whence it is seen that the lower specific contact resistance, the shorter (in the direction of temperature gradient) thermoelectric legs can be made. Moreover, it has been found that in the manufacture of thermoelectric legs it is desirable to maintain an optimal ratio $l_s/S_s$, where $S_s$ – cross-sectional area of the leg, owing to which a decrease in specific electric contact resistance by a factor of $K$ all other things being equal, leads to a reduction in TEM consumption by a factor of $K^2$. And TEM is known to be most scarce and expensive part of thermoelectric power converter. But an even more important factor that determines the urgency of the miniaturization of thermoelectric energy converters is the need to use them in order to create favorable temperature conditions for the operation of microelectronic components of various-purpose electronic equipment.

However, for the design of thermoelectric energy converters and the correct assessment of their effectiveness, it is of fundamental importance to know the temperature dependences of the thermoelectric characteristics of transient contact layers, and up to now they have only partially been considered in the theory of thermoelectric energy conversion, and in the design of thermoelectric energy converters they have not been fully taken into account, although experimental data on the temperature dependences, for example, of TEM-metal electric contact resistances do exist [4 – 7].

Therefore, *the purpose of this work* is to develop a model of TEM-metal transient contact layer structure with regard to percolation theory and to calculate on its basis the temperature dependences of thermoelectric characteristics of transient contact layers.

## Physical model of TEM-metal transient layer with due regard for percolation effect and its mathematical description

The electrical resistance of transient layer in the case when contact metal or solder does not form intermetallides with TEM and is not a doping impurity for it, which, for instance, is valid for contact structures with anti-diffusion layers [8], can be considered such that consists of three parts: 1) due to diffusion of metal particles in TEM without change in chemical composition and macroscopic characteristics of metal and TEM; 2) due to deviation of TEM surface from the ideal plane; 3) due to the interface between metal and TEM, in particular the potential barrier on this interface. In this paper, we consider only the first part. In our consideration we will take into account the percolation effect [9, 10].

First we consider a physical model which illustrates the necessity of taking into account percolation effect on examination of electrical conductivity and thermal conductivity of transient layer which is a thermoelectric material with metal particles diffused thereto. This model is shown in Fig.1.

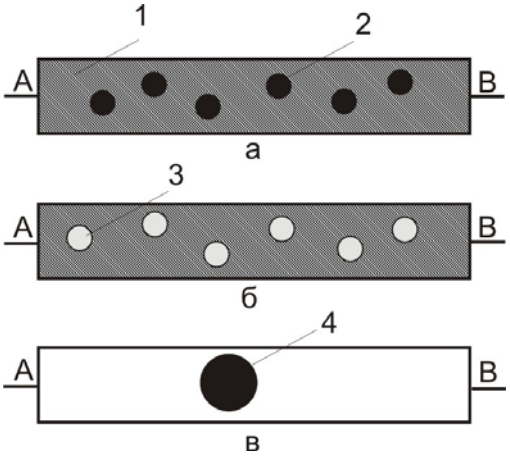


*Fig.1. Physical model that illustrates the need to use percolation theory: a) TEM bar with metal particles; b) TEM bar with vacuum cavities (pores); c) hypothetical evacuated or perfectly dielectric volume comprising a single conducting particle, A,B – electrical contacts,1-TEM, 2-metal particles, 3-vacuum cavities, 4-single conducting particle*

Before considering, incidentally, we note that prior to creation of percolation theory the electrical conductivity and thermal conductivity of the two-phase TEM-metal system shown in Fig. 1a were calculated through the volumetric fraction $v_m$ of metal in it according to the so-called "mixing formulae", which for this case have the form [11]:

$$\sigma(v_m) = \sigma_s(1 - v_m) + \sigma_m v_m . \tag{2}$$

$$\kappa(v_m) = \kappa_s(1 - v_m) + \kappa_m v_m \tag{3}$$

The limited applicability of this formula can be seen from the following physical considerations.

Imagine that at first our system consists of TEM, and part of the material in it is gradually replaced by vacuum cavities (pores) (Fig.1b). From traditional formulae of the type (2) and (3) it follows that the electrical conductivity and (or) thermal conductivity of this system will become zero only when all TEM or other electrically conducting (and, therefore, heat-conducting) material is replaced by vacuum or another ideally non-conducting for electricity and (or) heat phase. But on the other hand, it is clear that the electrical conductivity and (or) thermal conductivity of the "hypothetical" system shown in Fig.1c, in which, a single conducting particle in the volume of the non-conducting phase, that does not touch the electrodes, is also equal to zero (for electrical conductivity this is true, if we do not consider the phenomenon of breakdown of a dielectric or current in vacuum, and for thermal conductivity – if we do not consider the transfer of heat by radiation). From this it is clear that if the leading phase does not form end-to-end connected regions, there must exist a critical volume fraction of vacuum pores, or another non-conducting phase, provided that the conductivity and thermal conductivity of the system exceed zero. This phenomenon is called the percolation phenomenon. It is taken into account by the so-called percolation theory. In accordance with it, the electrical conductivity and thermal conductivity of the two-phase three-dimensional system "TEM-metal" is determined by the following formulae [9,10]:

$$\sigma = 0.25\left\{\sigma_s(2 - 3v_m) + \sigma_m(3v_m - 1) + \sqrt{[\sigma_s(2 - 3v_m) + \sigma_m(3v_m - 1)]^2 + 8\sigma_m\sigma_s}\right\}, \tag{4}$$

$$\kappa = 0.25\left\{\kappa_s(2 - 3v_m) + \kappa_m(3v_m - 1) + \sqrt{[\kappa_s(2 - 3v_m) + \kappa_m(3v_m - 1)]^2 + 8\kappa_m\kappa_s}\right\}, \tag{5}$$

where $v_m$ – the volumetric part of metal in transient layer.

Indeed, suppose that one of the phases does not conduct electricity and heat at all, that is, we assume that $\sigma_s = 0$ and $\kappa_s = 0$. Then formulae (4) and (5) will acquire the form:

$$\sigma = 0.5\sigma_m(3v_m - 1), \tag{6}$$

$$\kappa = 0.5\kappa_m(3v_m - 1). \tag{7}$$

The characteristic feature of formulae (6), (7) is that in conformity with them not only $\sigma = \sigma_m$ and $\kappa = \kappa_m$ at $v_m = 1$, which obviously should be done, but also, unlike traditional formulae (2) and (3), $\sigma = 0$ and $\kappa = 0$ at $0 < v_m \le 1/3$. So, critical volumetric fraction of an absolutely non-conducting phase equal to 2/3 and upon reaching or exceeding which the electrical conductivity and thermal conductivity of a two-phase system with this phase vanish, really exists, as mentioned above.

