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THE SYMMETRY ANALYSIS AND OPTIMUM CONCEPTION FOR THERMOELECTRIC CONVERTERS WITH NON-UNIFORM LEGS

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The symmetry analysis was applied to the thermoelectric converters of energy (generators (TEG), coolers (TEC), and heaters (TEH)) with non-uniform legs (inhomogeneous, segmented, graded, functionally graded, and of non- regular shape). The concept of symmetry was used in a widen sense that includes space order and proportion, harmony, synergism, and also all their infringements in modules. The analysis was carried out within four structural levels including ones for the materials, the legs, the thermocouples, and the group of converters of energy. The increase in Z for the converters with non-uniform legs was shown to be due to the additional contributions of "bulk" thermoelectric effects in a combination with the decrease of the contribution of irreversible processes (Joule's heat emission and heat conductivity) at the breakdown of the symmetry of the legs. The crystallographic symmetry of thermoelectric materials and the own symmetry of the legs and modules providing the increase of the figure of merit Z for converters was specified.

For the group of converters with non-uniform legs the modified tetratomic classification (TEG^a, TEG^b, TEC, and TEH) was proposed. The general rule for the proper set of the legs in thermoelectric converters was developed. Some new effects observed in inhomogeneous legs and on their borders as well as the practical application of inhomogeneous legs for cooling, domestic heating, waste heat utilization and power generation were discussed (Grant of Russian Basic Research Foundation № 06-08-00084).

Keywords: thermoelectric converters, thermocouples, thermoelectric effects, crystallographic symmetry.

Introduction

As is well known, the use of the non-uniform legs (inhomogeneous, segmented, graded, functionally graded, and of non- regular shape) in thermoelectric converters of energy may increase up to 10- 20 % and more the figure of merit Z and the power characteristics of thermoelectric generators (TEG) [1], coolers (TEC) [2-3] and heaters (TEH) [4]. As it was shown earlier, the increase in Z is due to the additional contributions of "bulk" thermoelectric effects in cooperation with the "contact" ones [5-8]. Both effects are of the same physical nature, but the first are due to variation of Seebeck coefficient α along the length of n- and p- legs ($\Delta\alpha_n$ and $\Delta\alpha_p$), and the last results from the drop of Seebeck coefficient α at the joint of a thermocouple ($\Delta\alpha_{np}$) [1,7] [1].

Shows some examples of distribution of Seebeck coefficient α along the length of the legs and at the joints of thermocouples [6-9]. Usually, the drop of Seebeck coefficient α along the legs is man- made or arises spontaneously due to the secondary effects in modules working continuously under the standing electric field E and the drop of temperature ΔT. For example, the spontaneous heterogeneity of legs arises because of the dependencies of Seebeck coefficient α on temperature

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[1] Some data on the discovery of "bulk" and "contact" thermoelectric effects are given in the Appendix.

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(the Thomson effect), thermo- and electro- diffusion of the dopants and so on [7-10]. As a rule, the “contact” effects precede the spontaneous “bulk” ones in some times [5-9]

$$\Delta\alpha_{\mathrm{n}}, \Delta\alpha_{\mathrm{p}} \leq (0, 1\text{- }0, 2)\ \Delta\alpha_{\mathrm{np.}} \tag{1}$$

For this reason, just the large “contact” effects were used in thermoelectric converters of energy for the first time [1]. Then in due course, the researchers began to make use of the “bulk” thermoelectric effects as well. According to [9], Schlegel and Ioffe seem to be the first researchers who used the “bulk” thermoelectric effects and non-uniform legs to improve the metallic thermocouples and semiconductor TEG respectively. Currently, the application of the non-uniform legs in the thermoelectric converters of energy are deeply worked out that enables ones to design of the improved thermoelectric converters of energy with non- uniform legs of various type [6-8]. It is necessary to notice that the thermoelectric phenomena in such structures with the lowered symmetry become essentially complicated [1, 6].

In order to understand the complex physical phenomena occurred in the thermoelectric modules the symmetry analysis is frequently used [11-13]. The matter is that the concept of symmetry is closely tied with some extreme principles of thermodynamics [13]. Actually, the problem of increase in Z for thermoelectric converters of energy represents a typical extreme task of the thermodynamics of irreversible processes [13]. For this reason, the concept of symmetry seems to be very important for the analysis of thermoelectric converters of energy.

Recently, the symmetry analysis was applied to the thermoelectric converters of energy with non-uniform legs [14]. In present paper, the previous researches are further developed. In particular, the concept of symmetry have been used in a widen sense that includes space order and the proportion, harmony, synergism, and also all their infringements in modules. The researches of symmetry are carried out within four structural levels. The symmetry of the materials, the legs, the thermocouples and the group of converters of energy was separately investigated. It was shown that sometimes for the increase in Z the symmetric configurations at any structural level are necessary, but in other cases the asymmetrical configurations are more favorable. For the group of energy converters the modified tetratomic classification (TEG^a, TEG^b, TEC, and TEH) was proposed. The general rule for set of inhomogeneous leg in the converters was developed. Some new effects observed in inhomogeneous legs and on their borders as well as practicable application of inhomogeneous legs for cooling, domestic heating, waste heat utilization and power generation are briefly discussed.

1. The symmetry of thermoelectric materials

As it is known, homogeneous thermoelectric materials are characterized by universal parameter of figure of merit

$$Z = \alpha^2 / (\rho k), \tag{1}$$

were α is the Seebeck coefficient, $\rho = \sigma^{-1}$ and σ are the partial resistance and conductance respectively, k is the partial thermal conductivity [1]. Therefore, ones choose the materials for thermoelectric converters of energy by criterion of maximum of figure of merit $Z_{\max}$ in a given interval of temperatures [1, 15]. According to [15, 16], the maximum of figure of merit $Z_{\max}$ is proposed by two asymptotic expressions being valid for the case of absence of Fermi degeneracy of carriers (2) and for the highly degenerated case (3)

$$\mathrm{Z}_{\max} \begin{cases} N(m_d)^{3/2} \mu T^{3/2} e^{\gamma} / k_L \left(E_F / k_0 T << 1 \right) \\ N\left(m_d / m_c \right) p^{-2/3} T e^{\gamma} / k_L \left(E_F / k_0 T > 10 \right) \end{cases} \tag{2), (3}$$

were N is the degeneracy of band extreme in the momentum space, m_{d} and m_{c} are the effective mass of density of state and one of conductivity within an extreme, μ and r are the mobility and the scattering parameter of carriers, k_L is the lattice thermal conductivity, T is the absolute temperature, E_F is the Fermi energy, k_0 is the Boltzmann constant.

