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Refinement and Supplement of Phenomenology of Thermoelectricity

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Abstract: Phenomenology of nonequilibrium thermodynamics based on independent thermodynamic forces with kinetic coefficients independent of the applied forces. Whereas the traditional thermoelectric phenomenology is based on the experimentally measured material parameters of the medium. At the same time, their historically emerging definitions have neither mathematical rigor nor consistency. And, as a result, the strict, developed in macroscopic phenomenological nonequilibrium thermodynamics patterns of relationship, in thermoelectricity are not completely considered. A rigorous phenomenological description of macroscopic thermoelectricity made it possible to reveal effects that had not been taken into account earlier when measuring thermoelectrics. In particular the effect of thermoelectric locking of current significantly influencing the measurement accuracy of conductivity of thermoelectrics has been ascertained. In addition, the phenomenology of thermoelectricity could be expanded both in terms of dimensionality and in terms of scale of size. Thereby it was succeeded to consider concentration effects even in the macroscopic case and to extend thermoelectricity phenomenology on micro- and the nano-level.

Keywords: Local Effects, Sharply Inhomogeneous Media, Thermoelectricity,
Phenomenological Nonequilibrium Thermodynamics, p-n Junction

1. Introduction

Seebeck and Peltye's thermoelectric effects are defined by the small difference between mean energy of the drift flow of electrons and their mean static energy (Fermi level). Therefore, the diffusion kinetic coefficients corresponding to these effects are small. As it became clear now, it is for this reason that the efficiency of thermoelectric devices has only increased insignificantly for many decades, solely due to constructive factors, but it does not cardinally change. And that is why the possibility of direct energy conversion attributed to diffuse effects is in principle not true. Empirical same attempts to increase the thermoelectric figure of merit due to nano-technologies rested in the absence of understanding of thermodynamic processes at the micro- and nano-level.

On the other hand, because of the smallness of the diffusive coefficients of Seebeck and Peltier, they were earlier justly rejected from consideration when describing the operation of microelectronic devices. The carried-out big cycle of thermoelectric researches on semiconductor micro objects and artificial microstructures showed that in addition to macroscopic thermoelectric effects there are local thermoelectric effects. The description of local thermoelectric effects also required refinement and supplementation of basic models of thermoelectricity. As the analysis shows, taking into account and using the local thermoelectric effects will allow, both dramatically increase the efficiency of thermoelectric devices, and reduce the energy consumption of microelectronic devices.

2. Materials and Methods

This paper concerns thermoelectric effects, macroscopic effects arising in homogeneous and slightly inhomogeneous media and local thermoelectric effects arising in sharply inhomogeneous media. Macroscopic effects were investigated by the author in a wide class of materials, from semimetals such as graphite and bismuth, to wide-band semiconductors such as silicon carbide, gallium arsenide and

gallium nitride, from strongly self- and additionally alloyed semiconductor-alloys such as higher manganese silicide and magnesium disilicide, to ultrapure Crystals of germanium, silicon, silicon carbide, gallium arsenide and a number of others. Researches and composition materials of type the sintered silicon carbide nanoparticles with metal and the grown-up alternating nano-layers of boron nitride and graphite were conducted.

At the same time researches were conducted complex: from the temperature dependences of the kinetic coefficients, to neutron studies of the features of the phonon spectrum. Results of these researches are only partially presented in references below, selectively not to distract from the solvable task. Although many of the results obtained, most of which are scattered in the works of Russian conferences, have previously determined the direction of the experimental search, and now they have determined the ways of solving the problem of increasing the efficiency of thermoelectric conversion. And it is these studies that have shown the fundamental limitations of the thermoelectric figure of merit of any macroscopic effective medium.

In thermoelectric studies, epoch-making giant thermo-emfs, were occasionally observed -"forbidden", since were not described either by thermoelectric phenomenology, or by barrier models based on the Richardson's formula. These, called "anomalous" thermoelectric power, were occasionally observed on contacts. And with these "anomalous" thermoelectric power I was instructed to understand more than 30 years ago the thermoelectricity cipher, which was elected by the President of the Thermoelectric Congress, Professor L. S. Stilbans. He had long felt the impasse of macroscopic thermoelectricity and pinned his hopes on contact effects even then.

It is cardinal it was succeeded to promote in repeatability of observed datas of "abnormal" thermo-emfs when departed from traditional thermoelectric manufacturing techniques of contact to technology of microelectronics i.e. when understood that p-n junction and is ideally controlled and managed contact for thermoelectric researches. Actually already the first results of the researches of p-n junctions with leading of the controlled heat flux by the standard thermoelectric technique - by means of the heat conductor, closed experimental "anomaly" - repeatability of observed datas was high.

But the magnitude of the registered EMFs raised the question of the theoretical "anomaly" - when the two semiconductors come into contact with the same physical and geometric parameters, the integral thermoelectric power should equal zero, while the recorded signals, even the recorded signals, even according to rough estimates of the temperature drop directly on the p-n junction, gave a thermo-emf of orders of magnitude greater than the thermoelectric power of the p-n junction facings. The use of the optical method of supplying a controlled heat flux made it possible to carry out both quantitative measurements of the magnitude of local thermo-EMFs and their frequency characteristics.

Longitudinal and transverse thermoelectric effects in p-n junctions based on silicon and a longitudinal thermoelectric effect in p-n junctions based on silicon carbide and gallium arsenide were investigated. Also, the longitudinal thermoelectric effect was investigated on an asymmetric potential barrier on gallium nitride border with magnesium. The results of these experiments are also presented in the references.

So the present work itself is devoted to a phenomenological analysis of previously obtained research results, which also removes the theoretical "anomaly" (prohibition) from local thermo-EMFs.