Therefore, it is clear that, as a result of the percolation phenomenon, the theoretically predicted values of the electrical and thermal contact resistances should be greater than according to the traditional theory of

composites. Note that the limiting values of the electrical conductivity and thermal conductivity of a two-phase system according to formulae (4), (5) are the same as according to formulae (2), (3).

The volumetric metal part $v_m(y)$, which, generally speaking, depends on the normalized to layer thickness $d_0$ of dimensionless coordinate $0 \le y \le 1$ and satisfies the boundary conditions $v_m(0) = 1$, $v_m(1) = 0$, is determined from the diffusion equation of the type [12] with a constant intensity of the source of metal particles as follows:

$$v_m(y) = \frac{(A_m/\gamma_m)\left[1-(1-A)y-Ay^2\right]}{(A_m/\gamma_m)\left[1-(1-A)y-Ay^2\right]+(A_s/\gamma_s)\left[(1-A)y+Ay^2\right]}, \tag{8}$$

where $A_m, A_s, \gamma_m, \gamma_s$ – atomic (molecular) masses of metal and TEM and their densities, respectively. The dimensionless parameter $A$ depends on the mode of contact creation and is determined in this way:

$$A = Qd_0^2/2Dn_0, \tag{9}$$

where $Q$ – the intensity of metal particles entering transient layer, $D$ – coefficient of diffusion of metal particles in TEM, $n_0$ – atomic concentration of metal.

If the uneven distribution of metal particles in the transient layer is preserved, then the electrical conductivity $\sigma_l(y)$ and thermal conductivity $\kappa_l(y)$ of such a layer in accordance with relations (4), (5), (8) depend on the normalized coordinate y, and, therefore, the magnitude of the electrical and thermal contact resistances of such a layer can be evaluated by the formulae:

$$r_{ce} = d_0 \int_0^1 \frac{dy}{\sigma_l(y)}, \tag{10}$$

$$r_{ct} = d_0 \int_0^1 \frac{dy}{\kappa_l(y)}, \tag{11}$$

and the value of thermoEMF by the formula:

$$\alpha = \frac{\int_0^1 \{(\alpha_m/\kappa_m)v_m(y)+(\alpha_s/\kappa_s)[1-v_m(y)]\}dy}{\int_0^1 \{\kappa_m^{-1}v_m(y)+\kappa_s^{-1}[1-v_m(y)]\}dy}. \tag{12}$$

If, however, the distribution of the metal particles in transient layer has been levelled, then the electrical conductivity $\sigma_l(y)$ and thermal conductivity $\kappa_l(y)$ dependent on the normalized coordinate should in this case be replaced by their established values $\sigma_{la}$ and $\kappa_{la}$ obtained by formulae (4) and (5) after substitution in them instead of the coordinate dependent volumetric metal fraction $v_m(y)$ of its established value $v_{ma}$ which is defined as:

$$v_{ma} = \int_0^1 \frac{(A_m/\gamma_m)\left[1-(1-A)y-Ay^2\right]}{(A_m/\gamma_m)\left[1-(1-A)y-Ay^2\right]+(A_s/\gamma_s)\left[(1-A)y+Ay^2\right]}dy. \tag{13}$$

Thus, formulae (10) – (12) will be given by:

$$r_{ce} = \frac{d_0}{\sigma_{la}}, \tag{14}$$

$$r_{ct} = \frac{d_0}{\kappa_{la}}, \tag{15}$$

$$\alpha = \frac{(\alpha_m/\kappa_m)v_{ma} + (\alpha_s/\kappa_s)(1-v_{ma})}{\kappa_m^{-1}v_{ma} + \kappa_s^{-1}(1-v_{ma})}. \tag{16}$$

## Procedure for calculating characteristics of transient contact layer

The calculation starts with theoretical approximation of the temperature dependences of the kinetic coefficients of TEM and metal.

We approximate the kinetic coefficients of TEM. Let at some temperature $T_0$ we know its thermoelectric parameters, namely the thermoEMF $\alpha_{s0}$, the electrical conductivity $\sigma_{s0}$ and the thermal conductivity $\kappa_{s0}$. To construct their temperature dependences, using this data we make the following model assumptions:

1) zone spectrum of carriers in TEM is parabolic and isotropic with temperature independent effective mass;
2) quasi-elastic scattering of carriers in the relevant temperature region occurs on the deformation potential of acoustic phonons with energy independent cross section and mean free path inversely proportional to temperature;
3) lattice thermal conductivity of semiconductor is determined by phonon-phonon scattering with umklapp and is inversely proportional to temperature.

Provided that these assumptions are valid, the carrier scattering index r = –0.5. Taking into account its value, the construction of the necessary temperature dependences on the basis of known general relations [13] is carried out in the following order.

From the relation for the thermoEMF

$$\alpha_{s0} = \frac{k}{e}\left[\frac{2F_1(\eta_0)}{F_0(\eta_0)} - \eta_0\right] \tag{17}$$

we find a reduced chemical potential $\eta_0$ of carrier gas at temperature $T_0$.

Using the condition of constant carrier concentration and their effective mass, from the equation

$$\frac{T^{1.5}F_{0.5}(\eta)}{T_0^{1.5}F_{0.5}(\eta_0)} = 1 \tag{18}$$

we determine the temperature dependence of reduced chemical potential $\eta$ of carrier gas on temperature $T$ in given temperature range.

From the relation

$$\alpha_s = \frac{k}{e}\left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta\right] \tag{19}$$

we determine the temperature dependence of the thermoEMF of TEM.

From the relation

$$L_s(\eta)=\left(\frac{k}{e}\right)^2\left[\frac{3F_2(\eta)}{F_0(\eta)}-\frac{4F_1^2(\eta)}{F_0^2(\eta)}\right] \tag{20}$$

we determine the temperature dependence of the Lorentz number of TEM.

The temperature dependence of the electrical conductivity of TEM for the above model assumptions is determined as:

$$\sigma_s=\sigma_{s0}\left(\frac{T_0}{T}\right)^{1.5}\frac{F_0(\eta)F_{0.5}(\eta_0)}{F_{0.5}(\eta)F_0(\eta_0)}\,. \tag{21}$$

The temperature dependence of the thermal conductivity of TEM with regard to everything said above is determined as:

$$\kappa_s=\sigma_s L_s(\eta)T+\left[\kappa_{s0}-\sigma_{s0}L_s(\eta_0)T_0\right]\frac{T_0}{T}\,. \tag{22}$$

In formulae (17) – (21), $F_m(\eta)$ denote the Fermi integrals that are determined by the following relation:

$$F_m(\eta)=\int_0^\infty x^m\left[\exp(x-\eta)+1\right]^{-1}dx\,. \tag{23}$$

Relations (17) - (22) completely determine the temperature dependences of the thermoEMF, the electrical conductivity and the thermal conductivity of TEM.

