus, an increase in the conversion efficiency at $r = -1/2$, the chemical potential should lie below the bottom of the conduction band at a distance of at least $kT/2$.

We limit ourselves to the case of non-degenerate charge carriers and the simplest standard band model. In order that the calculations of the thermoelectric would not be too abstract, the band parameters are approximated to the parameters of a real low-temperature thermoelectric based on bismuth and antimony tellurides: the band gap $E_g = 0.15$ eV, the effective masses of the density of electron states $m_n^* = 0.45m_0$, holes $m_p^* = 0.69m_0$ [9].

In the classical approximation, the electron concentration is determined by the expression [10]:

$$n = N_C \exp \eta_e, \tag{6}$$

holes

$$p = N_V \exp \eta_h, \tag{7}$$

where N_C, N_V — effective densities of states of the conduction band and valence band, respectively. Concentrations of electrons and holes are related to electroneutrality equation

$$n = p + N_d, \tag{8}$$

where N_d is the donor impurity concentration.

Specific electrical conductivity of electrons $\sigma_e = eN_e n$ and holes $\sigma_h = eN_h p$ in aggregate determine the total specific electrical conductivity.

$$\sigma = \sigma_e + \sigma_h. \tag{9}$$

For a better comparison of the calculation results with the experiment, it is necessary to take into account the temperature dependences of the mobility of charge carriers and lattice thermal conductivity. In a sufficiently wide temperature range, it is possible to take into account the temperature dependence of the mobility of charge carriers in the form of $U_e = 617.3 \cdot T^{-3/2}$, $U_h = 1449 \cdot T^{-1/8}$ [9,11]. Concentration dependences of electron and hole mobilities were not taken into account.

Specific thermal conductivity of a semiconductor

$$\chi = \chi_{ph} + 2\left(\frac{k}{e}\right)^2 T\left[\sigma_e + \sigma_h + \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h}\left(\frac{E_g}{kT} + 4\right)^2\right], \tag{10}$$

where χ_{ph} — phonon thermal conductivity, the lattice component of thermal conductivity is taken into account as a dependence $\chi_{ph} = 235 \cdot T^{-1}$ [9].

The differential thermal EMF equals [9]

$$\alpha = \frac{\alpha_p \sigma_p + \alpha_n \sigma_n}{\sigma_p + \sigma_n}, \tag{11}$$

where the partial thermal EMF of electrons and holes are determined by the Pisarenko formula (4).

Optimization of the efficiency parameter $Z = \alpha^2/\rho\chi$ at $T = 300$ K shows that the maximum value of $3 \cdot 10^{-3}$ K^{-1} is achieved at the value of the reduced chemical potential $\eta = -0.4$ and impurity concentrations $N_d = 5 \cdot 10^{24}$ m^{-3}. According to the elementary theory of A.F. Ioffe $\Delta T = ZT_c^2/2$ site1, it is possible to calculate the minimum temperature achievable at the cold end of the branch — 225 K. The calculation at this temperature gives the efficiency parameter $Z = 2.95 \cdot 10^{-3}$ K^{-1} at the value of the chemical potential $\eta = -0.5$ and impurity concentrations $N_d = 3 \cdot 10^{24}$ m^{-3}.

Naturally, the question arises: what should be the optimal concentration of impurities in a homogeneous branch? To answer it, it is necessary to use the solution of the boundary problem of thermal balance:

$$\frac{d}{d\xi}\left(\chi \frac{dT}{d\xi}\right) + \frac{Y^2}{\sigma} = 0 \tag{12}$$

with boundary conditions

$$\chi \frac{dT}{d\xi}\bigg|_{\xi=0} = \alpha Y T\big|_{\xi=0}, \; T\big|_{\xi=1} = T_1, \tag{13}$$

where $\xi = x/l$ $(0 < \xi < 1)$, $Y = I\,l/S$ — optimization parameter [12], l — branch length, S — branch cross section, I — branch current. Since the boundary value problem is nonlinear, it was solved by numerical technique. Minimizing the temperature of the cold end of the branch by the parameter Y with simultaneous optimization by the impurity concentration gave a value of 230 K. The optimal impurity concentration for a homogeneous branch turned out to be equal to $N_d = 3.3 \cdot 10^{24}$ m^{-3}.