As it is accepted now, the band degeneracy (N) is an attribute of high symmetry crystals (cubic, hexagonal, or tetragonal) [15, 16]. In addition, the low symmetry materials can be of interest for thermoelectricity due to high (m_d/m_c) as well [17]. Except for that, the small m_c and high μ are the characteristics of wide width of conductive and valence bands and the direct energy gap E_g between the bands [16, 18]. On the other hand, the low k_L is the characteristic for anharmonicity of a lattice fluctuations inherent in a solid solutions [1], a materials under phase transitions [16], and a bulk nanostructure composites [17]. Usually, Z achieves the peak value at the "optimal" carrier densities of n, $p \sim 10^{19}$, cm^{-3} (curve2, Figure.3a) [1], and at the temperature near intrinsic conduction begin [6, 16]

$$T_{\max} \sim (E_g + E_F)/\, 10k_{0.} \tag{4}$$

Thus, the homogeneous materials used for the legs of thermocouples should be optimized on E_g and E_F (n, p) [1], and on crystallographic orientation for non- cubic crystals as well [11, 13]. At the same time, at the transition from homogeneous to non-uniform legs the concept of thermoelectric figure of merit Z of materials (1) gets the local character.

As before, the principle of $Z_{\max}$ does act but only for a choice of the starting characteristics of materials for the various segments of legs. The final optimization of the materials for segments of the legs includes the analysis of their contributions in Z within the structural levels of the legs and of the thermocouples.

2. The symmetry of inhomogeneous legs

The variation of Seebeck coefficient α along the length l of inhomogeneous legs decreases the spatial symmetry of a leg by gradient transformations $\nabla\alpha_{n,\,p}$ (Fig.1a). As a result, the parameters of n, p, E_g and E_F on the various ends of non-uniform legs will be accordingly more or less that optimum ones for the materials at given temperature (see the arrows in Fig.2) [14]. In addition, there is a mismatch on ($E_g + E_F$) and accordingly on a working temperature interval and the intrinsic conductivity begin at the various ends of a leg [16].

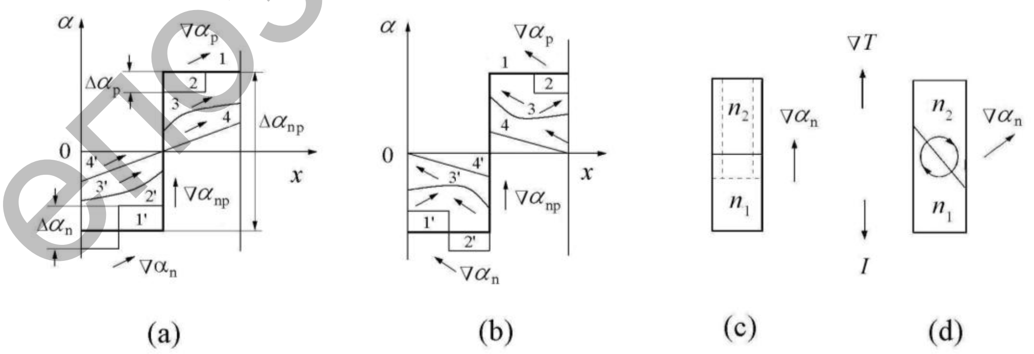
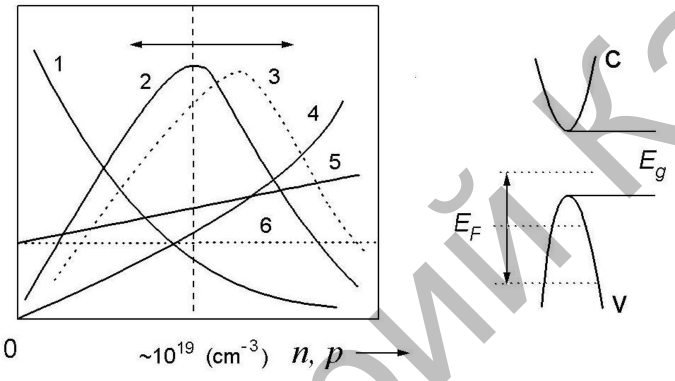


Fig.1. The distribution of Seebeck coefficient α along the thermocouples (a, b) and within the legs (c, d). Legs: (1- 4) - *p*- type; (1'- 4') - *n*- type; 1- homogeneous; 2-segmented; 3, 4 – graded. Set of legs: a – proper ($\nabla\alpha_n \uparrow\uparrow \nabla\alpha_p \uparrow\uparrow \nabla\alpha_{np}$); b – undue ($\nabla\alpha_n \uparrow\uparrow \nabla\alpha_p \uparrow\downarrow \nabla\alpha_{np}$). Set of segments: c- proper ($\nabla\alpha_n // \nabla T$); d- undue ($\nabla\alpha_n \angle \nabla T$). The dashed lines (c) show an optimizing of the leg on size, the ellipsoid with arrows (d) displays the parasitic curl current.

Thus, the optimization of non-uniform legs includes a choice of distribution of α on length and the orientation of $\nabla\alpha_{n,\,p}$ concerning the directions of a current I, a gradient of temperature ∇T and a thermal stream Q in a leg and concerning a gradient of Seebeck coefficient $\nabla\alpha_{np}$ on a joint of the thermocouple [6-10,19].

The optimized curves (Fig.1a) were calculated earlier for segmented and graded legs with linear [20] and random distributions of Seebeck coefficient $\alpha_{n,\,p}= f\,(l)$ along the legs [2, 3, 6, 9, 19]. For the proper set of segments within a leg and of boundaries of segments along the length l, the calculation predicts the increase in Z up to 10-20% and sometimes even more [19]. Figures 2c and 2d show the various orientations of boundaries of segment along the length l of the legs concerning the directions of electric current I, gradient of temperature∇T, and thermal flow Q. From Fig.2d it is seen that the curl currents I_c may aroused near the inclined phase borders of segments due to the longitudinal gradient of temperature ∇T in a leg that resulting in decrease in Z [15].



(a) (b)

Fig.2. The variation of some characteristics (a) and the band structure (b) of thermoelectric materials used for production of inhomogeneous legs: 1- Seebeck coefficient α; 2- figure of merit $Z= \alpha^2\sigma/\kappa$; 3- power factor $\alpha^2\sigma$; 4- specific electric conduction σ; 5- heat conductivity κ; and 6- lattice component of heat conductivity κ_L versus carrier densities n, p. The arrows show the control intervals for inhomogeneous legs [6,14,16].

In the same time, no curl currents I_c are observed for the orthogonal phase border of segments ($\nabla\alpha$ // I, ∇T and Q) (Fig.2c). Thus, there is only the orthogonal orientation of the phase border of segments in inhomogeneous legs that is suitable for thermocouples (Fig.2c).