3. Results and Discussion

3.1. Critical Analysis of Kinetic Effects Phenomenology

Kinetic effects in macro homogeneous media in the simplest case, for the so-called direct effects, are characterized by the linear coupling of the corresponding forces F_i and flows J_i :

$$J_i = L_i F_i \qquad (1)$$

These coupling equations describes any processes that arise in the medium under the weak action of one independent force. The known laws describing diffusion:

carriers of charges in electric field E : $J_E = \sigma \dfrac{\partial \varphi}{\partial x} = \sigma E$ - Ohm's law,

particles in the presence of the concentration gradient $\dfrac{\partial N}{\partial x}$:

$J_N = -D \dfrac{\partial N}{\partial x}$ - the 1st Fick's law,

heat in the presence of a temperature gradient $\dfrac{\partial T}{\partial x}$:

$J_T = -\mathrm{K} \dfrac{\partial T}{\partial x}$ - Fourier's law,

where material parameters σ - electrical conductivity, D - the diffusion coefficient, and K - thermal conductivity, show this linear relation of flows at rather small influences (gradient forces) that, actually, and is the basis for strict use of system of mathematical linear equations (1). But the relation of the kinetic coefficients in the canonical form (1), to which the symmetry tool is applicable, with the material parameters in the noted direct laws is not as unambiguous as often believe is applicable. The canonical coefficients strictly correspond to the condition of nulling of all independent thermodynamic forces, except one, chosen for consideration that is not always observed also at their measurement in the experiment, and when calculating.

The ambiguity of the connection L_i with the measured and calculated material parameters of the medium will be shown below at the accounting of cross effects. Now we will only note that some and direct effects, and for small forces and flows sometimes demand initially, in principle, the accounting of additional factors. For example, the diffusion

(number) of photons N_k : $J_K = D_k \dfrac{\partial N_k}{\partial x}$, photons - in optically active media or nonequilibrium phonons - in acoustically active media, demand the accounting of the blurring of the frequency of the wave packet. But even in these cases the linear connection can be quite strictly used with the introduction of a parametric dependence on the additional factor of the coupling coefficient $D_k(p)$.

For the majority of processes in a homogeneous medium at small influences, the independence of the coupling coefficient L_i from the force F_i written in canonical form and, thereby, linear approach, is strictly carried out with good accuracy. The physical cause of the validity of the linear connection of small diffuse flows with forces is their physical nature - all direct kinetic coefficients L_i are nothing more than a friction coefficient for the corresponding diffuse flow.

Naturally, and cross coefficients to which the analysis is actually devoted below are also the consequence of mutual friction of the flows corresponding to the selected forces. For this reason and in linear approach it is possible to consider deposits of different processes at the same time.

But at the same time instead of the elementary coupling equations (1), characteristic of direct effects, it is necessary to use the combined equations which are written down, generally, in the canonical form of Pfaff [1]:

$$J_i = L_{ik} F_k \qquad (2)$$

I.e. strict calculation of physical processes in the medium requires the solution, as a first approximation full and written down strictly in the canonical form of combined equations (2). However developed and so far used phenomenology of the individual kinetic phenomena are based on the models simplified, corresponding only to the separate considered effect.

At the same time, for each effect, the historically developed type of forces and flows was used. The arbitrariness in the choice of the processes under consideration, without estimating the order of infinitesimal of the discarded orthogonal forces, certainly leads to a violation of the principles of symmetry. But the analysis of completeness (sufficiency) of the used minimum set for each effect, even in linear approach, it was not carried out. Just as assessment of order infinitesimal of reaction to influences of all forces excluded from consideration was not carried out. In homogeneous environments for which the simplest models were originally developed, the quantitative differences in the results of the calculations and measurements that were encountered were attributed to their errors (assuming they were small). In homogeneous environments for which the prime models were initially developed the arising quantitative differences of results of calculations and measurements connected with their errors (believing their small). In certain cases the arising errors were implicitly corrected at creation of nonlinear or microscopic models. But in certain cases, the arising basic contradictions just were ignored.

The analysis of kinetic effects in microinhomogeneous media has revealed a number of fundamental contradictions in simplified models. Interaction of different thermodynamic forces is insufficiently full and were insufficiently strictly considered in the linear response even for homogeneous macroscopic medium. As it will be shown below, application of the simplified models even for homogeneous media essentially limits the circle of the considered effects. And the effects connected with the inhomogeneities of micro- and nano-scale at the same time in principle were excluded from consideration.

The analysis of cross effects in homogeneous media once formed base of creation of nonequilibrium thermodynamics [2]. Their analysis in inhomogeneous media - artificial semiconductor structures [3, 4] has now become an impetus, both for the revision of the basic macroscopic phenomenology of individual effects, and for the expanded and generalized phenomenology of kinetic phenomena in general.

The carried-out critical analysis has allowed to eliminate a number of inaccuracies and contradictions in widely used models and to offer new models. This allowed us to estimate the theoretical limit of the efficiency of macroscopic thermoelectricity and, taking into account the local thermodynamics of Ilya Prigogine [5], to demonstrate the possibility of a cardinal increase in the efficiency of thermoelectric conversion on artificial semiconductor structures on the basis of local thermoelectric effects found.