Figure 1 shows the distribution of the reduced chemical potential along the branch (curve *3*), which generally satisfies the condition (5), but goes beyond the boundaries of the chemical potential interval calculated above, corresponding to the maxima Z at temperatures of 230 and 300 K. Therefore, only a small part of the branch near its cold end works effectively. This clearly indicates that only a branch with a heterogeneous composition can be optimal in the parameter Z. What should be the nature of heterogeneity? This can be determined by solving the boundary value problem of thermal balance considering the distributed Peltier effect:

$$\frac{d}{d\xi}\left(\chi \frac{dT}{d\xi}\right) + \frac{Y^2}{\sigma} - YT\frac{d\alpha}{dn}\frac{dn}{d\xi} = 0 \tag{14}$$

with former boundary conditions (13). Since there is an analytical dependence between electron concentration and impurity concentration

$$n(N_d) = \frac{N_d}{2}\left(\sqrt{1 + \frac{4n_i^2}{N_d}} + 1\right) \tag{15}$$

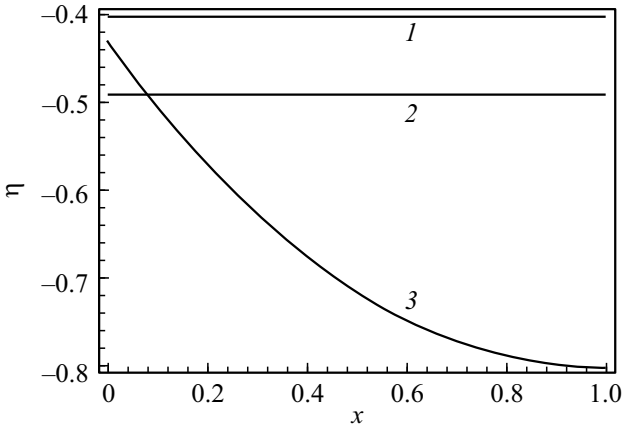

Figure 1. Distribution of the chemical potential along a homogeneous branch with an optimal impurity concentration (curve *3*); the straight lines *1* and *2* correspond to the optimal values of the chemical potential at 300 and 225 K, respectively.

derivative of electrons concentration can be expressed through derivative of impurity concentration

$$\frac{dn}{d\xi} = \frac{dn}{dN_d}\frac{dN_d}{d\xi}, \tag{16}$$

which makes it possible to solve the boundary value problem (13), (14) for different types of impurity distribution along the branch $N_d(\xi)$.

Solving the problem (13), (14) with a linear distribution of the impurity concentration in the above calculated ranges from $N_d(0) = 3 \cdot 10^{24}$ m^{-3} at the cold end to $N_d(1) = 5 \cdot 10^{24}$ m^{-3} on the hot with simultaneous optimization by the parameter Y, we get that instead of the expected decrease in the minimum achievable temperature at the cold end of the branch, it rises to 234 K, which is related to with the release of heat due to the distributed Peltier effect. As can be seen from Figure 2, the difference between the electron concentration and the impurity concentration is small, because the concentration of its own electrons is an order of magnitude smaller. In the insert (Figure 2) it can be seen that in this case the position of the reduced chemical potential better satisfies the condition (5). Thus, in the case of optimization of the parameter Z by temperature along the branch, a one-band approximation is sometimes sufficient for calculations. The distribution of the reduced Joule heat density ql/S and the distributed Peltier effect is shown in Figure 3. The heterogeneity of the branch leads to a redistribution of the Joule heat density, and since the resistivity near the cold end of the branch is higher, the maximum amount of Joule heat is shifted to the cold end of the branch (curve *1*). The distributed Peltier effect also makes its negative contribution (curve *2*), as a result of which the total maximum of heat release approaches the cold end of the branch (curve *3*). Therefore, optimization of the parameter Z in order to increase the thermoelectric efficiency in temperature is ineffective. The estimation of the contribution of the reduced Thomson heat near the cold end of the branch, where the temperature gradient is greatest, gives a value not exceeding 16 W/m.

Increasing the efficiency of thermoelectric energy conversion using the distributed Peltier effect is not limited only to optimizing the efficiency parameter Z, but in addition to sufficiently high values of Z, it is also necessary to maximize the range of variation of the differential thermal EMF module. However, this expansion of the region from the side of large concentrations of charge carriers is limited by