Approximation of the temperature dependences of the electrical conductivity, the thermal conductivity and the thermoEMF of metal is done as follows. We assume that in metal, just as in TEM, scattering of free carriers takes place on the deformation potential of acoustic phonons, and in the real temperature region the mean free path of carriers is inversely proportional to temperature. Then, taking into account strong degeneracy of carriers in metal, the temperature dependence of its electrical conductivity will be determined as [14]:

$$\sigma_m=\sigma_{m0}\cdot(T_0/T)\,, \tag{24}$$

and, therefore, taking into account the Wiedemann-Franz relation, the thermal conductivity of the metal $\kappa_m$ will be considered to be temperature independent. We will also consider the thermoEMF of the metal $\alpha_m$ to be independent of temperature. Then, knowing the above mentioned temperature dependences, from relations (8) – (16) we find the temperature dependences of the characteristics of transient contact layer.

## Results of calculation and their discussion

The temperature dependences of the electrical and thermal contact resistances, the thermoEMF and the dimensionless thermoelectric figure of merit of the TEM-metal transient contact layer for bismuth telluride-nickel pair obtained in the framework of the calculation procedure described above, provided that the uneven distribution of the metal atoms in the layer is preserved, are shown in Figs. 2 – 8.

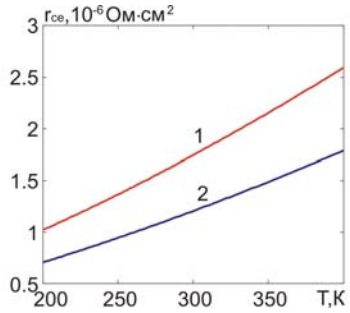


*Fig.2. Temperature dependences of electrical contact resistance with due regard for percolation effect at transient layer thickness of 20 μm: 1 – A=0; 2 – A=1.*

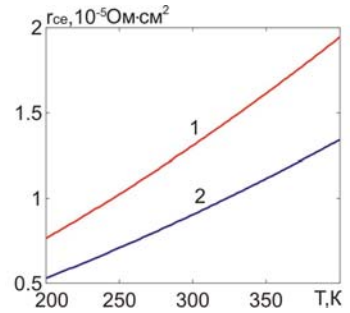


*Fig.3. Temperature dependences of electrical contact resistance with due regard for percolation effect with due regard for percolation effect at transient layer thickness of 150 μm: 1 – A=0; 2 – A=1.*

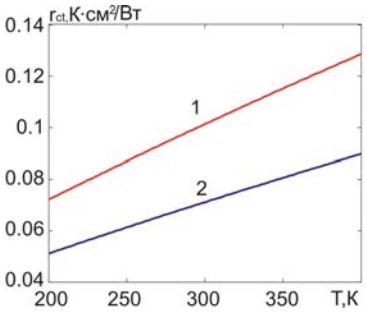


*Fig.4. Temperature dependences of thermal contact resistance with due regard for percolation effect at transient layer thickness of 20 μm: 1 – A=0; 2 – A=1.*

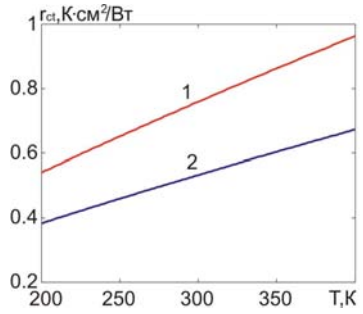


*Fig.5. Temperature dependences of thermal contact resistance with due regard for percolation effect at transient layer thickness of 150 μm: 1 – A=0; 2 – A=1.*

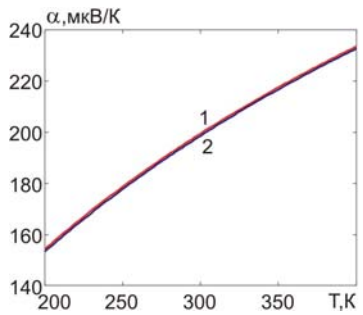


*Fig.6. Temperature dependences of transient layer thermoEMF: 1 – A=0; 2 – A=1.*

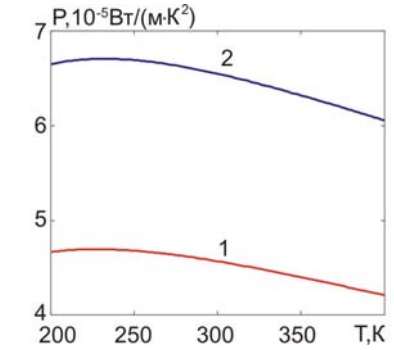


*Fig.7. Temperature dependences of transient layer power factor with due regard for percolation effect: 1 – A=0; 2 – A=1.*

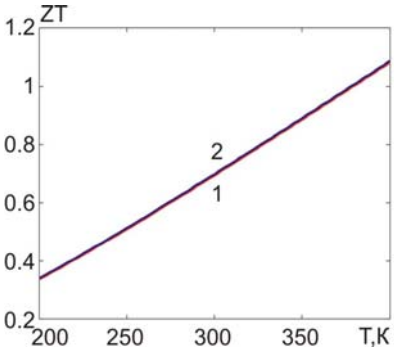


*Fig.8. Temperature dependences of transient layer thermoelectric figure of merit with due regard for percolation effect*
*1 – A=0; 2 – A=1.*

Similar temperature dependences after levelling metal concentration in transient layer are shown in Figs. 9 – 15.