3.2. Refinement of the Two-Component Thermoelectric E-T Phenomenology

The most studied cross effects are Seebeck's and Peltye's thermoelectric effects. Moreover, the very Onsager's principle of the symmetry of kinetic coefficients derived from the analysis of these effects. In the thermoelectric theory, the reduced system of kinetic equations [6] is used, which connects through the measured material parameters the density of two flows: electric J_E and heat J_T with two gradient forces: the gradient of the electrostatic potential - the electric field intensity $E = \Delta\varphi$ and the temperature gradient ΔT :

$$\left.\begin{array}{l} J_E = \sigma \cdot E + \sigma \cdot (S \cdot \Delta T) \\ J_T = \Pi \cdot J_E + K^* \cdot \Delta T \end{array}\right\} \qquad (3)$$

where coefficients corresponding to direct effects σ - the electric current conductivity in the absence of temperature force, and K^* - heat conductivity of material, at this record of the heat flow in the absence of electric current (that is noted by the asterisk), and the corresponding to cross effects S - Seebeck's coefficient, and Π - Peltye's heat.

That to transform the system of equations (3) to the canonical form - Pfaff form (2), we will substitute expression for electric current in the equation for the heat flow and we use record of thermodynamic forces in the canonical,

gradient form: $F_E = \dfrac{E}{T}$, $F_T = \dfrac{\Delta T}{T^2}$:

$$\left.\begin{array}{l} J_E = \sigma \cdot T \cdot \dfrac{E}{T} + \left(\sigma \cdot S \cdot T^2\right) \cdot \dfrac{\Delta T}{T^2} \\[3mm] J_T = \Pi \cdot \sigma \cdot T \cdot \dfrac{E}{T} + \left(\Pi \cdot \sigma \cdot S + K^*\right) \cdot T^2 \cdot \dfrac{\Delta T}{T^2} \end{array}\right\} \quad (4)$$

Also we will receive the expression of the coefficients of Pfaff form through the measured parameters:

$$L_{EE} = \sigma \cdot T, \; L_{TT} = \left(\Pi \cdot \sigma \cdot S + K^*\right) \cdot T^2, \; L_{ET} = \sigma \cdot S \cdot T^2,$$
$$L_{TE} = \Pi \cdot \sigma \cdot T \quad (5)$$

Onsager's principle of symmetry, which is applicable to kinetic coefficients exclusively in canonical form, abridge their number to three independent coefficients: $L_{ET} \equiv L_{TE}$. Thus, the physical relationship between the thermoelectric coefficients of Seebeck and Peltier becomes visible: $\Pi = S \cdot T$ - both these effects are a reflection of the same interaction of electric and temperature forces in a material medium, but under different measurement conditions.

From formulas (5) it is also visible that even not all direct measured kinetic coefficients, because of different conditions of their measurement, correspond to canonical kinetic coefficients. If the conductivity measurement corresponds to the canonical zeroing of the external thermal force, the measurement of the thermal conductivity at the canonical nulling of the external electric force will give the thermal conductivity coefficient K [7] qualitatively different from the one traditionally measured in the absence of an electric current K^*.

$$K = \Pi \cdot \sigma \cdot S + K^* \equiv S^2 \cdot \sigma \cdot T + K^* \equiv \Pi^2 \cdot \sigma / T + K^* \equiv \kappa + K^* \;\; (6)$$

The difference arises, firstly, due to the fact that in the canonical determination of the heat conductivity K in the absence of an electric field $E = 0$, the electric current is completely determined by the thermal force $J_E = \sigma \cdot \left(S \cdot \Delta T\right) \neq 0$ and a short-circuited regime is realized by the electric current. Whereas traditional non-canonical definition of heat conduction K^* at $J_E = 0$ essentially differs - corresponds to an open-circuit regime on electric current that excludes the drift contribution of Peltier heat $\Pi \cdot \sigma \cdot S$ to heat transport. The accounting of this connection made allowed to find nonlinearity of temperature distribution in the thermoelement and to refine the model of optimization of thermoelectrics [8, 9].

Thus, and canonical definition of the electrical conductivity corresponds to the short circuit of the heat flow generated by electric current, and canonical definition of heat conductivity corresponds to also short circuit of the electric current generated by the heat flux. I.e. conditions of receiving/ measuring of both direct kinetic coefficients in the canonical form are completely symmetric. At the same time square dependence on thermoelectric coefficients S and Π addition κ to the traditionally measured uncanonical thermal

conductivity K^* means that this additive positive for carriers of current of any sign (independent of the sign of the thermoelectric power).

But from the symmetry of the conditions for measuring direct coefficients, the principal "second" also follows. Additive $\Pi \cdot \sigma \cdot S = \kappa$ is drift component full electronic heat conductivity $\kappa + K^e$, where K^e - heat conductivity of stationary electronic plasma, and the additive κ defines canonical coefficient of the system of equations for a conducting medium with the 2-th order (2x2) matrix of kinetic coefficients. So taking into account actually uncanonical part this matrix, strictly speaking, has to be expanded to the 4-th order (4x4) matrix of the type shown below:

$$\begin{bmatrix} L_{11} & L_{12} & 0 & 0 \\ L_{12} & L_{22} & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & L_{44} \end{bmatrix} \quad (7)$$

Thus, the traditional record of the equation of the heat flow corresponds to the reduced system of equations. At the same time the equation for the heat flow is received with symmetry violation - summing from the combined equations degenerated to one heat conduction equation with the additional canonical thermal conductivity $L_{44} = L_{TT}^* = K^* \cdot T^2$, which leads to a difference in the abbreviated 2x2 matrix. In this case the uncanonical part of heat conductivity is defined by all, the processes which are immovable of the charge and the additional member contains: $K^* = K^e + K^{Ph}$, where K^{Ph} - phonon heat conductivity.

But before starting the strict analysis of the canonical system of equations, we will show how also conductivity will change if to measure it at uncanonical, similar to measurement of uncanonical heat conductivity conditions. I.e. we and I will measure electrical conductivity σ not in traditionally canonical conditions that corresponds as it is noted above, to a regime short-circuited by the heat flux.