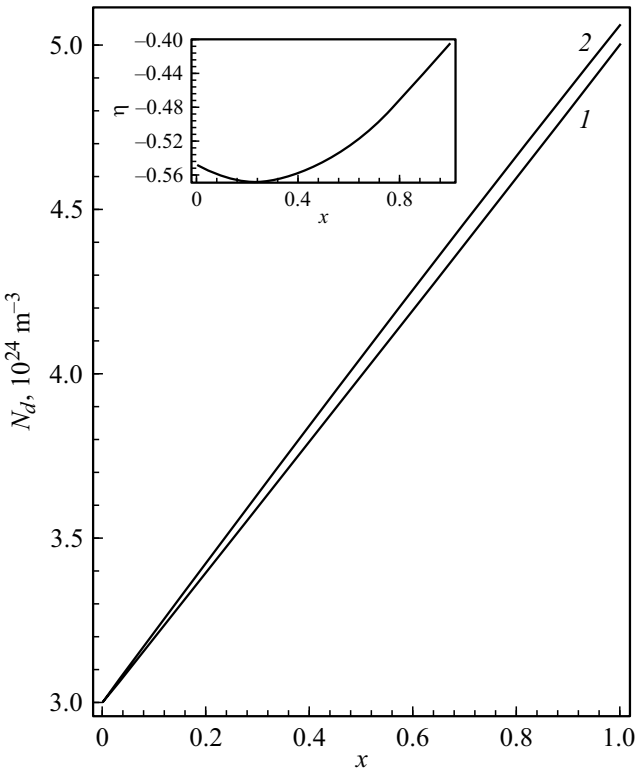

Figure 2. Distribution of impurity concentrations (*1*) and electrons n (*2*) along the branch (in the insert, the distribution of chemical potential along the branch).

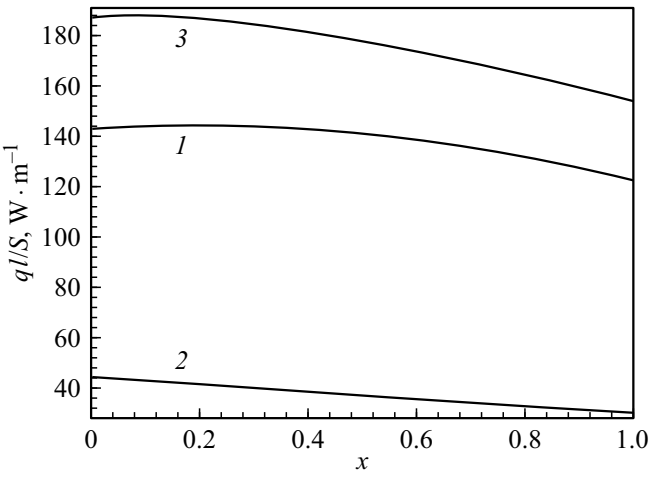

Figure 3. Distribution of the reduced Joule heat density (*1*), distributed Peltier (*2*) and their sum (*3*).

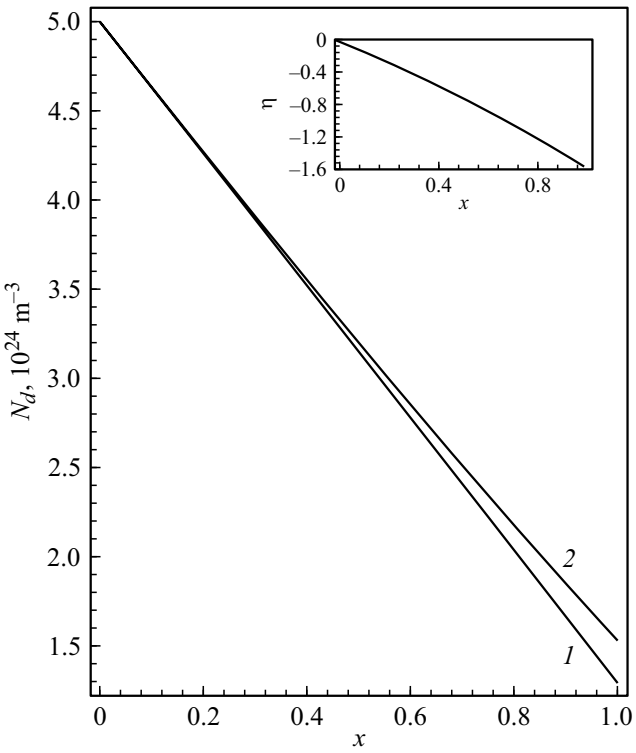

Figure 4. Distribution of impurity concentrations (*1*) and electrons *n* (*2*) along the branch (in the insert, the distribution of chemical potential along the branch).