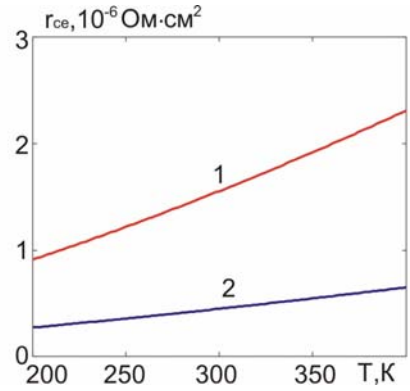


*Fig.9. Temperature dependences of electrical contact resistance with due regard for percolation effect after levelling metal concentration at transient layer thickness of 20 μm:*
*1 – A=0; 2 – A=1.*

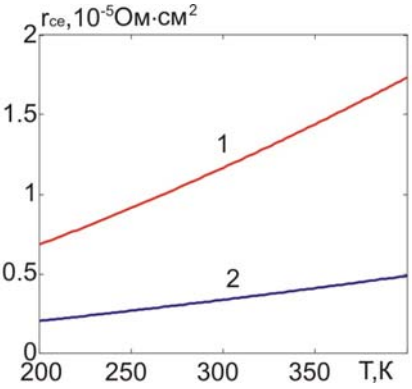


*Fig.10. Temperature dependences of electrical contact resistance with due regard for percolation effect after levelling metal concentration at transient layer thickness of 150 μm:*
*1 – A=0; 2 – A=1.*

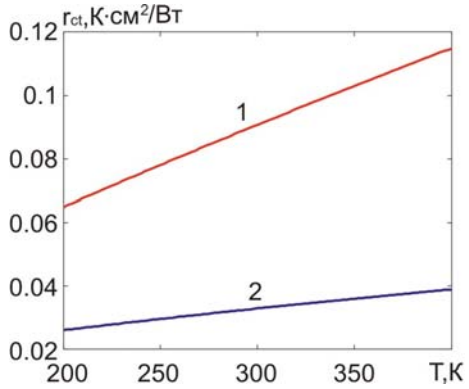


*Fig.11. Temperature dependences of thermal contact resistance with due regard for percolation effect after levelling metal concentration at transient layer thickness of 20 μm:*
*1 – A=0; 2 – A=1.*

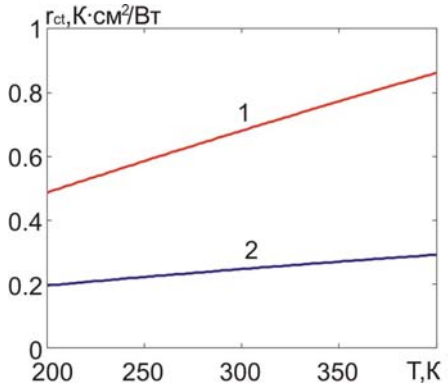


*Fig.12. Temperature dependences of thermal contact resistance with due regard for percolation effect after levelling metal concentration at transient layer thickness of 150 μm:*
*1 – A=0; 2 – A=1.*

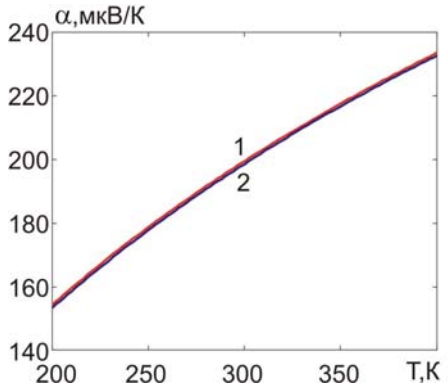


*Fig.13. Temperature dependences of transient layer thermoEMF after levelling metal concentration: 1 – A=0; 2 – A=1.*

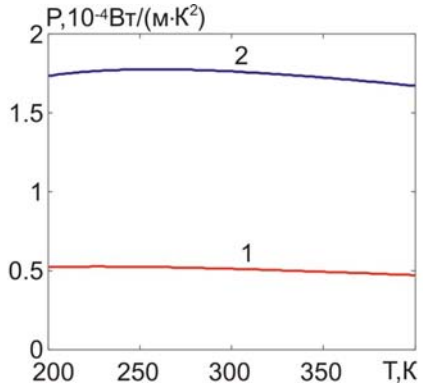


*Fig.14. Temperature dependences of transient layer power factor with due regard for percolation effect after levelling metal concentration: 1 – A=0; 2 – A=1.*

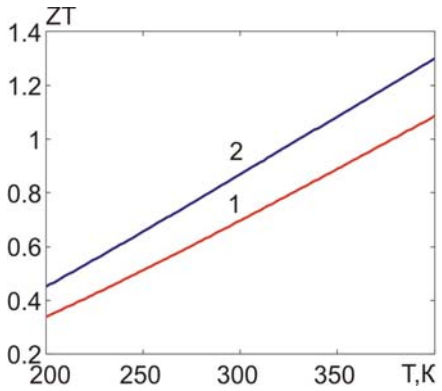


*Fig.15. Temperature dependences of transient layer dimensionless thermoelectric figure of merit with due regard for percolation theory after levelling metal concentration:*
*1 – A=0; 2 – A=1.*

When plotting, the following material parameters for 300K were taken: $\sigma_m$=1.25·10$^5$ S/cm, $\sigma_s$=800 S/cm, $\kappa_m$=92 W /(m·K), $\kappa_s$=1.4 W /(m·K), $\alpha_m$= – 23 μV/K, $\alpha_s$= 200 μV/K, and, besides, $A_m$=58.5, $A_s$=801, $\rho_m$=9100 kg/m$^3$, $\rho_s$=7700 kg/m$^3$. It can be seen from the figures that in the temperature range studied, the electrical and thermal contact resistances, the thermoEMF, and the dimensionless thermoelectric figure of merit of transient layer increase, and the power factor has a maximum in the range of 200 - 250 K. Such temperature dependences can be explained by an increase in the resistivities of metal and semiconductor, a decrease in their thermal conductivity, and an increase in the thermoEMF of semiconductor with a rise in temperature. With an increase in the thickness of transient layer, the electrical and thermal contact resistances increase in proportion to this thickness. The presence of a maximum in the temperature dependence of power factor is explained by two competing processes: an increase in the thermoEMF and a decrease in TEM electrical conductivity with a rise in temperature. It should be noted that the thermoEMF of transient layer is mainly determined by the semiconductor due to the fact that thermal conductivity of metal is significantly greater than thermal conductivity of semiconductor.

In addition, it can be seen from the figures that with increasing parameter A, that is, the intensity of metal atoms entering transient layer, the thermal and electrical contact resistances, as well as the thermoEMF decrease, and the power factor and the dimensionless thermoelectric figure of merit increase. On the whole, in the studied ranges of temperature, the intensity of metal entering transient layer, and the transient layer thickness, the electrical contact resistance varies from 7·10$^{-7}$ to 1.9·10$^{-5}$ Ohm·cm$^2$, the thermal contact resistance – from 0.052 to 0.98 K·cm$^2$/W, the thermoEMF – from 155 to 235 μV/K, the power factor – from 4.2·10$^{-5}$ to 6.8·10$^{-5}$ W/(m·K$^2$), the dimensionless thermoelectric figure of merit – from 0.35 to 1.08. Thus, the electrical and thermal contact resistances, predicted with due regard for percolation theory, are, as expected, essentially higher, and the power factor and the dimensional thermoelectric figure of merit – essentially lower than without regard to this theory. Taking into account the percolation theory does not affect the predicted temperature dependence of the thermoEMF of transient contact layer.