In addition, in order to get the synergistic effect from various parts of a thermocouple one needs the proper orientation of non- uniform legs concerning a gradient of Seebeck coefficient on a top joint of the thermocouple $\nabla\alpha_{np}$. For the first time, the rule for proper orientation of non-uniform legs in modules was developed by A.F.Ioffe for TEG [1]. According to [1], the rule of Z_{max} for the materials should be applied to each segment of the legs so the carrier density (n, p) along the legs increase in the *hot zone* [1]. Naturally, the rule [1] provided the increase in Z for TEG and prevents modules from intrinsic conduction, but it failures for TEC [2-3]. In accordance with [2-3], the segments of high carrier density (n, p) should be placed in the *cold* zone of a thermocouple.

Recently, the conflict of [1] with [2-3] was successfully resolved by development of the universal rule for the proper set of non-uniform legs in the thermocouple [9-10]. According to [9-10], the proper set of segments is not defined in any way by the directions of gradient of temperature∇T, electric current I and/or thermal stream Q, but determined only by the orientation of legs concerning a gradient of Seebeck coefficient $\nabla\alpha_{np}$ on the top joint of a thermocouple:

$$\nabla\alpha_n \uparrow\uparrow \nabla\alpha_p \uparrow\uparrow \nabla\alpha_{np.} \qquad (5)$$

It was shown that it is the case, when the increase in Z for the converters of energy is possible. On the contrary, the undue set of segments ($\nabla\alpha_n \uparrow\downarrow \nabla\alpha_{np}$; $\nabla\alpha_p \uparrow\downarrow \nabla\alpha_{np}$ or $\nabla\alpha_n \uparrow\uparrow \nabla\alpha_p \uparrow\downarrow \nabla\alpha_{np}$) (Fig.1b) causes a decrease in Z and significant power losses in modules [9, 10]. The effects were explained by the two-value expression obtained for effective figure of merit of a thermocouple with segmented legs (Fig.1c)

$$Z \cong (\Delta\alpha_\Sigma)^2/\ (K\,R), \qquad (6)$$

here $\Delta\alpha_\Sigma = (\Delta\alpha_{n\ p} \pm C^*\Delta\alpha_l\ (T^*/T_1))$ is effective Seebeck coefficient drop along the thermocouple, $\Delta\alpha_{np}$ is the Seebeck coefficient drop on joint of thermocouples; $\Delta\alpha_l = (\Delta\alpha_p - \Delta\alpha_n)$ is the total Seebeck coefficient drop in the legs; T_1 and T^* are the temperatures on top of modulus and at the boundary of segments; $C^* \sim ½$ is the calculated factor, depending on partial electric resistivities and heat conductivities as well as the sizes of the legs; K, K_1 and K_2 are the total thermal conductivities of modules and segments; R is the total resistivity; (±) correspond to proper or undue sets of segments in a modulus (Fig.1), the dependence of Z on signs (±) being significant as amplified with square-law dependence in (6) [14,19].

Thus, the rule (5) forces the legs of n- and p- type, and the top joint of thermocouples to run in a synergistic mode to get the gain in Z. So in accordance with (6), the carrier density in segments of legs should be raised on the top side ($n_2 > n_1$, $p_2 > p_1$) for all types of thermoelectric converters (Fig.1).

3. The symmetry of the thermocouples

Figure 3 shows the circuit design of single wire thermocouple (a) and elementary thermoelectric converter of energy of standard π- type **(**b**)** and of Oersted type (c). Arrows in Fig.3 show the directions of gradients of Seebeck coefficient $\nabla\alpha$ in a circuit. From Fig. 3a it is visible that the free thermocouple with homogeneous legs is completely symmetric concerning the joints 1 and 2 (point symmetry group G= mm*2*; here asterisk (*) marks the reversion of electric current I and conversion of conductivity $n \leftrightarrow p$ in a leg). Therefore, at the inversion of a gradient of temperature ∇T or a direction of current I in the thermocouple the Seebeck and Peltier effects on joints will be inverted as well.

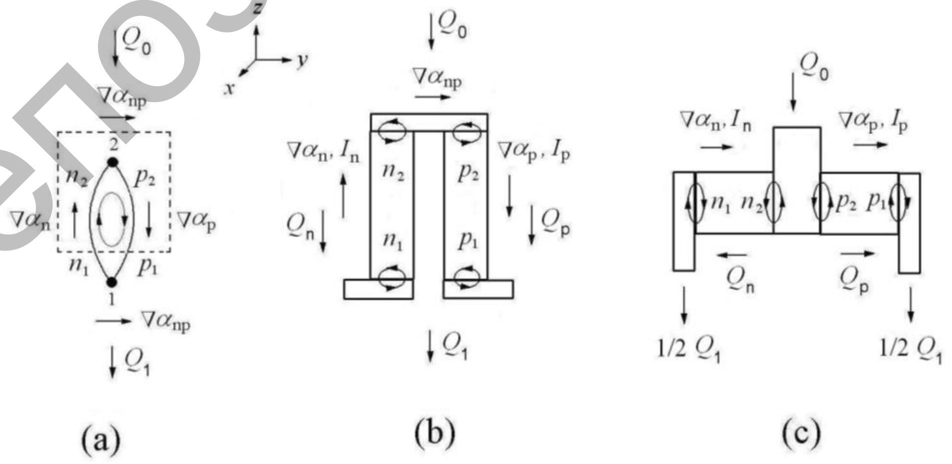


Fig.3. The single wire thermocouple (a), and standard of π- type (b) and of Oersted type (c) energy converters. The doted contour (a) marks the synergetic area of the top joint of a thermocouple. Ellipsoids with arrows (b, c) show the curl currents near the border of the legs.

The transition from the free thermocouple (Fig.3a) to the thermoelectric converter of energy (Fig.3b and 3c) is accompanied by decrease of symmetry mm*m → mm*2* because the top joint 2 of a thermocouple becomes an active part of a converter, but the base joint 1 becomes a thermal drain. For the inhomogeneous legs ($\nabla\alpha_n$, $\nabla\alpha_p \neq 0$) in proper set (5) the symmetry of the thermocouple is decreased in the same way as mm*m → mm*2* (Fig.3a). Therefore, the symmetry does not interfere with the use of non-uniform legs in thermoelectric converter of energy. The synergetic area of the top joint of a thermocouple used in thermoelectric converters of energy is marked on Fig.3a by the doted contour.

Because of the legs of *n*- and *p*- type are cut into electric circuit of a thermocouple in series, but into the heat flow Q in parallel, there are 2 variants of the basic thermocouple design [12]. The first is the standard π- type set friendly to heat flow $Q_n \uparrow\uparrow Q_p$ ($I_n \uparrow\downarrow I_p$) (Fig.3b), the second is of Oersted type set friendly to electric current $I_n \uparrow\uparrow I_p$ ($Q_n \uparrow\downarrow Q_p$) (b) (Fig.3c). It is useful to notice that ones can transform π- type thermocouples into Oersted type and on the contrary by proper rotations of the legs around of an x- axis.

