Contribution of the distributed Peltier effect to the efficiency of the thermoelectric cooler branch

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An attempt is made to calculate the contribution of the distributed Peltier effect to the efficiency of the branch of the thermoelement Z for various types of impurity distribution. For this purpose, the boundary problem of thermal balance in the branch of the thermoelectric element was solved numerically, taking into account the distributed Peltier effect. The case of non-degenerate charge carriers was considered within the framework of the standard two-band model. The parameters of charge carriers were selected close to thermoelectrics based on bismuth and antimony tellurides. As the calculation in the framework of the two-zone model showed, the use of the distributed Peltier effect leads only to partial absorption of Joule heat, which contributes to an increase in the overall efficiency of the branch. In this case, the Z parameter along a significant part of the branch takes values significantly less than the maximum value.

Keywords: thermoelement, Peltier effect, thermoelectric efficiency parameter, standard two-zone model.

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1. Introduction

Idea of using the variable composition of thermoelectrics for increase of conversion efficiency of thermoelectric device, operating in a wide range of temperatures, was initially proposed by A.F. Ioffe [1]. There are at least two ways to increase the efficiency: using the variable charge carrier concentration: optimization of efficiency parameter Z in each point of a branch within operating temperature range [2], and using the distributed Peltier effect [3]. Application of the distributed Peltier effect is considered as one of the prospective ways to increase thermoelectrics efficiency. Implementation of this idea implicates some problems related to mathematical modeling, determination of optimum distribution of charge carriers concentration, resulting in maximum efficiency of the branch, production of branch with optimum distribution of charge carriers concentration. Since the actually used thermoelectrics are doped semiconductors of *n*- and *p*-type, only the main charge carriers are usually considered at optimization. It is assumed that their concentration can be changed using doping with the corresponding impurities within very wide range of impurities concentration, without considering the intrinsic charge carriers. At the same time, the temptation arises to fully compensate Joule heat using 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 2 times higher than on a hot end, while differential thermal EMF module is 4 times lower. In study [5] only the single-sign carriers (electrons, which concentration is defined by a doping impurity concentration) are also used for maintaining the optimum value of Z in PbTe. In study [6] it is noted that materials based on Bi_2Te_3 at higher temperature drop in thermoelement branch have significantly lower general efficiency parameter compared to its maximum value. It is recommended to maintain the efficiency parameter, close to maximum, in each branch point by means of material composition change over the length of thermoelement branch. In review [7] it is noted that determination of optimum profile of impurity inhomogeneity is a complicated mathematical problem, several methods of calculation of the temperature profile of thermoelement branch are specified and technologies of inhomogeneities formation are discussed.

Actual low-temperature thermoelectrics with high efficiency do not have a wide forbidden band, therefore the intrinsic charge carriers [8,9] should also be considered. In this study the attempt was made to calculate a contribution of the distributed Peltier effect to the efficiency of thermoelement branch in the framework of two-band model under various types of impurities distribution along the branch, based on the boundary problem of the thermal balance using the classical statistics. Since at the direct calculation of efficiency parameter Z the contribution of Thomson effect is not considered, this effect was not considered in solving the boundary problem.

2. Calculation procedure

For simplification of the problem solving let's confine with a case of nondegenerate charge carriers and the simplest standard band model. To make the calculation results closer to reality, band parameters correspond to parameters of low-temperature thermoelectric based on bismuth and antimony telluride: forbidden band width $E_g = 0.15\,\text{eV}$, density-of-state effective mass of electrons $m_c^* = 0.45m_0$, holes $m_v^* = 0.69m_0$ [10].

In classical approximation the concentration of electrons and holes is defined with the expressions [11]

$$n = 2\left(\frac{2\pi m_c^* kT}{h^2}\right)^{3/2} e^{\eta_e} = N_c e^{\eta_e}, \tag{1}$$

$$p = 2\left(\frac{2\pi m_v^* kT}{h^2}\right)^{3/2} e^{\eta_h} = N_v e^{\eta_h}, \tag{2}$$

where N_c, N_v — effective number of states of conductivity band and valence band, respectively, η_e, η_h — normalized chemical potential of electrons and holes, respectively. Concentrations of electrons and holes are related to electroneutrality equation

$$n = p + N_d, \tag{3}$$

where N_d is the donor impurity concentration. It is assumed that all impurity atoms are ionized.