It is also seen from the figures that after levelling metal concentration in the bulk of transient layer, the anticipated values of the electrical and thermal contact resistances at all temperatures decrease, the thermoEMF is practically unvaried, and the power factor and the dimensionless thermoelectric figure of merit increase as compared to the case of uneven distribution, but not so essentially as without regard to percolation theory.

As regards the effect of parameter *A*, that is, the intensity of metal entering transient layer, on the predicted thermoelectric properties of transient layer, both in the case of uneven and uniform distribution, with due regard for percolation theory the same tendency is preserved as without regard to this theory. The sole exception is power factor. Unlike the case of uneven distribution of concentration, when it has a maximum both at *A*=0 and at *A*=1, after its levelling in the temperature range under study the power factor

has a maximum only at $A$=1.

In general, in the studied ranges of temperature, the intensity of metal entering transient layer and the thickness of transient layer after levelling metal concentration the electrical contact resistance varies from $2.5\cdot10^{-7}$ to $1.75\cdot10^{-5}$ Ohm·cm$^2$, the thermal contact resistance – from 0.025 to 0.85 K·cm$^2$/W, the thermoEMF – from 155 to 235 V/K, the power factor – from $5\cdot10^{-5}$ to $1.9\cdot10^{-4}$ W/(m·K$^2$), the dimensionless thermoelectric figure of merit – from 0.35 to 1.3. Thus, after the concentration is levelled, the electrical contact resistance drops by a factor of 1.12 – 3.6, the thermal contact resistance decreases by a factor of 1.15 – 2.08, the thermoEMF is practically unvaried, the power factor grows by a factor of 1.19 – 2.79, the dimensionless thermoelectric figure of merit grows maximum 1.2 times. Note that though for thermoelectric contact structures such characteristics thereof as power factor and dimensionless thermoelectric figure of merit do not have self-importance in terms of designing thermoelectric power converters, they are useful for the integral quality evaluation of these structures.

## Effect of contact resistance on the efficiency of thermoelectric generator module

The above temperature dependences of the electrical and thermal contact resistances were used to calculate the efficiency of thermoelectric generator modules with the height of thermoelectric legs 3 and 1.5 mm, respectively. The calculations were performed by methods of object-oriented simulation in Comsol Multiphysics software environment.

For this purpose, a physical model shown in Fig.16 was considered.

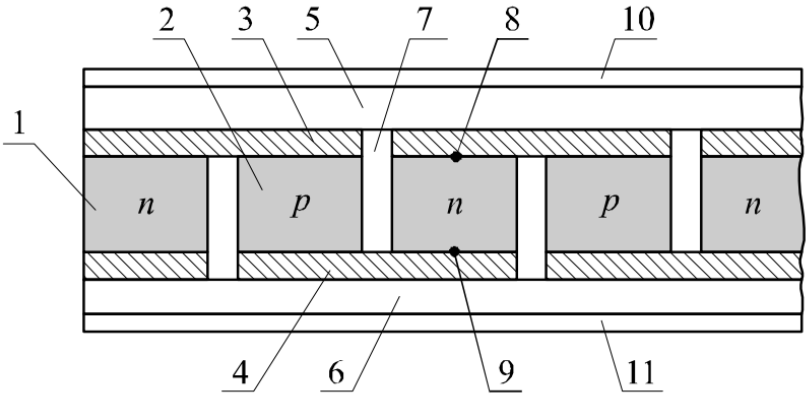


*Fig. 16. Physical model of thermoelectric generator module.*
*1 – n-type leg; 2 – p-type leg; 3, 4 – electrical interconnects;*
*5, 6 – ceramic plates; 7 – gas; 8, 9 – electrical contacts between legs and interconnect plates;*
*10 – thermal contact between ceramic plate and hot thermostat;*
*11 – thermal contact between ceramic plate and cold thermostat.*

The distribution of temperature and electrical potential in the module was found from the system of differential equations with respect to temperature $T$ and electrochemical potential $U$. These equations were obtained on the basis of the law of conservation of energy which is given by the following two equations:

$$\nabla\vec{w} = 0\,, \tag{25}$$

$$\vec{w} = \vec{q} + U\vec{j}\,. \tag{26}$$

In formulae (25) and (26), $\vec{j}$ – electric current density, $\vec{q}$ – heat flux density:

$$\vec{q} = -\kappa\nabla T + \Pi\vec{j}\,, \tag{27}$$

where Π is the Peltier coefficient; κ is thermal conductivity.

$$\Pi = \alpha T, \tag{28}$$

where α is the Seebeck coefficient, T is temperature.

The electric current density is found from the equation

$$\vec{j} = -\sigma\nabla U - \sigma\alpha\nabla T \quad \vec{j} = -\sigma\nabla U - \sigma\alpha\nabla T, \tag{29}$$

where σ is electrical conductivity.

Substituting (26), (27) into (25), we obtain

$$-\nabla(\kappa\nabla T) + (\nabla\Pi + \nabla U)\vec{j} = 0 \quad -\nabla(\kappa\nabla T) + (\nabla\Pi + \nabla U)\vec{j} = 0. \tag{30}$$

From expression (30), using (28) and (29), we obtain the following equation to find the distributions of temperature and potential:

$$-\nabla\left[\left(\sigma\alpha^2 T + \kappa\right)\nabla T\right] - \nabla(\sigma\alpha T\nabla U) - \sigma\left[(\nabla U)^2 + \alpha\nabla T\nabla U\right] = 0\,. \tag{31}$$

To obtain the second equation, we will use the law of conservation of electrical charge:

$$\nabla\vec{j} = 0 \quad div\,\vec{j} = 0. \tag{32}$$

Substituting (29) into (32), we obtain the following equation:

$$\nabla(\sigma\alpha\nabla T) + \nabla(\sigma\nabla U) = 0 \quad -\nabla(\sigma\alpha\nabla T) - \nabla(\sigma\nabla U) = 0. \tag{33}$$

System (31), (33) is a system of differential equations with variable second-order partial differential coefficients, which describes the distribution of temperature and potential in an inhomogeneous thermoelectric medium. A feature of the system of equations (31), (33) is that the parameters α, σ, κ depend on the spatial coordinates *x, y, z* both directly and implicitly through the temperature *T* (*x, y, z*). This leads to the fact that it becomes inevitable to use numerous computer methods to solve equations of this kind.