The advantage of a π- type set (Fig.3b) is the straight heat flow Q over the top joint of a thermocouple, but the disadvantage is the bending of electric current I in switching plate. On the contrary, the advantage of Oersted set (Fig.3c) is the straight electric current I flow along the legs, but the disadvantage is the bending of heat flow Q by way of the legs. In both cases, the infringement of symmetry may cause the occurrence of transverse gradients of temperature and accordingly parasitic curl currents I_c near the contacts [21]. The curl currents in a π- type set (Fig.3b) arise due to non-uniform heating of switching plates and may be reduced with the help of special methods.

Contrary, the curl currents in an Oersted set (Fig.3c) are due to the systematic transverse temperature gradients ∇T along the heat-conducting paths that resulting in the significant decrease in Z. For this reason, the π- set of legs is more preferable for practical use in converters of energy in comparison to the Oersted one. The last are used in automobiles, where the losses in thermoelectric generators seem to be insignificant in comparison with the overwhelming losses of the combustion engine [21].

4. The symmetry of the group of converters of energy

The various thermoelectric converters of energy form a group inside which there are certain relations of symmetry. There are 4 possible sets for standard π- type thermocouples as well as for Oersted ones being in thermoelectric circuits under the heat flow Q and current I. Accordingly, for thermocouples with inhomogeneous legs the generalized tetratomic classification of energy converters (TEG^a, TEG^b[1], TEC, and TEH) was suggested [14]. Let's notice, that for homogeneous leg the sets of TEG^a and TEG^b are similar (Fig.5), so in this case the tetratomic classification transforms into the standard trinomial one (TEG, TEC, and TEH) [5,6]. The tetratomic classification for converters with thermocouples of π- type was earlier discussed in [14]. The ones for the thermocouples of Oersted type is given below for the first time (Fig.4).

For TEG at heating or cooling of the top joint of thermocouples the electric voltage $\pm E$ arises between *p*- and *n*- legs and electric current I arises if electric circuit being closed (a, b, Fig.4). On the contrary, in TEC and TEH the current flows give rise the cooling ($\nabla\alpha \uparrow\uparrow I$) (c) or heating ($\nabla\alpha \uparrow\downarrow I$) (d) of the top joint, the sign of effects being specified by thermodynamic principle of Le Chatelier-Braun [9,10,19]. According to (6), the “bulk” effects in the legs will increase or decrease the output of a converter depending on proper or undue set of segments in a leg. Fig.4 shows the proper set of the legs (5) and corresponding distribution of carrier density along the legs ($n_2 > n_1$, $p_2 > p_1$) that will improve a converter.

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[1] The set of TEG^b is not of common use now as assumes the heat removal from the system.

Table 1 shows the results of application of inhomogeneous legs to various types of thermoelectric converters of energy [9, 10, 19]. From Table 1 and Fig.4 one can see that the thermoelectric energy converters with inhomogeneous legs show a number of the general properties within the group.

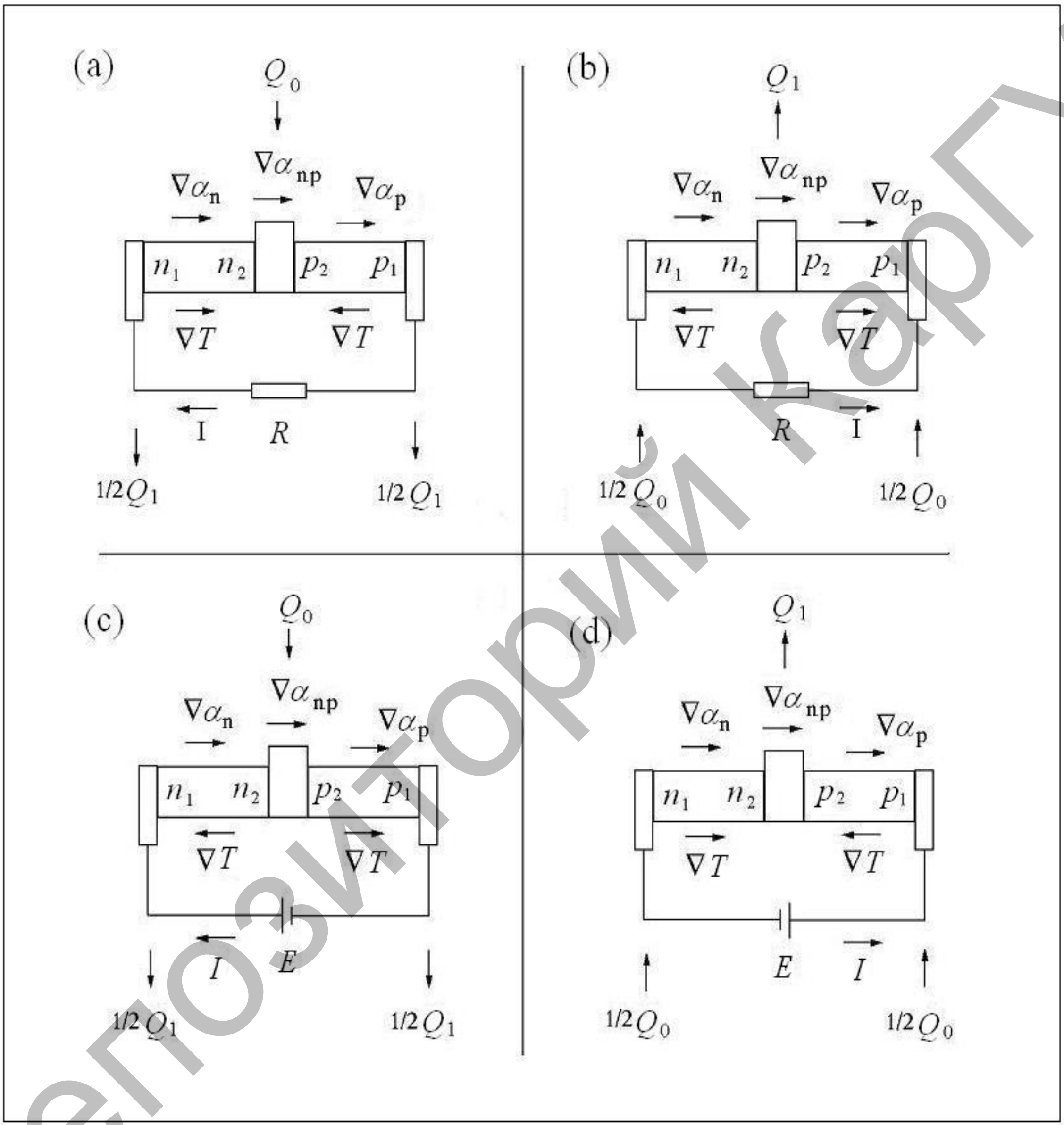

Fig.4. The tetratomic classification of the group of converters of energy of the Oersted type with inhomogeneous legs ($n_2 > n_1$, $p_2 > p_1$). a, b- TEG; c- TEC; d- TEH. Here T_0, T_1, and Q_0, Q_1 are the input and output temperatures and heat flows; ∇T and $\nabla\alpha$ are the gradients of temperature and Seebeck coefficient; R is the external load, E is the e.m.f. of a battery.