Electrical conductivity of electrons $\sigma_n = eU_n n$ and holes $\sigma_p = eU_P p$ as a sum defines total electrical conductivity

$$\sigma = \sigma_n + \sigma_p. \tag{4}$$

Correspondence of results of kinetic coefficients calculation with experimental data can be improved by considering temperature dependencies of charge carriers mobility as $U_n = aT^{-3/2}$, $U_p = bT^{-1.8}$ [10,12], where $a = 617.3\,\text{m}^2\text{K}^{1.5}/\text{B}\cdot\text{c}$, $b = 1449\,\text{m}^2\text{K}^{1.5}/\text{B}\cdot\text{c}$. Concentration dependencies of electrons and holes mobility were not considered. Thermal conductivity of semiconductor [11]

$$\chi = \chi_{\text{ph}} + \left(\frac{k}{e}\right)^2 T\left[2\sigma + \frac{\sigma_n\sigma_p}{\sigma}\left(\frac{E_g}{kT} + 4\right)^2\right], \tag{5}$$

where χ_{ph} — phonon thermal conductivity is considered as dependence $\chi_{\text{ph}} = cT^{-1}$ [9], with coefficient $c = 235\,\text{W/m}$.

Differential thermal EMF of electrons [10]

$$\alpha_n = -\frac{k}{e}(r + 2 - \eta_e), \tag{6}$$

where $r = 0$ (acoustic-phonon scattering), normalized chemical potential of electrons was defined using the formula

$$\eta_e = \ln\frac{n}{N_c}. \tag{7}$$

Differential thermal EMF of holes

$$\alpha_p = \frac{k}{e}(r + 2 - \eta_h), \tag{8}$$

where normalized chemical potential of holes

$$\eta_h = -\left(\frac{E_g}{kT} + \eta_e\right). \tag{9}$$

Total differential thermal EMF

$$\alpha = \frac{\alpha_p\sigma_p + \alpha_n\sigma_n}{\sigma_p + \sigma_n}. \tag{10}$$

Calculation of efficiency parameter $Z = \alpha^2\rho\chi$ as per presented formulas at $T = 300\,\text{K}$ shows that the maximum value $3\cdot 10^{-3}\,\text{K}^{-1}$ is achieved at chemical potential value of $\mu = -0.009\,\text{eV}$ and impurity concentration $N_d = 5\cdot 10^{24}\,\text{m}^{-3}$. As per elementary theory, such efficiency allows to achieve the minimum temperature $T_c = 225\,\text{K}$. At that temperature $Z = 2.95\cdot 10^{-3}\,\text{K}^{-1}$, optimum $\mu = -0.01\,\text{eV}$ and concentration $N_d = 3\cdot 10^{24}\,\text{m}^{-3}$. Naturally, the question arises on optimum impurity concentration in homogeneous branch. The answer can be obtained with solving the boundary problem of the thermal balance

$$\frac{d}{d\xi}\left(\chi\frac{dT}{d\xi}\right) + \frac{Y^2}{\sigma} = 0 \tag{11}$$

with boundary conditions

$$\chi\frac{dT}{d\xi}\bigg|_{\xi=0} = \alpha YT|_{\xi=0},\ T|_{\xi=1} = T_1, \tag{12}$$

where $\xi = x/l$ $(0 < \xi < 1)$, $Y = Il/S$ — optimization parameter [13], l — branch length, S — branch cross section, I — branch current.

Since the boundary problem (11), (12) is non-linear, its solving is possible with numerical methods. Minimization of temperature of the branch cold end should be performed for parameter Y and impurity concentration N_d. In maximum temperature drop mode the optimum concentration for homogeneous branch was $N_d = 3.3\cdot 10^{24}\,\text{m}^{-3}$, minimum achievable temperature on the cold end was 230 K. Calculated distribution of temperature along homogeneous branch is represented with a curve *1* (Fig. 1), that, according to curve *1* (Fig. 2) of temperature gradient, is sufficiently close to parabola. At constant impurity concentration the efficiency parameter Z does not remain constant along the branch (Fig. 3, curve *1*); at first it rises insignificantly, then slightly reduces to the hot end of the branch. Chemical potential also reduces with temperature increase (Fig. 4, curve *1*) to $-0.02\,\text{eV}$. Hence it appears that the homogeneous branch of thermoelement can not be optimum for efficiency parameter over the whole length of the branch within the whole operating temperature range, and composition-inhomogeneous branch should be used for optimization of Z.