In a computer model, the thermoelectric field is described by a two-element column matrix in the functional space of twice differentiable functions, namely, the coordinate dependences of temperature and potential:

$$M = \begin{pmatrix} T(x,y,z) \\ U(x,y,z) \end{pmatrix}. \tag{34}$$

Matrix M satisfies one matrix differential equation

$$\nabla(c\nabla M) = f \quad -\nabla(-c\nabla M) = f, \tag{35}$$

whose components are equations (31) and (33) if the matrix nonlinear coefficients of equation (35) have the

form

$$c = \begin{pmatrix} \sigma\alpha^2 T + \kappa & \sigma\alpha T \\ \alpha\sigma & \sigma \end{pmatrix}, f = \begin{pmatrix} \sigma\left[(\nabla U)^2 + \nabla T \nabla U\right] \\ 0 \end{pmatrix}. \quad (36)$$

A system of equations of the form (35) with allowance for (36) is solved for each of the layers that make up the thermoelectric module. For this, we additionally introduce the boundary conditions for the continuity of temperature, electric potential, heat flux, and electric current density at the boundaries of the layers. In addition, for reasons of optimality of the conditions under which the thermoelement operates, and which are determined from the requirement to achieve the maximum value of the efficiency, the potentials on the switching electrodes and the temperatures of the "hot" and "cold" thermostats are set. Therefore, the potentials on the switching electrodes of one of the legs are 0 and 0.0573 V, on the second - 0.0573 and 0.1146 V, and the temperatures of the "cold" and "hot" thermostats are 273 and 573 K, respectively.

The impact of the electrical and thermal contact resistances is taken into account in the physical model in the framework of two approaches. The first is that the contact layer is not explicitly introduced into the physical model, but its electrical conductivity and thermal conductivity are considered to be known from experiment or, in this case, temperature functions preliminarily calculated by calculation. Then, the proportionality of the electrical and thermal contact resistances to the layer thickness is taken into account. The second approach is that a contact layer with temperature-dependent thermal conductivity and electrical conductivity, taking into account its thickness, is explicitly introduced into the physical model. The thermoEMF of the contact layer at this stage of research is not taken into account.

Such mathematical description allows solving the above described system of equations for temperature and potential in Comsol Multiphysics simulation environment. The results of solving Eq.(11) are three-dimensional temperature and electrical fields in given geometry of thermoelectric module. Their examples for one thermoelement which is part of the module with the height of leg 3 mm are shown in Figs. 16, 17. Knowing these fields, it is easy to calculate the basic energy characteristics of the module.

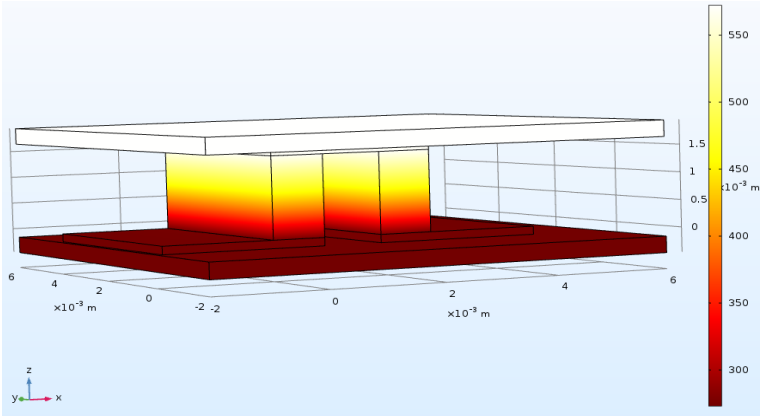


*Fig.17. Temperature field in thermoelement*

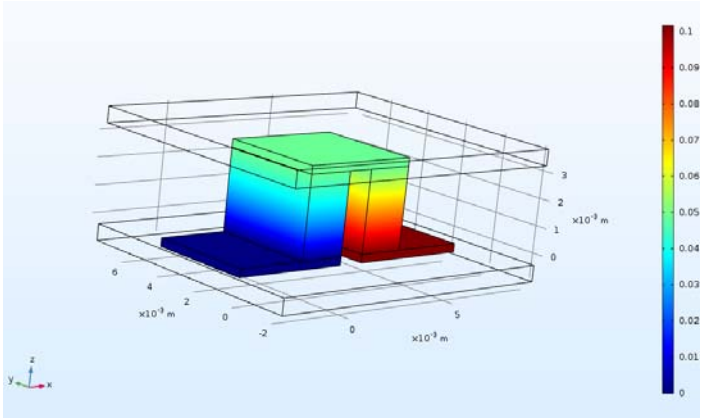

*Fig.18.Electric potential distribution in thermoelement*

The results of these calculations are presented in Figs.19 – 22.

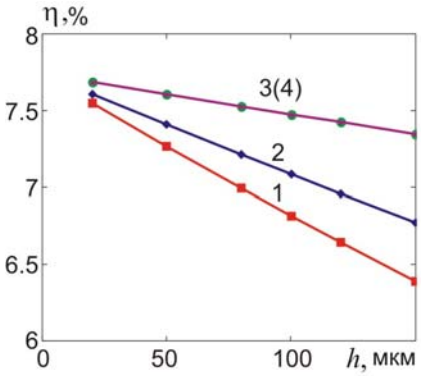


*Fig.19. Dependence of generator module efficiency with the height of leg 3 mm on transient layer thickness for the case when contact resistance is considered to be a lumped parameter:1 – A=0, the distribution of metal atoms in transient layer is uneven; 2 – A=1, the distribution of metal atoms in transient layer is uneven; 3 – A=0, the distribution of metal atoms in transient layer is uniform;4 – A=1, the distribution of metal atoms in transient layer is uniform*

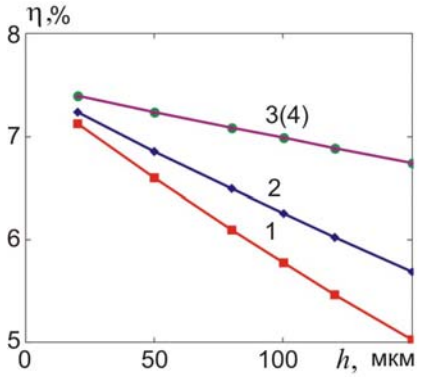


*Fig.20. Dependence of generator module efficiency with the height of leg 1.5 mm on transient layer thickness for the case when contact resistance is considered to be a lumped parameter:1 – A=0, the distribution of atoms in transient layer is uneven; 2 – A=1, the distribution of metal atoms in transient layer is uneven; 3 – A=0, the distribution of metal atoms in transient layer is uniform;4 – A=1, the distribution of metal atoms in transient layer is uniform*