the fall of the EMF module due to degeneration of charge carriers, and the upper boundary is associated with the maximum achievable value of the differential EMF module, which can be determined only within the two-band model. To carry out the calculation in this case, it is necessary to solve the boundary value problem (13), (14). The thermal EMF calculation showed that the maximum value of the module at 300 K is achieved at an impurity concentration of $N_d(1) = 1.3 \cdot 10^{24}\,\mathrm{m}^{-3}$. The choice of the impurity concentration at the cold end of the branch was made as a result of sorting through different values in a series of solutions to the boundary value problem using a linear distribution. It turned out that the maximum temperature difference was achieved with a linear distribution of the impurity from $N_d(0) = 5 \cdot 10^{24}$ m^{-3} at the cold end to $N_d(1) = 1.3 \cdot 10^{24}$ m^{-3} on hot. It should be noted that neither at the cold end of the branch nor at the hot end is the impurity concentration optimal for the maximum Z at a given temperature. The calculated distribution of the electron concentration (15) is shown in Figure 4. In this case, the difference from the impurity concentration is somewhat greater than in the previous case, since the contribution of own carriers at the hot end of the branch increases. With such a distribution of impurities in the branches, there is a significant redistribution of the Joule and Peltier heat, which contributes to an increase in efficiency (Figure 5).

The minimum achievable temperature at the cold end of the branch with such an impurity distribution is 226 K, i.e. practically coincides with the calculation according to the theory of A.F. Ioffe. The differential thermal EMF module from the cold to the hot end increases only by 1.5 times, and the resistivity by 4.8 times, which significantly differs from the calculation data for a one-band thermoelectric in operation [4]. Based on the calculations made, it can be concluded that one should not rely on full compensation of the Joule heat in a low-temperature thermoelectric. Since linearization has not been carried out in the boundary problem (13), (14) and, accordingly, the use of advanced optimization technique [4] is impossible when solving a nonlinear problem, it remains only to limit ourselves to selecting the type of impurity distribution, achieving maximum temperature reduction. Finding the optimal impurity distribution is a rather difficult task, which, according to -, is apparently even more difficult to implement technologically.

Conclusion

Using a two-band model of a thermoelectric, the boundary thermal problem for a branch of a thermoelectric element is solved. Using examples of different impurity distributions, the temperature field, the reduced chemical potential, and the distribution of heat emissions are calculated. This approach made it possible to analyze in detail the effect of distributed Peltier on the efficiency of thermoelectric cooling.

The conducted research allows us to conclude that:

— in the scope of the two-band standard model of the thermoelectric band structure, a heterogeneous distribution of the donor impurity concentration can be used to increase the efficiency of the *n*- type branch;

— optimization of the carrier concentration to create maximum values of Z at the cold and hot ends and the

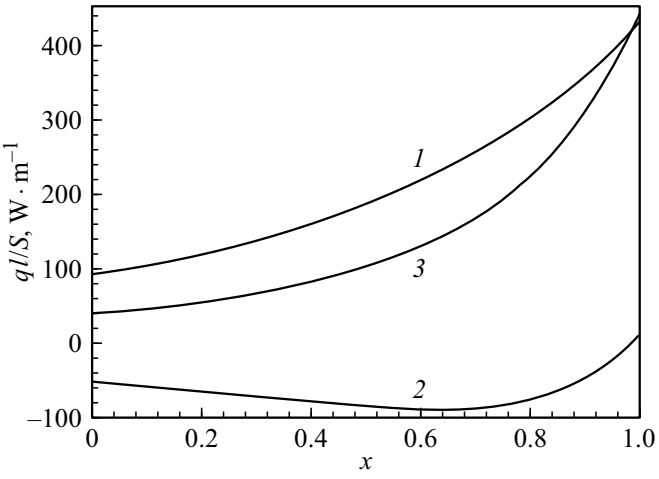

Figure 5. Distribution of the reduced density of Joule heat fluxes (*1*), distributed Peltier (*2*) and their sum (*3*).

linear distribution of the donor impurity concentration along the branch does not lead to an increase in its efficiency from -due to increased heat release of the Joule effect and the distributed Peltier effect near the cold end of the branch;

— the use of a linear distribution of the donor impurity concentration makes it possible to increase the efficiency of the branch transformation both as a result of partial compensation of the Joule effect heat release due to the distributed Peltier effect, and as a result of the redistribution of the Joule heat release density to the hot end of the branch;

— the use of the distributed Peltier effect to increase efficiency is limited by an interval of sufficiently high values of the differential thermal EMF module, which, from the side of the highest impurity concentration, is due to the degeneracy of charge carriers and the appearance of the contribution of own charge carriers for the lowest concentration;

— the optimal distribution of the impurity along the branch is uniquely related to its temperature profile and any change in the thermal load of the branch makes it suboptimal, so its calculation is more of a theoretical task than a practical problem.

Conflict of interest

The author declares that he has no conflict of interest.

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