They are the following: 1) the rule for proper sets of segments in modules; 2) the decrease of transitive resistance r and curl currents I_c near the top joint of a hermocouples; 3) a possible increase in Z for modules, all resulting from the asymmetry of top.

Table 1. Results of application of inhomogeneous legs to various types of thermoelectric energy converters

Energy converters	TEG^a	TEG^b	TEC	TEH
Sets of joints	$\nabla\alpha_{np} \uparrow\uparrow I$	$\nabla\alpha_{np} \uparrow\downarrow I$	$\nabla\alpha_{np} \uparrow\uparrow I$	$\nabla\alpha_{np} \uparrow\downarrow I$
A.F.Ioffe rule for segments	Does act	Failed	Failed	Does act
Proper sets of segments	$\nabla\alpha_{n,\,p}\uparrow\uparrow \nabla\alpha_{np}$	$\nabla\alpha_{n,\,p}\uparrow\uparrow \nabla\alpha_{np}$	$\nabla\alpha_{n,\,p}\uparrow\uparrow \nabla\alpha_{np}$	$\nabla\alpha_{n,\,p}\uparrow\uparrow \nabla\alpha_{np}$
Effective drop of Seebeck coefficient $\Delta\alpha_\Sigma$	Decrease	Increase	Increase	Decrease
Transitive resistance *r* and curl currents	Decrease	Decrease	Decrease	Decrease
Intrinsic conduction	Decrease	Increase	Increase	Decrease
Influence of Thomson effect on *Z*:				
a) extrinsic conduction	Negative $\nabla\alpha_{np} \uparrow\downarrow\nabla\alpha_\tau$	Positive $\nabla\alpha_{np} \uparrow\uparrow\nabla\alpha_\tau$	Positive $\nabla\alpha_{np} \uparrow\uparrow\nabla\alpha_\tau$	Negative $\nabla\alpha_{np} \uparrow\downarrow\nabla\alpha_\tau$
b) intrinsic conduction	Positive $\nabla\alpha_{np} \uparrow\uparrow\nabla\alpha_\tau$	Negative $\nabla\alpha_{np} \uparrow\downarrow\nabla\alpha_\tau$	Negative $\nabla\alpha_{np} \uparrow\downarrow\nabla\alpha_\tau$	Positive $\nabla\alpha_{np} \uparrow\uparrow\nabla\alpha_\tau$

and base joints of a thermocouple (Fig.3). On the contrary, the other characteristics show the cross parities of symmetry within the groups of (TEG^a, TEH) and (TEG^b, TEC) (Table1). They are: 1) the Ioffe rule; 2) the variation of the effective drop of Seebeck coefficient $\Delta\alpha_\Sigma$ along the legs; 3) the influence of intrinsic conduction and Thomson effect on *Z*, all resulting from the same temperature distributions in working modules (Fig.4). In addition, the make use of tetratomic classification (Fig.4) as a guide-book resulting in some discoveries concerning the practical applications of inhomogeneous legs [16, 19].

The practical applications of inhomogeneous legs

First of all, ones expand the application of inhomogeneous legs previously known for TEG and TEC to TEH as well [10, 16]. Thus, it was confirmed that for a proper set of segments (5) one can get the increase in *Z* for each thermoelectric converter of energy up to 10- 20% near the room temperature by using **the existing thermoelectric materials** (Table II). There are some reasons to believe that the same approach is applicable and to a new thermoelectric materials with abnormal low heat conductivities κ_L of a lattice [17]. In all cases, the increase in *Z* obtained by inhomogeneous legs results in the growth in power characteristics of the converters of energy

$$\eta = A/\,Q_1 = (\Delta T/\,T_1)\,(\mathrm{M}-1)/\,(\mathrm{M}-\,T_0/\,T_1), \tag{7}$$

$$K = Q_0/\,A = (T_0/\,\Delta T)\,(\mathrm{M}-\,T_0/\,T_1)/\,(\mathrm{M}+1), \tag{8}$$

$$L = Q_1/\,A = K+1, \tag{9}$$

where η is the efficiency of TEG, K and ΔT_c are the cooling coefficient and the peak of cooling for TEC, L is the heating coefficient of TEH, $A = (Q_1 - Q_0)$ is the work of a current I, Q_1 and Q_0 are the heat emission and absorption at cold and hot sides of thermocouples respectively, $\mathrm{M} = (1 + Z(T_0 + T_1)/\,2\,)^{1/2})$, Z is the figure of merit for the device, $(\Delta T\,/\,T)$ is the Carnot factor, $\Delta T = (T_1 - T_0)$, T_0 and T_1 are the temperatures at the base and at the top of modules [1,7].

Table 2. The room temperature characteristics and the peaks of cooling ΔT_c for modules with homogeneous and non-uniform legs under various set of segments (asterisk marks the modulus optimized by size).

№	Modulus	Characteristics of modules			Cooling test			Calculations
		Seebeck coefficient $\Delta\alpha_\Sigma$, μV /K	Resistance R, Ohm	Heat conduction K, mW/ K	Peak of cooling ΔT_c, K	Optimal current I_0, A	Figure of merit $Z.10^3$, 1/ K	Figure of merit $Z_{calc}.10^3$, 1/ K
1	(190/-192)	382	0,049	4,78	68	3,0	2,5	2,8
2	(250/-263)	513	0,164	3,78	51	1,7	1,7	2,1
3	(250/190/-192/-263)	513	0,105	4,29	71 75*	2,5 1,9*	2,7 3,0*	3,2 3,3
4	(190/250 /-263/-192)	382	0,105	4,29	32	1,5	0,9	1,0

Fig.5a shows the experimental peaks of cooling $\Delta T_c = ½ Z T_1^2$ for TEC versus electric current I. obtained for modules with homogeneous (3, 4) and inhomogeneous legs (1, 2, 5). The legs for modules of 1, 4x1, 4x2, 5 mm^3 in size were cut from special grown single crystals of bismuth and antimony chalkogenides (BAC) in perpendicular to a trigonal axis. For designations of modules the room temperature Seebeck coefficients α of various segments cut in series into thermoelectric circuit have been used.

Fig. 5b shows the experimental curves of η, K, L obtained using the same modules with homogeneous (3, 4) and inhomogeneous legs (1, 2, 5) cut in thermoelectric circuits as TEG, TEC, and TEH in turn. It was discovered, that due to the contribution of the "bulk" effects and inversed Carnot factor (ΔT / T) in (8) and (10), the TEH with inhomogeneous legs becomes the most effective thermoelectric converters for the small temperature drops (Fig.5a) [4,16].