The heat flux is defined by electric force: $J_T = \pi \cdot \sigma \cdot E$ and, thereby, the mode, short-circuited on it, corresponded to the identical temperature of the electrical contacts. When the heat flow is set to zero, as the electric current is nullified when measuring the heat conductivity, will arise the temperature gradient ΔT which will give additive to the measured electrical resistance. If we use the initial in the experimentally measured parameters non-canonical equation for the heat flux from (3) and we will receive this temperature gradient:

$$J_T = 0 = \Pi \cdot J_E + K^* \cdot \Delta T \rightarrow \Delta T = -\Pi \cdot J_E / K^* \quad (8)$$

Setting up it in the equation for current, we have the following equation:

$$J_E = \sigma \cdot E - \sigma \cdot \left(S \cdot \Pi \cdot J_E / K^*\right) \rightarrow J_E \left(1 + \sigma \cdot S \cdot \Pi / K^*\right) = \sigma \cdot E \;\; (9)$$

which gives the electrical conductivity σ^* measured in the temperature gradient it is less than conductivity σ measured at identical temperatures on contacts:

$$J_E = \frac{\sigma}{1 + \sigma \cdot S \cdot \Pi / K^*} \cdot E = \frac{1}{1/\sigma + (S^2 \cdot T)/K^*} \cdot E = \sigma^* \cdot E \quad (10)$$

From the carried-out non-strict, qualitative calculation of the "measured" conductivity it is visible that to unit resistance $\rho = 1/\sigma$ we have thermoelectric additive $(S^2 \cdot T)/K^*$, positive for any sign of carriers of current. This additive of subjects is more, than it is less not canonically measured K^* which no other than full heat conductivity minus the drift electronic part. I.e. K^*, as well as assumed above, there is the total heat conductivity of phonons and motionless electronic plasma.

Thus, for a freely suspended thermoelectric sample, we have that the higher its thermoelectric figure of merit (the lower the thermal losses in it), the greater the thermoelectric self-choking of the electric current. If the heat flux is completely neglected due to the thermal conductivity of the lattice heat conductivity and the motionless plasma (and due to the contacts), then it follows from the system of equations (3) that the temperature gradient tends to a maximum but finite value:

$$J_T = 0 = \Pi \cdot \sigma \cdot E + (\Pi \cdot \sigma \cdot S) \cdot T \cdot \frac{\Delta T}{T} \Rightarrow \Delta T = -\frac{E}{S} \quad (11)$$

and the joint current goes in zero:

$$J_E = \sigma \cdot E + \sigma \cdot (S \cdot \Delta T) = \sigma \cdot E - \sigma \cdot \left(S \frac{E}{S} \right) = 0 \quad (12)$$

The solution of a strictly canonical system of equations, if we use only the canonical part of thermal conductivity κ with a heat flux equal to zero, as will be shown below, also gives zero electric current:

$$J_E = \frac{L_{EE} L_{TT} - L_{ET}^2}{L_{TT}} \cdot F_E \xrightarrow[K^* \to \kappa]{} \frac{0}{L_{TT}} \cdot F_E \equiv 0 \quad (13)$$

Thus, we have self-choking of the thermoelectric current, which, naturally, disappears if the cross coefficient L_{ET} is equal to zero. This self-locking is shown like differentiation in the form of peaks on pulse edges of heating of thermoelectric detectors [10]. Before it connected with nonequilibrium electron concentration, but self-locking is observed also on samples with high concentration of carriers of current where essential change of this concentration does not happen.

For a strict description of thermoelectric effects, we now use the system of equations, not reduced to the measured parameters (3), but the system of equations in the canonical form:

$$\left. \begin{array}{l} J_E = L_{EE} \cdot F_E + L_{ET} \cdot F_T \\ J_T = L_{ET} \cdot F_E + L_{TT} \cdot F_T \end{array} \right\} \quad (14)$$

If we take the electro-and heat-insulated homogeneous macroscopic sample, then, from equality zero of both flows, taking into account symmetry (lack of the preferential polar direction), the trivial solution - equality zero both thermodynamic forces. But if to consider fluctuation (or some additional polar influence in sharply inhomogeneous mediums), then from equality zero both flows

$$\left. \begin{array}{l} 0 = L_{EE} \cdot \delta F_E + L_{ET} \cdot \delta F_T \\ 0 = L_{ET} \cdot \delta F_E + L_{TT} \cdot \delta F_T \end{array} \right\} \quad (15)$$

we obtain the ratio of the amplitudes of the fluctuations of the thermodynamic forces, determined by the canonical kinetic coefficients. Solving the system of equations (15) and eliminating the forces, we obtain, up to a sign, the relationship of the cross canonical coefficient with direct coefficients:

$$\delta F_E = -\frac{L_{ET}}{L_{EE}} \cdot \delta F_T = -\frac{L_{TT}}{L_{ET}} \cdot \delta F_T \to L_{ET} = \pm\sqrt{L_{EE} \cdot L_{TT}} \quad (16)$$

But when the canonical coefficients are replaced by the measured parameters and using the traditionally measured heat conductivity

$$\Pi \cdot \sigma \cdot T = \pm \left(\Pi^2 \cdot \sigma^2 \cdot T^2 + K^* \cdot \sigma \cdot T^3 \right)^{1/2} \quad (17)$$

Let's receive that the relation between the kinetic coefficients (16) is carried out only at $K^* = 0$. I.e. drift part of electronic heat conductivity, completely is defined by mutual friction of electric current and heat flux and is the canonical heat conductivity κ corresponding to direct coefficient L_{TT} (the friction sign - conductivity type does not enter conductivity and heat conductivity and is shown only in cross coefficient).