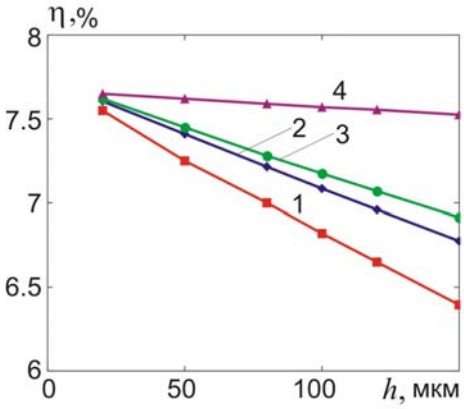


*Fig.21. Dependence of generator module efficiency with the height of leg 3 mm on transient layer thickness for the case when transient layer is explicitly introduced into model:1 – A=0, the distribution of metal atoms in transient layer is uneven; 2 – A=1, the distribution of metal atoms in transient layer is uneven; 3 – A=0, the distribution of metal atoms in transient layer is uniform;4 – A=1, the distribution of metal atoms in transient layer is uniform*

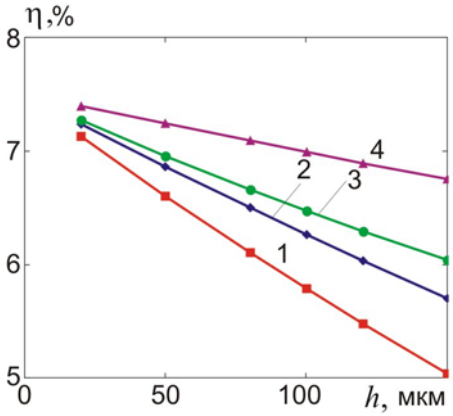


*Fig.22. Dependence of generator module efficiency with the height of leg 1.5 mm on transient layer thickness for the case when transient layer is explicitly introduced into model:1 – A=0, the distribution of metal atoms in transient layer is uneven; 2 – A=1, the distribution of metal atoms in transient layer is uneven; 3 – A=0, the distribution of metal atoms in transient layer is uniform;4 – A=1, the distribution of metal atoms in transient layer is uniform*

Note that in this case, just as in the absence of clusters in transient layer, its thermoEMF was considered to be zero.

It can be seen from the figures that in this case, just as in the absence of clusters, the efficiency of the thermoelement in the mode of electric energy generation is maximum when the distribution of metal atoms in transient layer is uniform. In addition, other things being equal, it is the greater, the greater the intensity of the source from which the metal enters transient layer. In the case of uneven distribution of metal atoms in transient layer, the efficiency decreases with increasing transient layer thickness the more, the smaller the height of the thermoelectric leg. However, the efficiency value is somewhat reduced as compared to the case when there are no clusters in transient layer. In general, in the considered range of thermoelectric leg heights and layer thicknesses, the efficiency changes from 5% to 7.5% when the contact layer is explicitly introduced into the model, and from 5 to 7.4% when the contact resistance is considered to be a lumped parameter. In the case when transient layer is introduced into model, the efficiency after levelling the distribution of metal atoms in transient layer essentially depends on the intensity of the source from which a steady-state diffusion of metal to TEM occurs.

## Conclusions

1. With due regard for percolation effect, the temperature dependences of the electrical and thermal contact resistances, the thermoEMF, the power factor and the thermoelectric figure of merit of bismuth telluride-nickel transient contact layers were calculated on the assumption that carrier scattering in semiconductor and metal occurs on the deformation potential of acoustic phonons, the thermal conductivity of metal is determined by electron gas, and the lattice thermal conductivity of semiconductor – by phonon-phonon scattering with umklapp. In this case it was believed that nickel does not form new phases with bismuth telluride.
2. It is shown that both with uneven and uniform distribution of metal atoms in transient layer, the electrical and thermal contact resistances, the thermoEMF and the dimensionless thermoelectric figure of merit of transient layer are growing functions of temperature and the intensity of metal atoms entering transient layer during contact creation.
3. Power factor in the temperature range under study is a growing function of the intensity of metal atoms entering transient layer, and at the same time has a maximum on the temperature dependence in case of uneven distribution of metal atoms in transient layer. However, at low intensities of metal atoms entering transient layer it becomes a monotonically decreasing function of temperature in case of levelling the distribution of the concentration of metal atoms in transient layer.

4. In the case of uneven distribution of metal atoms in the temperature range of 200 – 400 K, the intensity of metal atoms entering transient layer, which corresponds to a change in parameter *A* from 0 to 1 and the thickness range of transient layer from 20 to 150 μm, the electrical contact resistance changes from $7 \cdot 10^{-7}$ to $1.9 \cdot 10^{-5}$ Ohm·cm$^2$, the thermal contact resistance – from 0.052 до 0.98 K·cm$^2$/W, the thermoEMF – from 155 to 235 μV/K, the power factor – from $4.2 \cdot 10^{-5}$ до $6.8 \cdot 10^{-5}$ W/(m·K$^2$), the dimensionless thermoelectric figure of merit – from 0.35 до 1.08.
5. After levelling the distribution of the concentration of metal atoms in transient layer, the electrical contact resistance decreases by a factor of 1.12 – 3.6, the thermal contact resistance decreases by a factor of 1.15 – 2.08, the thermoEMF is practically unvaried, the power factor increases by a factor of 1.19 – 2.79, the thermoelectric figure of merit grows maximum by a factor of 1.2 as compared to the case of uneven distribution.
6. Studies of the effect of transient contact layer with clusters on the efficiency of thermoelement in generation mode have shown that, all other things being equal, if the influence of the thermoEMF of transient layer is ignored, in the considered range of thermoelectric leg heights and layer thicknesses in the case when a contact layer is explicitly introduced into the model, the efficiency varies from 5 to 7.5%. However, if contact resistance is considered to be a lumped parameter, the efficiency changes from 5 to 7.4%. In the case when transient layer is introduced into the model, the efficiency after levelling the distribution of metal atoms in transient layer essentially depends on the intensity of the source from which steady diffusion of metal into TEM occurs, whereas in the case when contact resistance is considered to be a lumped parameter, this dependence is weak.