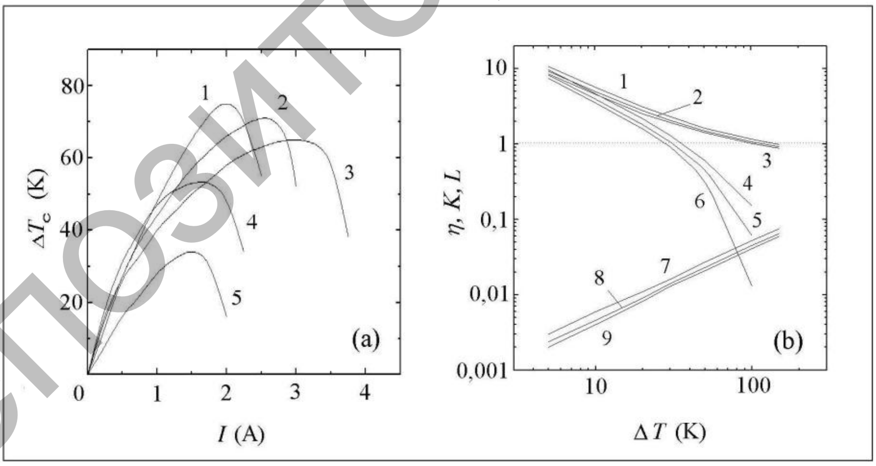

Fig.5. The curves of cooling ΔT_c versus electric current I for TEC (a) and the efficiency η for TEG (7-9), the heating coefficient L for TEH (1-3), and the cooling coefficient K for TEC (4-6) versus temperature drop ΔT (b). Modules: (a)- 1, 2- (250/190/-192/-263) (2- optimized by size); 3-(190/-192); 4- (250/-263); 5- (190/250 /-263/-192); (b): 1, 4, 7 – (260/200/-200/-260); 2, 5, 8– (260/-260); 3, 6, 9– (200/-200).

The applications of the enhanced modules with inhomogeneous legs for cooling, domestic heating, waste heat utilization and power generation were declared preferable in [6-10].

In the modules working continuously, the secondary effects in the legs transforms the homogeneous legs into inhomogeneous ones that may causes either increases or decreases in Z.

The TEG seems to be the most sensitive converter for secondary effects as working under the big temperature drops $\Delta T \cong$ 300- 500 K [7]. According to (Table I), it is the Thomson effect α_τ in the TEG that decreases *Z* under extrinsic conduction. On the other hand, the Thomson effect α_τ improves TEC (Table I) as it was declared earlier [2, 3].

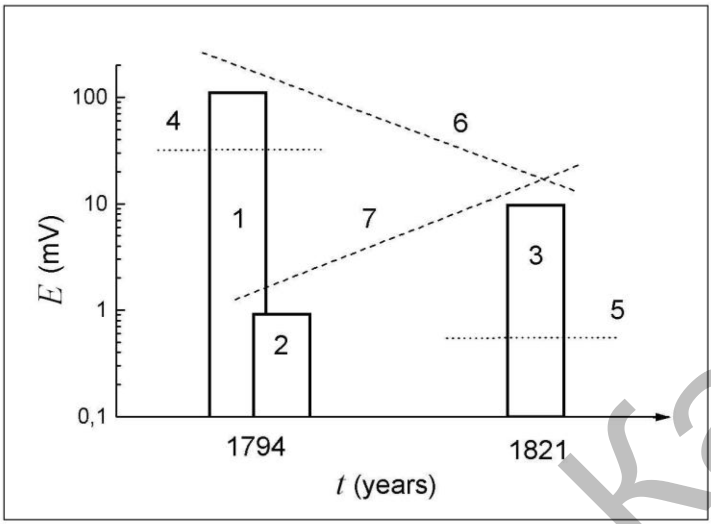

Fig.6. The voltages *E* bringing the contribution to experiments of Volta (1794) and .Seebeck (1821). Effects: 1- galvanothermic E_{GTE} in Fe/H_2O/Fe cell; 2- bulk Seebeck E_Z in iron wire; 3- joint Seebeck E_J in Bi/ Sb thermocouple. 4, 5 are the thresholds of sensitivity of the used measuring devices (frog and magnetic needle). Trends: 6- "*the big the first*"; 7- (1).

From the given examples it is visible that the "bulk" thermoelectric effects in the legs of converters may cause both increase and decrease in *Z* of the converters. For this reason, the finding out of the mechanism of the effect is the matter of great concern.

The mechanism of increase in *Z* for the converters

First of all, it is necessary to emphasize that the mechanism of increase in *Z* for converters with inhomogeneous legs is determined by many factors [6]. As it was established above, the mechanism of increase in *Z* is determined by two general factors: 1) nonequivalence (asymmetry) of the top and the base joints of a converter (Fig.3); 2) the existence of symmetric synergetic mode (5) of the "bulk" thermoelectric effects in the legs and the "contact" ones at the top joint of a thermocouple. The necessary conditions for synergetic mode (5) are the absence of circular currents both in the legs (Fig.1c) as well as in the converters (Fig.3). For this reason, ones should use the legs with phase front of heterogeneity being perpendicular to a gradient of temperature and preferably the thermocouples of π-type (Fig.3b).

Under the specified conditions, it is possible to expect the maximal increase in Z due to the additional contributions of "bulk" thermoelectric effects in cooperation with the "contact" ones. So, the figure of merit *Z* for inhomogeneous legs should be considered as the effective figure of merit *Z* for *n*/ *n*' or *p*/ *p*' thermocouples, and the figure of merit Z for converter as the effective figure of merit *Z* for series cascading of thermocouples with the general electric current feed. According to [19], the increase in *Z* for modules with non-uniform legs may results from an increase in $\Delta\alpha_\Sigma$ due to use of the materials with big α not suitable for homogeneous legs (curves 1' and 2', Fig.1a). Furthermore, it was shown that the increase in *Z* is possible and without increase in $\Delta\alpha_\Sigma$ (curves 1 and 2 , Fig.1a) due to the decrease of the irreversible processes (Joule's heat emission and heat conductivity) at the breakdown of the symmetry of the legs [14].