Thus, the strictly canonical system of equations (14) corresponds to the fluctuation of the heat flux, determined only by the drift part of the heat conductivity κ, and, therefore, this part is connected with the fluctuations of the electric current. Therefore, the rigid, set in equilibrium conditions (15) canonical coefficients interaction communication (16) amplitudes of fluctuations of electric and thermal force, unambiguously defines cross coefficient through the corresponding direct coefficients.

And the contribution phonon and the contribution of motionless plasma to heat conductivity are described, strictly speaking, by the additional independent equations which as it will be shown below, are not completely described also by expansion of the system of equations (14) by means of the matrix of coefficients (7), but require an increase in the dimensionality of the system of equations (14).

As by definition canonical coefficients of linear approach do not depend on the value of the applied force, the received

relation (15) is fair also at small deviations from the balance used for its stay. Therefore the received result has the basic moment. Namely, the relation (16) reduces number of independent kinetic coefficients (in absolute value) of actually conducting medium in the used Pfaff's form from three to two (the sign of the cross ratio is determined by the "hidden" parameter - the type of conductivity). At the same time we have only two independent kinetic coefficients for conducting medium which define its conductivity and the drift part of heat conductivity, and to within the sign thermoelectromotive force and Pelte's heat.

Having rewritten equilibrium condition (15) in the parameters measured for electronic system we will receive

$$\frac{\kappa}{\sigma} = \frac{\pi^2}{3} \cdot \left(\frac{k_B}{e}\right)^2 \cdot T \rightarrow \Pi = \pm \frac{k_B}{e} \cdot \frac{\pi \cdot T}{\sqrt{3}}, \quad S = \pm \frac{k_B}{e} \cdot \frac{\pi}{\sqrt{3}} \approx \pm 1.81 \cdot \frac{k_B}{e}, \tag{19}$$

which is close to the expression of the thermoelectromotive force received in the Herring emission model on the basis of the Richardson's formula [11]:

$$S = 2\frac{k_B}{e} + \frac{\Phi}{T} \tag{20}$$

if work function Φ from the Fermi level in the allowed band is equal to zero.

The relation received in equilibrium point for kinetic coefficients (16) explains abnormally high volt - watt sensitivity of thermoelectric detectors at registration of extremely small radiation flows [12]. For extremely small heat flow in the absence of an electric current, we have the

expressions for thermoelectric coefficients

$$\Pi = \pm \left(\frac{\kappa}{\sigma} \cdot T\right)^{1/2} \text{ or } S = \pm \left(\frac{\kappa}{\sigma \cdot T}\right)^{1/2} \tag{18}$$

From the relations (18), the simplest case, taking into account the Wiedemann-Franz law-the relation between electron conductivity and heat conductivity, with the Sommerfeld's constant, we obtain the expression for the thermoelectromotive force

pole of the relation of the electric force (EMF) to the heat flux (heat flow power)

$$\frac{\delta F_E}{\delta J_T} = \frac{L_{ET}}{L_{EE}L_{TT} - \left(L_{ET}\right)^2} \underset{K^* \to 0}{\longrightarrow} \frac{L_{ET}}{0} \to \infty \tag{21}$$

This, not taking into account noise processes and additional heat losses (and as it will be shown below, concentration effects) idealization, is shown also in calculation of watts - watt conversion factor at small electric currents

$$\frac{\delta F_E \cdot \delta J_E}{\delta J_T} = \frac{L_{ET} - L_{TT} \cdot \frac{\delta J_E}{\delta J_T}}{\left(L_{ET}\right)^2 - L_{EE}L_{TT}} \cdot \delta J_E \underset{K^* \to 0}{\longrightarrow} \frac{L_{ET} - L_{TT} \cdot \frac{\delta J_E}{\delta J_T}}{0} \cdot \delta J_E \to \infty \tag{22}$$

Existence, in the absence of additional heat losses, in the conversion factors (21) and (22) of the poles makes it possible to estimate the maximum achievable conversion coefficients and at big heat flows, when the noise can already be neglected, and the independence of the kinetic coefficients from the forces still remains.

Therefore, the thermo-emf (18) obtained, and without simplification (19), make it possible to estimate the theoretical limit of the Ioffe parameter-the maximum value of the thermoelectric figure of merit of an ideal medium-a conducting macroscopic medium in the absence of additional

thermal losses at the expense of motionless plasma and phonons:

$$Z^{max} = \frac{S^2 \cdot \sigma}{\kappa} = \frac{1}{T} \text{ or } Z^{max} \cdot T = 1 \tag{23}$$

At the same time we will receive the most achievable efficiency of the conversion of the ideal thermoelectric in Ioffe's model

$$\eta_{max} = \frac{T_{max} - T_{min}}{T_{max}} \cdot \frac{Z^{max}(T_{max}) \cdot T_{max}}{\left[1 + \sqrt{1 + Z^{max}(T_{min}) \cdot T_{min}}\right]^2} = \frac{T_{max} - T_{min}}{T_{max}} \cdot \frac{1}{\left[1 + \sqrt{2}\right]^2} = 0,1716 \cdot \frac{T_{max} - T_{min}}{T_{max}} \tag{24}$$

Follows from the formula (24) that when heating hot junction of the thermocouple up to a temperature of 300°C we will receive the maximum diffusion efficiency less than 9% (in real devices less than 6%), and with the maximum use of its heating up to a temperature of 1000°Cthe efficiency

will not exceed 14% (in real devices less than 12%) [13].

Addition of heat losses for the account K^* can make, naturally, the maximum thermoelectric figure of merit (23) only less unit. Therefore its values given for the number of thermoelectrics like alloys on the basis of Bi_2Te_3 much

greater than one, or reflect the physical process giving the additional positive contribution to the cross-correlation coefficients due to the phonon subsystem (that is improbable), or the investigation of confusion in definition/measurement of different material parameters of the medium under nonequivalent conditions, i.e. without the effects described above.