Boundary problem of the thermal balance considering distributed Peltier effect should be used for calculation of impurity distribution of inhomogeneous branch:

$$\frac{d}{d\xi}\left(\chi\frac{dT}{d\xi}\right) + \frac{Y^2}{\sigma} - YT\frac{d\alpha}{dn}\frac{dn}{d\xi} = 0 \tag{13}$$

with former boundary conditions (12). Since there is an analytical dependence between electrons concentration and

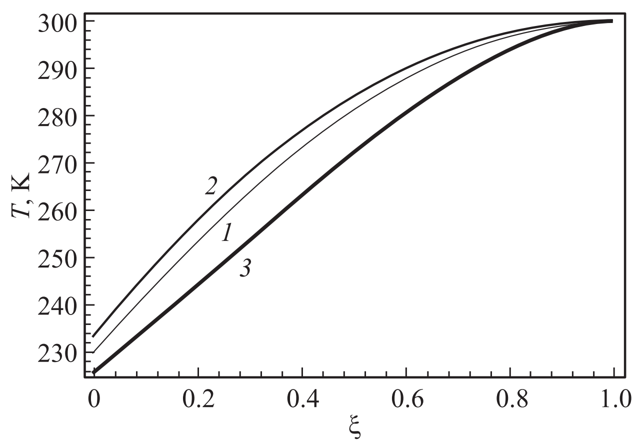

Figure 1. Temperature distribution along: homogeneous branch with optimum impurity concentration $N_d = 3.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *1*), inhomogeneous branch with concentrations $N_d(0) = 3 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 5 \cdot 10^{24}\,\text{m}^{-3}$ (curve *2*), inhomogeneous branch with concentrations $N_d(0) = 5 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 1.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *3*).

impurities concentration

$$n(N_d) = \frac{N_d}{2}\left(\sqrt{1 + \frac{4n_i^2}{N_d^2}} + 1\right), \tag{14}$$

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

$$\frac{dn}{d\xi} = \frac{dn}{dN_d}\,\frac{dN_d}{d\xi}, \tag{15}$$

that allows to solve the boundary problem (12), (13) with different options of impurity distribution along the branch $N_d(\xi)$.

It can be assumed that thermoelectric efficiency parameter can be increased by distribution of impurity concentration within optimum value $N_d(0) = 3 \cdot 10^{24}\,\text{m}^{-3}$ on the cold end to optimum value $N_d(1) = 5 \cdot 10^{24}\,\text{m}^{-3}$ on the hot end. In assumption of linear dependence of impurity concentration between the specified values the solving of the boundary problem (12), (13) with simultaneous optimization for parameter Y demonstrated that instead of expected reduction of minimum achievable temperature on the cold end of the branch, it increases to 234 K (Fig. 1, curve *2*), the temperature dependence curve becomes parabolic, that can be inferred by linear dependence of temperature gradient (Fig. 2, curve *2*). Small increase of temperature gradient near the cold end of the branch compared to the former case results in minimum temperature increase, i.e. reduction of branch efficiency in general. Calculation of efficiency parameter Z shows that linear distribution of impurities near the cold end of the branch gives values, almost identical to homogeneous distribution, and then allows to increase it over the whole length of the branch almost to maximum value (Fig. 3, curve *2*). This result, consisting in increase of the efficiency parameter and general decrease of the branch efficiency, could be paradoxical without considering heat release of the distributed Peltier effect. Thus, the use of inhomogeneous branch with linear increase of impurity concentration allows to increase the efficiency parameter Z over the whole length of the branch, but distributed Peltier heat release results in general reduction of the branch efficiency. This is confirmed with the fact that calculation at reduced interval of concentrations to $N_d(0) = 4 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 5 \cdot 10^{24}\,\text{m}^{-3}$ shows the temperature reduction to 233 K, i.e. the general branch efficiency increase. Obviously it is caused by reduction of the distributed Peltier effect. Calculation of chemical