Table 2 shows some room temperature characteristics and the experimental peaks of cooling ΔT_c for investigated modules with homogeneous and non-uniform legs with the same segments being in various set. From the Table 2 it is visible that the increase in Z at the transition from homogeneous modules of low-resistance 1 and of high-resistance 2 to non-uniform one 3 is due to the increase in $\Delta\alpha_{\Sigma}$ and decrease of R. It is necessary to note that at variation of the resistivity R, the heat conduction $K = K_e + K_{lat}$ changes to a lesser degree (curves 5, 6, Fig.2) and accordingly less influences to the characteristics of modules (Table 2). At the same time, the decrease in Z at the transition from proper set of non-uniform modulus 3 to undue one 4 is due to decrease in $\Delta\alpha_{\Sigma}$. From the other hand, the increase in Z for the modulus optimized by size (3, Table 2) is due to the working of various segments of a leg at the general optimum current I_0 (curves 1,3,4, Fig.5a). The optimization of inhomogeneous legs on size was shown to increase Z of modulus up to 5-10% [14]. In addition, ones observed the increase in Z up to 40 % at the temperature of T_1 = 150 K, due to the reduction of the relative contribution κ_e into K at the decrease of temperature [9]. At the same time, the calculating values of Z exceed experimental ones that are attributed to parasitic electric resistances r_i and curl currents I_c near to contacts of modules [6, 7]. Lines of a current near to joints are bent (a, Fig.2), that results in increase of effective electric resistance near to contacts and reduces thermoelectric figure of merit

$$Z= Z_0/ (1+ (\Sigma\, r_i)/R), \qquad (10)$$

here $\Sigma\, r_i$ is the sum of all transitive and switching resistances in area of the top contact of the thermocouple; R is the total resistance. It is necessary to notice that the proper set of segments decreases the parasitic resistances r_i and curl currents I_c near the top joint of thermocouples due to increase of electric σ and heat κ conductivities of the top segment.

Some cases of infringement of symmetry

The important part of any symmetry analysis is detection of the infringement of requirements of symmetry. Despite of an evidence of the rule (5), its performance frequently caused mess in some papers. For example, both segments of non- uniform legs and joints of TEC were in a set of TEH in [22-23], as well the inclusion of small segments (up to 1/3 in length) near the top of the legs in undue set were calculated to be optimal for TEC in [24-25], the undue polarity of voltage for TEG was posed in [26]. These deviations from requirements of symmetry are of great interest for advanced researches. In the Appendix the example is given, when the detection of deviations from requirements of symmetry help ones to specify even the priorities for discoveries of thermoelectric phenomena.

Table 3. The economical range of production of non- uniform modules [9, 10, 14]

Method of manufactur	Relative man-hours for production of modulus		
	Homogeneous	Segmented	Graded
Crystal growth	1	~2	~1,3- 1,5
Cutting of legs	1	~3- 4	~2- 3
Mounting cost	1	~1,5	~2
Optimization	1	~2- 3	~3- 5
Yield	0,6- 0,7	~0,4- 0,5	~0,02- 0,04

The economical range of non- uniform modules production

The economical range of production based on experience in pilot assembling of modules [9, 10, 14] is submitted in Table 3. From Table 3 one can see that the man-hours for production of modulus with inhomogeneous (segmented and graded) legs are of 2 to 2,5 time more and the outcome is of 0,05 to 0,7 time less than for modulus with homogeneous legs. Hence it is clear, why the segmented and graded modules of TEC and TEH are not in the wide practice use now [3].

Spontaneous methods for formation of inhomogeneity in modules

The methods for spontaneous formation of inhomogeneous legs were completed in Table 1. They includes the application of inhomogeneous magnetic fields *H* and mechanical stresses [7], the Thomson effect [3, 9], and the thermal diffusion of the fast ions (Cu, Ag) [27, 28]. The basic requirement to the methods consists in holding the rule (5) at their application to a leg.

Table 4. Some spontaneous methods for formation of inhomogeneity in modules ((+) possible, (-) unworkable).

Methods	Symmetry relation	Converters				Ref
		TEG^{a}	$\mathrm{TEG}^{б}$	TEC	TEH	
Inhomogeneous magnetic fields *H* (low temperatures)	$\nabla H\,//\,I$	+	+	+	+	[7]
Inhomogeneous deformation ε	$\nabla \varepsilon\,//\,I$	+	+	+	+	[7]
Thermal diffusion of the fast ions (Cu, Ag so on))	$\nabla T\,//\,I$	+	-	-	+	[27,28]
Thomson effect:	$\nabla T\,//\,I$					
a) extrinsic conduction		-	+	+	-	[3]
b) intrinsic conduction		+	-	-	+	[9]

Conclusion

Now it is possible to enumerate the main principles for optimization of thermoelectric power converters with the non-uniform legs. At the transition from homogeneous to non-uniform legs some principles of optimization of the converters remain former and some are essentially modified. As shown above, the problem of optimization of the converters may be properly solved only considering the structural levels of the materials, the legs, the thermocouples, and the group of converters.

The materials for segments of the legs should be optimized by the carrier densities *n* and *p*, forbidden band gap E_g and Fermi energy E_F in accordance with the working temperature interval. The orientations of boundaries of segments with different carrier densities ($n_2 > n_1$, $p_2 > p_1$) concerning the length of leg should be in accordance with the symmetry demands to prevent the curl currents in the materials. The proper orientation of non-uniform legs concerning the electric current *I* in the modules should be made according to rule (5), otherwise characteristics of modules will be essentially worsened.

For the proper set of legs (5), one can get a gain in *Z* first of all by the growth of total drop of Seebeck coefficient $\Delta\alpha_\Sigma$ along the thermocouple, the last should be increased whenever possible. In the same time, the required increase in $\Delta\alpha_\Sigma$ may be limited by the width of homogeneity region of the materials, and sometimes by mismatch on size for different segments. Accordingly, the geometric optimization of inhomogeneous legs on cross section, and also on size of segments is necessary. In this case, the increase in *Z* of the devices up to 20-30 % is possible for the existing thermoelectric materials at room temperature.

Also, for thermocouples with non-uniform legs it is necessary to account a number of accompanying effects in running modules. They are the decrease of transitive resistance r_i and curl currents I_c at the top joint of modules, and the contribution of Thomson effect in *Z* . Taking into account high expenditures on manufacture of modules with non-uniform legs, ones offered some spontaneous methods of formation of the inhomogeneous legs by using a number of external fields and secondary physical effects arising in working modulus. The specified approach in due course, probably, becomes the basic for formation of non-uniform legs for the serial production of modules in future.

Appendix

T.Seebeck (1821) or A.Volta (1794)?

As is well known, the direct and reversed contact thermoelectric effects were discovered by T.Seebeck (1821) and J. Peltier (1834) one of the variety of bulk thermoelectric effects attributed to the dependence of Seebeck coefficient α on temperature was found by W.Thomson (1851) [29,30]. On the other hand, ones supposed [7, 12] that the phenomenon of thermoelectricity was earlier discovered by A.Volta (1794) in his experiments with excitation of a frog by heated iron wire [31]. According to calculation [29], Volta might observe the bulk Seebeck voltage in heated iron wire of $E = \alpha\Delta T \leq 0{,}7\text{-}1$ mV ($\alpha \sim 10\text{-}15\,\mu$V/K, $\Delta T \leq 70$ K) that being less the contact ones observed by Seebeck for thermocouple Bi/Sb $E = \alpha\Delta T \leq 5\text{-}10$ mV ($\alpha \sim 50\,\mu$V/K, $\Delta T \leq 100\text{-}200$ K) in accordance with relation (1).