Since real efficiency of macroscopic thermoelectric devices there are less maximum achievable efficiency calculated on the formula (24) for purely electronic subsystem of the used thermoelectrics, the last is more probable. And the high, not corresponding to final efficiency values of thermoelectric figure of merit, receive as they substitute the material parameters measured under different conditions.

Theoretical account of the contribution of phonons to the cross-correlation coefficients requires the construction of an independent phonon part of the system of equations in the canonical form and the solution of the system of equations with at least a matrix of kinetic coefficients of the type (7). But neither the theoretical analysis of homogeneous media [13], nor the experimental complex analysis the electron - phonon interaction in classical crystals, in superstructures, in amorphous materials, in incommensurate crystals and micro and nano-heterogeneous macroscopic environments [14, 15], did not reveal the mechanism of the efficiency providing increase over its maximum for the electronic subsystem.

Some researchers associated hopes for an increase in the efficiency with a low-temperature phonon drag effect in the high-temperature region on silicon carbide, which in principle would give additional contributions to the electric current due to the fact that the zero terms of the matrix (7) would be finite, and their contributions "resolved". However the conducted researches showed that incidentally observed abnormally big thermoelectromotive forces including on silicon carbide, arise on contacts and are defined not by macroscopic, but by micro and nano-effects [3, 16], as demanded expansion of macroscopic phenomenology [17].

The carried-out system, canonical approach, makes it possible to avoid confusion in the phenomenology of thermoelectricity which attributed the diffusion, i.e. indirect, friction-based energy conversion to direct conversion.

Without the strictly considering a simplified thermoelectric system from the two equations for coupling forces and flows, it would be impossible to extend it, which is necessary for taking into account local thermodynamic effects at micro-inhomogeneities. And as the system approach has shown, it is on the basis of local effects that cardinal, in many cases, an increase in the real efficiency of the thermoelectric energy conversion can be achieved due to its transfer from indirect to direct conversion of energy. And as showed system approach, on the basis of local effects perhaps cardinal, many times increase in real efficiency of thermoelectric energy conversion can be achieved due to its transfer from indirect to direct conversion of energy.

3.3. Additional Two-Component Phenomenology

Before starting the analysis of expanded system of equations, let us consider two more of its the particular case when one of independent forces and the flow corresponding to it neglect.

This detailed analysis of particular cases is connected not only with inaccuracies of the basic models used in them, but also with lack of understanding among experts of adjacent areas of the common problem - for the correct description of the phenomenon it is required to make a start from correctly constructed first, linear approach. In this case, it is necessary to use a complete necessary and sufficient set of independent thermodynamic forces. It is correct to specify only such approach describing the main effect as a first approximation on order infinitesimal and further. And to make in effect 100% of the correction in order of smallness (infinitesimal order) to a partial, in the first approximation, not describing the effect of the model, it is only its fit to describe the phenomenon beyond the applicability of the actual empirical model.

3.3.1. E-N Phenomenology

In the macroscopic thermoelectric theory, the concentration force is excluded from consideration and, accordingly, even the direct coefficient D from Fick's 1st law is excluded. Served as justification for such approach seemingly "obvious" communication of electric current J_E with the concentration flow $J_N : J_E \equiv e \cdot J_N$, where e - the electron charge. But this assumption, which is valid in homogeneous media and, in a rough approximation, allows one to exclude from thermoelectricity the equation for the concentration flow, in inhomogeneous media, is in principle not true.

That this assumption is not true for inhomogeneous media at the micro-level level is evident also from the theory of the p-n junction, which, in fact, is built on an E-N phenomenology, an alternative thermoelectric. Phenomenological incompleteness of thermoelectricity was confirmed also by the analysis of local thermoelectric effects at micro-objects [3, 15, 16, 17, 18]. And though for the description of properties of micro-objects are not limited to linear (diffusion) approach, correctly constructed linear phenomenology is necessary in the analysis of the asymptotics in zero.

So, for a nonlinear theory, it is also required to consider full, necessary and sufficient set of independent forces. Therefore, in thermoelectricity, an independent concentration force $F_N = -\dfrac{\Delta N}{T}$, which, with other forces equal to zero, completely determines the diffusion current $L_{NN}F_N \to D \cdot \Delta N$ and the direct kinetic coefficient $L_{NN} = D \cdot T$, is required. And it is this current, in principle, that determines the formation of potential barriers in inhomogeneous media, in particular, in the p-n junction. This

is a direct indication of the need to take it into account in the first approximation.

At first, we note some features of the system of equations which are actually used in a simplified form for describing p-n junctions by the Poisson equation. In this system of equations unlike thermoelectricity, the concentration force is taken into account, and the temperature force is thrown out of consideration:

$$\left.\begin{array}{l} J_E = L_{EE}F_E + L_{EN}F_N \\ J_N = L_{EN}F_E + L_{NN}F_N \end{array}\right\} \qquad (25)$$

Solving this system of equations, just as in the thermoelectric case, using the equality of fluctuation amplitudes for the equilibrium point, we obtain, similarly to (16), the relation for the cross coefficient with direct coefficients

$$L_{EN} = \pm\left(L_{EE} \cdot L_{NN}\right)^{1/2} = \pm T \cdot \sqrt{\sigma \cdot eD} \qquad (26)$$

The resulting relation, as a consequence of the independence of the kinetic coefficients from the applied force, is also valid for small deviations from the equilibrium point, which allows us to analyze the opening move of the I-V characteristic. If we put the concentration flux in (25) equal to zero, then near the equilibrium point we get the electric current equal to zero:

$$J_E = \frac{L_{EE}L_{NN} - L_{EN}^2}{L_{NN}}F_E = \frac{0}{L_{NN}}F_E \equiv 0 \qquad (27)$$