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# ПРО ТЕМПЕРАТУРНІ ЗАЛЕЖНОСТІ ТЕРМОЕЛЕКТРИЧНИХ ХАРАКТЕРИСТИК ПЕРЕХІДНОГО ШАРУ ТЕЛУРИД ВІСМУТУ МЕТАЛ З УРАХУВАННЯМ ЯВИЩА ПЕРКОЛЯЦІЇ

*Розрахунковим шляхом отримано основні співвідношення, які визначають температурні залежності термоелектричних характеристик перехідних контактних шарів термоелектричний матеріал-метал з урахуванням явища перколяції. Конкретні кількісні результати та графіки температурних залежностей електричного та теплового контактних опорів, термоЕРС, фактору потужності та безрозмірної термоелектричної ефективності перехідного контактного шару наведено для контактної пари телурид вісмуту – нікель. Встановлено, що у температурному інтервалі 200-400 К за умови збереження нерівномірного розподілу частинок металу у перехідному шарі і його товщини в діапазоні 20-150 мкм електричний контактний опір змінюється від $7\cdot10^{-7}$ до $1.9\cdot10^{-5}$ Ом·см$^2$, тепловий контактний опір – від 0.052 до 0.98 К·см$^2$/Вт, термоЕРС – від 155 до 235 мкВ/К, фактор потужності – від $4.2\cdot10^{-5}$ до $6.8\cdot10^{-5}$ Вт/(м·К$^2$), безрозмірна термоелектрична ефективність – від 0.35 до 1.08. Після вирівнювання концентрації електричний контактний опір спадає у 1.12 – 3.6 рази, тепловий контактний опір спадає у 1.15 – 2.08 рази, термоЕРС практично не змінюється, фактор потужності зростає у 1.19 – 2.79 рази, безрозмірна термоелектрична ефективність зростає максимально у 1.2 рази. Бібл. 14, рис. 22.*

**Ключові слова:** контакт термоелектричний матеріал – метал, приконтактний перехідний шар, електричний контактний опір, тепловий контактний опір, термоЕРС, теорія протікання.

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# О ТЕМПЕРАТУРНОЙ ЗАВИСИМОСТИ ТЕРМОЭЛЕКТРИЧЕСКИХ ХАРАКТЕРИСТИК ПЕРЕХОДНОГО СЛОЯ ТЕЛЛУРИДА ВИСМУТА МЕТАЛЛ С УЧЕТОМ ЯВЛЕНИЯ ПЕРКОЛЯЦИИ

*Расчетным путем получены основные соотношения, определяющие температурные зависимости термоэлектрических характеристик переходных контактных слоев термоэлектрический материал-металл с учетом явления перколяции. Конкретные количественные результаты и графики температурных зависимостей электрического и теплового контактных сопротивлений, термоЭДС, фактора мощности и безразмерной термоэлектрической эффективности переходного контактного слоя приведены для контактной пары теллурид висмута - никель. Установлено, что в температурном интервале 200-400 К при условии сохранения неравномерного распределения частиц металла в переходном слое и его толщины в диапазоне 20-150 мкм электрический контактное сопротивление меняется от $7 \cdot 10^{-7}$ до $1.9 \cdot 10^{-5}$ Ом · см2, тепловое контактное сопротивление - от 0.052 до 0.98 к·см$^2$/Вт, термоЭДС - от 155 до 235 мкВ/К, фактор мощности - от $4.2 \cdot 10^{-5}$ до $6.8 \cdot 10^{-5}$Вт/(м·К$^2$), безразмерная термоэлектрическая эффективность - от 0.35 до 1.08. После выравнивания концентрации электрический контактное сопротивление приходит в 1.12 - 3.6 раза, тепловой контактное сопротивление приходит в 1.15 - 2.08 раза, термоЭДС практически не меняется, фактор мощности возрастает в 1.19 - 2.79 раза, безразмерная термоэлектрическая эффективность возрастает максимально в 1.2 раза. Библ. 14, рис. 22.*

**Ключевые слова:** контакт термоэлектрический материал – металл, приконтактный переходной слой, электрический контактное сопротивление, тепловой контактное сопротивление, термоЭДС, теория протекания.

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# EFFECTIVE MEDIUM THEORY FOR THE THERMOELECTRIC PROPERTIES OF COMPOSITE MATERIALS WITH VARIOUS PERCOLATION THRESHOLDS

*In the work, a modified effective medium theory is constructed for calculating the effective properties of thermoelectric composites with different values of percolation thresholds. It is shown that even at concentrations beyond the critical region, the threshold value is essential for determining the effective properties. Two fundamentally different cases of a set of local properties of the composite are considered. In one of these cases, the conductivity and thermal conductivity of one of the phases is simultaneously greater than the conductivity and thermal conductivity of the other phase. The second, anomalous case, when the electrical conductivity of the first phase ($\sigma_1$) is greater than that of the second, but the thermal conductivity of the first phase is less than that of the second, shows unusual concentration behavior of effective conductivity, i.e. with an increase in the well-conducting phase, the effective conductivity $\sigma_e$ shows a decrease (rather than growth as in the standard case, see Fig. 1a), which at $p \approx \tilde{p}_c$ goes over to growth. Bibl. 5, Fig. 5.*

**Key words**: thermoelectricity, percolation theory, percolation thresholds, composites, effective properties

## Introduction

The calculation of effective values for composite materials is a complex problem that cannot be solved in the general case. Solutions are also possible as an exceptional case, for one-dimensional inhomogeneity, or for strictly periodic structures, for example, for spherical inclusions of one phase in the matrix of the other. Even in the case of simple-shaped inclusions, the solutions are rather bulky expressions of infinite series that are difficult to analyze [1 – 7].

To describe randomly inhomogeneous environment with randomly located inclusions of one phase in the other, there are approximate methods that allow one to approximately describe the concentration behavior of effective coefficients with different accuracy. For example, the Maxwell approximation [8] allows describing the concentration behavior of effective coefficients accurate to the first degree of concentration.

For the entire range of concentrations, a good approximation is the Bruggeman – Landauer approximation [9, 10], which is a self-consistency method (effective medium approximation).

The lack of the Bruggeman-Landauer approximation is the percolation threshold fixed in this approximation. With a large difference in the physical properties of the phases, for example, when the conductivity of the first phase $\sigma_1$ is much larger than that of the second $\sigma_2 \cdot (\sigma_1/\sigma_2) >> 1$, a sharp change in