From the other hands, according to the well known law of heuristics “*the big the first*”, the big effects are usually being primarily observed by researchers. For this reason, it was possible to assume that effect of Volta might be caused by the big voltage of non Seebeck nature [29]. So, the experiment of Volta were repeated in [29] that shown the Volta effect in the system to be the difference of two effects: the big galvanothermal effect (GTE) related to temperature dependence of electrode potentials of Fe/H_2O/Fe cell ($E_{\mathrm{GTE}} \sim 114$ mV) and a small bulk Seebeck effect in iron wire heated by side ($E_Z \sim 1$ mV), the last being outside of a threshold of sensitivity of the nervous of a frog ($E_0 \sim 35$ mV) as well as all modern to Volta measuring devices (Fig.6).

Thus heuristics law “*the big the first*” was confirmed, the priorities of Seebeck, Peltier and Thomson in discoveries of the thermoelectric phenomena was restored.

Nevertheless, the role of Volta in discovery of thermoelectricity seems to be essential as Seebeck was his follower in searches of the *metal electricity* [7, 12, 32].

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References:

33. A.F. Ioffe. Semiconducting Thermoelements. 1960, M.- L., Izd. AN SSSR. p. 79.
34. A.D. Reich. Bull. Amer. Phys. Soc. **Vol.17**, №3, p.702 (1972).
35. R.J. Burst “The Extrinsic Thomson Effect”, *Proc. XIV Int. Conf. on Thermoelectricity. Russia, SPb.* pp. 301- 304, June 27- 30, 1995.
36. M.A.Korzhuev. Technical Physics. **Vol.54**, №8, p.1241 (2009).
37. E. Schlegel. Z. fur ges. Kalta- Ind. **Vol.40,** №1, S.2 (1933).
38. L.I.Anatychuk, V.A. Semenyuk. Optimal Control for the Thermoelectric Materials and Device Properties. 1992, Chernovtsy, Prut, 264 p.
39. L.I. Anatychuk. To 70- anniversary of the birth. Jubilee volume. 2007, Chernovtsy, Institute on Thermoelectricity, 726 p.
40. L.N. Vikhor. J. Thermoelectricity, №1, p.7 (2005).
41. M.A. Korzhuev., L.D. Ivanova, L.I. Petrova, Yu.V Granatkina, T.E. Svechnikova, ‘The Multistage Thermoelectric Devices with Inhomogeneous Legs’, *Proc. of 5-th European Conf. on Thermoelectrics, Odessa, Thermion* , pp.148- 151, September 10-12, 2007.
42. M.A. Korzhuev., I.Yu. Nichezina, “The Power Increase of Thermoelectric Heaters with Inhomogeneous Legs”, *Proc. of 6-th European Conf. on Thermoelectrics, Paris: ICMPE- CNRS,* P. 2-06-1 - 2-06-4, July 2-5, 2008.

43. J.F.Nye. Physical properties of crystal. 1966, Oxford, Claredon Press, 388 p.
44. A.A.Buriyak, N.B.Karpova. Sketches on development of thermoelectrisity. 1988, Kiev, Naukova Dumka, 290 p.
45. Yu.I.Sirotin, M.P.Shaskolskaya. The bases of crystal physics. 1975, M., Nauka, 680 p.
46. M.A. Korzhuev. ”Principles of optimization for thermoelectric energy converters with inhomogeneous legs”, Proc. of the 6th International Scientific Conference: Chaos and structures in nonlinear systems. Theory and experiment, Astana, ENU Publishing, pp. 264-268, October 3-4, 2008.
47. B.M.Goltsman, V.A.Kudinov, I.A.Smirnov. Semiconductor thermoelectrics on Bi_2Te_3 base.1972, M., Nauka, 320 p.
48. M.A. Korzhuev. Highly pure substances, №2, p.74 (1996).
49. J. R. Sootsman, D.Y. Chung, M.G. Kanatzidis. Angew. Chem. Int. Ed., **Vol.48**, p.8616 (2009).
50. W. Heywang. Amorphe und polykristalline Halbleiter.1984, Berlin, Springer-Verlag, 160 s.
51. M.A. Korzhuev, “The application of bulk Seebeck and Peltier effects in thermoelectric energy converters”, *Proc. of XI Inter State Seminar: Thermoelectrics and their applications, ed. M.V.Vedernikov and L.N. Lukyanova, SPb, PIYF,* pp. 369-374, November 25-26, 2008.
52. O.I. Markov. J. Technical Physics, **Vol.74**, №2, p.138 (2004).
53. J. Lieb, S. Neugebauer, A. Eger, M. Linde, B. Masar, W. Stűtz, *MTZ.* ***Vol.*****70**, p. 1 (2009).
54. V.A. Semenyuk, O.L.Nichiporyuk. Izv.VUZ. Power engineering, №2, p.105 (1976).
55. M.P.Volkov, S.M.Manyakin. Izv.VUZ. Materials electronic engineering, №2, p.21 (2003).
56. L.I. Anatychuk, L.N. Vikhor, R.G.Cherkez. J. Thermoelectricity, №3, p.41 (1997).
57. L.I. Anatychuk, L.N. Vikhor, R.G.Cherkez. J. Thermoelectricity, №3, p.47 (2000).
58. T.E.Svechnikova, L.E.Shelimova, P.P.Konstantinov, M.A.Kretova, E.S.Avilov, V.S.Zemskov, X.Shtive, A.Zuber, E.Muller. Inorganic Materials, **Vol.41**, №10, p.1183 (2005).
59. M.A. Korzhuev, T.E. Svechnikova, I.Yu. Nichezina, “ Spontaneous bulk Seebeck effect in p- legs of thermoelectric generators on $Cu_{2-x}Se$ base”, *Proc. of XI Inter State Seminar: Thermoelectrics and their applications, ed. M.V.Vedernikov and L.N. Lukyanova, SPb, PIYF,* pp. 375-380, November 25-26, 2008.
60. M. A. Korzhuyev, I. V. Katin, “Physical phenomena in the legs of thermoelectric generators made from cupric selenide”, *Proc. of the IV International Scientific Conference: Actual problems of solid state physics, Minsk, Varaksin A.N.,* ***Vol.2***, pp. 264-268, October 20- 23, 2009.
61. M. A. Korzhuev, I. V. Katin. J. Thermoelectricity, №3, p.11 (2009).
62. Yu.A.Chramov. The Physicists. Book of reference. 1983, M., Nauka, 400 p.
63. L.Galvani, A.Volta. The elected works on animal electricity. With introductory article by A.V.Lebedinskiy, 1937, M., OGIZ, p. 345.
64. M.B.Berkinblit, E.G.Glagoleva. Electricity in alive organisms. 1988, M., Nauka, 288 p.