If we put $J_E \equiv e \cdot J_N$, then only the denominator changes, and the numerator still tends to zero

$$J_E = \frac{L_{EE}L_{NN} - L_{EN}^2}{L_{NN} + L_{EN}/e}F_E = e\frac{0}{eL_{NN} + \sqrt{L_{EE}L_{NN}}}F_E \equiv 0 \quad (28)$$

It is obvious that in E-N phenomenology (25) the electrical conductivity even for a homogeneous medium (say, for the n-facing of the p-n junction) depends on both the concentration force and the cross coefficient L_{EN}. Moreover, strictly within the framework of the E-N phenomenology, Ohm's law does not work. Using the simplified system (25), the opening move of the I-V characteristic, when discarding the additional deposits analogous to the contributions to the thermal conductivity in the E-T phenomenology, is described by zero current.

Formally, this corresponds to the self-locking of the thermoelectric current in the absence of heat losses. And just as in E-T phenomenology, the dynamic (or quasi-dynamic at $J_E \equiv e \cdot J_N$) balance of the forces of the E-N phenomenology is violated and, respectively, the current growth begins when there are additives outside the framework of the canonical system of equations. The extreme case of "violation" - neglect in (27, 28) by the cross coefficient L_{EN} "corrects" the IVC and gives a diffuse, independent of force! electrical conductivity $\sigma = const(E)$ on its the opening move:

$$J_E = e\frac{L_{EE}L_{NN}}{eL_{NN}} \cdot F_E = L_{EE} \cdot F_E \equiv \sigma \cdot E \neq 0 \qquad (29)$$

Whereas, the received non-linear I-V characteristic of the same p-n junction has an electrical conductivity that depends on the electric force: $\sigma = \sigma(E)$. To determine the form of the current-voltage characteristic, we used the reduced equation of carrier current diffusion:

$$J_E^* = \sigma E^* - eD\frac{\partial N}{\partial x} \qquad (30)$$

where u is the "measured" (marked with an asterisk) electric current and field, and in fact the solution of Eq. (30) in the form of an I-V characteristic of an "ideal" diode was received speculatively-compiling. We will not dwell on an analysis of this non-strict solution. Let us dwell only on the prerequisites for obtaining it-equation (30).

Equation (30) uses a "corrected" set of forces and flows, which near the equilibrium state does not describe, in principle, only one E-N phenomenology (25). This is a general philosophical problem of considering selected process fragments beyond the cause-and-effect relationship.

Just as the equality of the force of acceleration to the inertia force demands the transition to a system of accelerated coordinates, for diffuse stationary processes, the rough accounting of uncanonical additives "provides" the transition from a fixed coordinate system to a drifting system with a constant speed.

And since in order to "correct the zeros" in (27, 28), in an explicit form it is impossible to neglect the member, cross with concentration, then, instead of the true (canonical) flows and forces, "correction" instead of using the "measured" electric force and current. At the same time, since it was believed that taking into account the additivity of the contributions of individual charges to the total electric field E and taking into account the connection between the concentration flux J_N and the electric current J_E by the equation: $J_E = eJ_N$ it is also sufficient to use as the basic one (upper) equation of the system (25) transformed by the "measurable" forces and flows into equation (30).

This is a crude phenomenological approximation. It still excludes the cross-effect, since the modified equation (30), gives dependence of the "measured" electric field on cross coefficient L_{EN} near equilibrium point too. And only at ejection L_{EN} from consideration:

$$F_E^* = -\frac{L_{EN} + L_{NN}}{L_{EE} + L_{EN}}F_N \xrightarrow[L_{EN}\to 0]{} -\frac{L_{NN}}{L_{EE}}F_N, \qquad (31)$$

the ratio for the "corrected" forces, corresponds to Einstein's ratio between diffusion D and mobility of electrons μ and their conductivity σ

$$D = k_B \cdot N \cdot T \cdot \mu \to D = \frac{k_B T}{e}\sigma \qquad (32)$$

The strict correspondence (31) and (32) is due to the fact that the Einstein relation itself is obtained for uncanonical coefficients with alternating neglect of one of the forces, i.e. the conditions of neglect of the cross-effect, and initially put in (30) for its speculative decision.

Thus, a whole section of physics was built in "corrected" coordinates, but the resulting "corrected" decisions do not turn asymptotically into strict linear approach near equilibrium point. Similarly, the relation of forces, but canonical, in the framework of the E-N phenomenology (25) gives the root dependence of the canonical coefficients instead of the Einstein relation (31, 32) near the equilibrium point:

$$F_E = -\frac{L_{EN}}{L_{EE}} \cdot F_N = -\frac{L_{NN}}{L_{NE}} \cdot F_N \rightarrow F_E = -\sqrt{L_{NN} / L_{EE}} \cdot F_N \quad (33)$$

Used (originally Schottky) rough approach with neglect by the cross member (31), allowed speculating, nevertheless, qualitatively, in order of value, to describe the current-voltage characteristics of the barrier layer at the metal-semiconductor interface (Mott), and later to construct a theory of (thick) p-n junction. However, the application of this approach in calculating the potential barrier in the p-n junction and the Schottky barrier, even after taking into account many additional factors in detail, requires the introduction of a correction multiplier about 2, which was called the non-ideality coefficient [19]. I.e. the incorrectness of the calculations demanding 100% correction (due to an error in the calculations but missed without a system approach) was due to the imperfection of the semiconductors and devices being used.