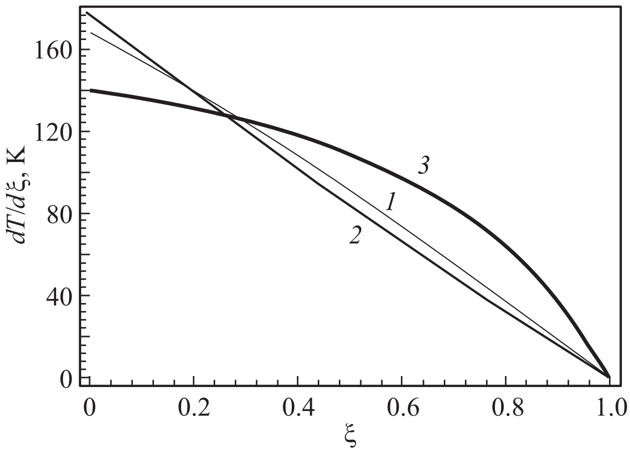

Figure 2. Temperature gradient distribution along: homogeneous branch with optimum impurity concentration $N_d = 3.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *1*), inhomogeneous branch with concentrations $N_d(0) = 3 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 5 \cdot 10^{24}\,\text{m}^{-3}$ (curve *2*), inhomogeneous branch with concentrations $N_d(0) = 5 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 1.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *3*).

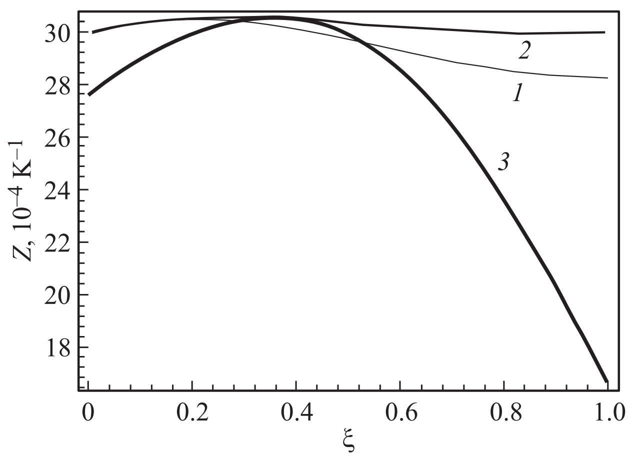

Figure 3. Efficiency parameter distribution along: homogeneous branch with optimum impurity concentration $N_d = 3.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *1*), inhomogeneous branch with concentrations $N_d(0) = 3 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 5 \cdot 10^{24}\,\text{m}^{-3}$ (curve *2*), inhomogeneous branch with concentrations $N_d(0) = 5 \cdot 10^{24}\,\text{m}^{-3}$ and $N_d(1) = 1.3 \cdot 10^{24}\,\text{m}^{-3}$ (curve *3*).

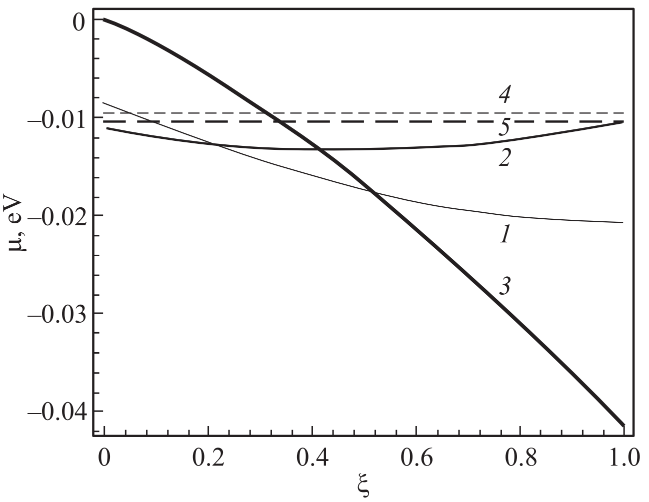

Figure 4. Chemical potential distribution along: homogeneous branch with optimum impurity concentration $N_d = 3.3 \cdot 10^{24}\,\mathrm{m}^{-3}$ (curve *1*), inhomogeneous branch with concentrations $N_d(0) = 3 \cdot 10^{24}\,\mathrm{m}^{-3}$ and $N_d(1) = 5 \cdot 10^{24}\,\mathrm{m}^{-3}$ (curve *2*), inhomogeneous branch with concentrations $N_d(0) = 5 \cdot 10^{24}\,\mathrm{m}^{-3}$ and $N_d(1) = 1.3 \cdot 10^{24}\,\mathrm{m}^{-3}$ (curve *3*). Dash *4* and *5* correspond to the optimum values of chemical potential at 300 and 225 K, respectively.

potential shows (Fig. 4, curve *2*), that the chemical potential is reduced to -0.013 eV in the central part of the branch.

Efficiency increase can be expected with impurity concentration gradient change to reverse. At the same time, for increase of distributed Peltier effect it is necessary to increase the growth area of the differential thermal EMF module to the maximum, that is provided with higher interval of donor impurity change. At the same time, it is obvious that some part of the branch will have efficiency parameter Z that is significantly lower than its maximum value. Extension of the concentration interval from the higher values side is restricted by the thermal EMF module drop due to degeneracy of the charge carriers, and lower limit of electrons concentration is related to maximum value of the differential thermal EMF module, that appears with increase of intrinsic concentration of charge carriers, that can be considered only under two-band model. Selection of impurity concentration change interval was made after solving the series of boundary problems (12), (13) at various values of impurity concentration on the cold end of the branch. It was observed that maximum reduction of the temperature is possible within linear distribution of impurity concentration from $N_d(0) = 5 \cdot 10^{24}\,\mathrm{m}^{-3}$ on the cold end to $N_d(1) = 1.3 \cdot 10^{24}\,\mathrm{m}^{-3}$ on the hot end. The temperature distribution curve *3* (Fig. 1) becomes flat, while temperature gradient curve *3* (Fig. 2) shows that near the cold end of the branch it significantly reduces compared to former cases (Fig. 2, curves *1, 2*). This results in minimum achievable temperature on the cold end at such impurity distribution of 226 K. It is interesting to note that on the cold and hot ends the efficiency parameter (Fig. 3, curve *3*) is significantly less than maximum Z, while the average value for the whole branch length is $2.7 \cdot 10^{-3}\,\mathrm{K}^{-1}$. Maximum value of parameter Z is in the branch region, where the chemical potential curve (Fig. 4, curve *3*) crosses „the efficiency corridor“ $-(0.009{-}0.01)$ eV (curves *4* and *5*). Thus, increase of efficiency of thermoelectric energy conversion using distributed Peltier effect does not result only in increase of the efficiency parameter Z, but it is also required to extend the region of the main charge carriers concentration change to the maximum.

Thus, in maximum temperature drop mode the differential thermal EMF module from the cold end to the hot one increases in 1.5 times, while conductivity — in 4.8, that is significantly different from these calculations for single-band model of thermoelectric [4]. Therefore, under more realistic two-band model only the partial compensation of Joule heat is possible using the distributed Peltier effect [9]. According to the results of the performed calculations, the reduction of the cold end temperature in relation to the types of impurity distribution is not critical, therefore instead of search for the optimum impurity distribution along the branch it is easier to select the distribution, that is easier to perform technologically.

3. Conclusion

The performed study allows to conclude that under two-band model:

– composition-homogeneous branch of thermoelement in the maximum temperature drop mode can not have uniformly high efficiency parameter Z over the whole length of thermoelement branch;

– branch optimization according to maximum values of Z on the cold and hot ends and linear distribution of charge carriers concentration does not result in improvement of its efficiency due to heat release in the distributed Peltier effect;

– distributed Peltier effect can be used for partial compensation of Joule heat and redistribution of the thermal balance along thermoelement branch, that increases efficiency of energy conversion with reduction of average value of efficiency parameter Z.

Conflict of interest

The author declares that he has no conflict of interest.

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