To correct the actual E-N phenomenology of the p-n junction, or to analyze in more detail the dependences of the initial portions of the IVC (27, 28, 29) received in its framework, does not enter the task of this thermoelectric work. But to move further, to a generalized system of equations, it is necessary making a start not from speculative calculations, but on a strictly simplified system of equations (25) and from calculations of fluctuations, when nulling of the true, but not specified forces. Therefore, in this paper devoted to thermoelectric phenomenology, we will not carry out a more detailed calculation of the actual p-n junctions. Moreover, as for the thermoelectric theory and for the theory of the p-n junction, the analysis carried out shows that in a strict linear approximation it is impossible - wrong to confine ourselves to a system of two phenomenological equations.

Running forward now, we note that the diffuse approximation itself, within which the Einstein's relation holds, and which works at initial low currents of the IVC, is applicable only when a certain current is reached, i.e. then, when the scattering-friction processes become decisive. And on extremely small currents ballistic effects give the essential contribution [20]. But the true electrical conductivity is measured not at low currents. And IVC of the ideal diode, received by means of equation (30), treats rather big currents. So, the asymptotically used dependences for diffuse currents

must satisfy the linear approximation in the canonical form.

3.3.2. N-T Phenomenology

Before passing to the consideration of the extended system of equations, it is required to briefly consider one more particular (limiting) case, where the electric force is excluded from consideration, and only the concentration and thermal force are taken into account:

$$\left. \begin{array}{l} J_N = L_{NN} F_N + L_{NT} F_T \\ J_T = L_{NT} F_N + L_{TT} F_T \end{array} \right\} \quad (34)$$

Let's shortly consider, similarly to the two previous special cases, fluctuation and we will receive ideally and within N-T of phenomenology analytical expression for one more cross canonical coefficient L_{NT} through direct coefficients:

$$L_{NT} = \pm \left(L_{TT} \cdot L_{NN} \right)^{1/2} = \pm T \cdot \sqrt{\kappa \cdot T \cdot D} \quad (35)$$

The coefficient L_{NT} corresponds to the diffusion-temperature Soret effect and the diffusional Duffur effect. To some extent, there is nothing unusual in that the received cross coefficient as well as in thermoelectricity, has two signs. Just it indicates that it is similar to the electrical conductivity, which has the same sign for both electrons and holes, the thermoelectric power is "senses" by difference of the sign of the charge carrier, and thermal diffusion, can be defined either by moving additional impurity in the temperature field, or by moving the missing impurities - vacancies.

Qualitatively this effect is used when annealing - formation of perfect crystals in the temperature gradient. And most clearly this effect is demonstrated by the motion in the temperature field of two-dimensional regular vacancies-the grid of concentration solitons in a incommensurate crystal of the higher manganese silicide [20].]. Soret effects and Dyuffura still are not considered in the description of operation of semiconductor devices at all. Therefore, we will not give a refinement of the analog of the current-voltage characteristic for the concentration flux using the thermal force in this paper.

3.4. Parametric Supplement of E-N to E-T Phenomenology

If in some cases, say for a photoelectric effect, it is possible to be limited, because of the small impulse of photons, to a nonpolar and even isotropic consideration of the influence of light in the p-n junction and, as a consequence, a parametric description of the reaction to light, then for the heat flux, its polar, changing symmetry of the object influence is an established fact.

Therefore, if the parametrical approach within the E-N phenomenology is allowed for the photo-effect, then for thermoelectric effects, there is no basis for neglecting the additional temperature force to E-N phenomenology or the additional concentration force to E-T phenomenology of sharply inhomogeneous media.

But a detailed analysis of the three-component thermoelectric phenomenology that gives the previously ignored "three-phase" thermoelectric effects, even for macroscopic media, and without which strict consideration of thermoelectric processes at nano- and micro-levels is simply not possible, will be devoted to (in connection with its large volume) the following paper. Now, from the analysis carried out, we use only a few basic conclusions to describe these fundamentally new thermoelectric effects:

(1) Earlier it was believed that thermoelectric effects, in principle, in thermodynamic terms, are especially macroscopic. Introduction of the Ilya Prigozhin's concepts of the local entropy production, in principle, removes the theoretical thermodynamic "prohibition (exclusion)" on the global existence of local thermoelectric effects.

(2) The local symmetry breaking in sharply inhomogeneous media, in particular in p-n junctions, lifts the ban on the measurement of local thermo-EMF.

(3) The accounting of concentration force removes the macroscopic diffusion limit for the absolute value of local thermoelectric effects set by Seebeck and Peltye's coefficients.

These conclusions have received numerous experimental confirmations, as shown in several studies, which is reflected in a number of previously noted papers and in the latest publication [4], where it is shown that the local thermo-EMF, arising in particular in p-n junctions, is approximately the same order as the photo-EMF, i.e. on $3 \div 4$ orders of magnitude exceed the Seebeck's coefficient.

This huge difference in EMF is quite natural, since the macroscopic diffuse thermoelectric power is determined only by the small difference between the mean equilibrium energy of the electrons and the mean energy of electrons the flow, then the local thermo- EMF, which depend on the local gradients of the carrier density, which are very big in micro-inhomogeneities, are defined, also as well as the photo-EMF, height of the potential barrier. This is directly related to the second conclusion, extending the phenomenological approach for the framework of exclusively diffusion description.

Already on the basis of these qualitative conclusions, one can give a non-strict, qualitative parametric description of local thermo- EMF that appear on micro- and nano-inhomogeneities. Local thermo-EMF have a sign opposite to the photoelectric effect, which corresponds, as shown in Fig. 1, to thermo-injection of the majority carriers of the hot facing of p-n junction. I.e. if the photoelectric effect corresponds to the stretching of the excited electron-hole pair by the electric field of the potential barrier of the p-n junction, then the local thermal EMF corresponds to the transfer of the majority carriers of the hot facing of p-n junction through this barrier and their subsequent recombination with the main carriers of the cold facing.
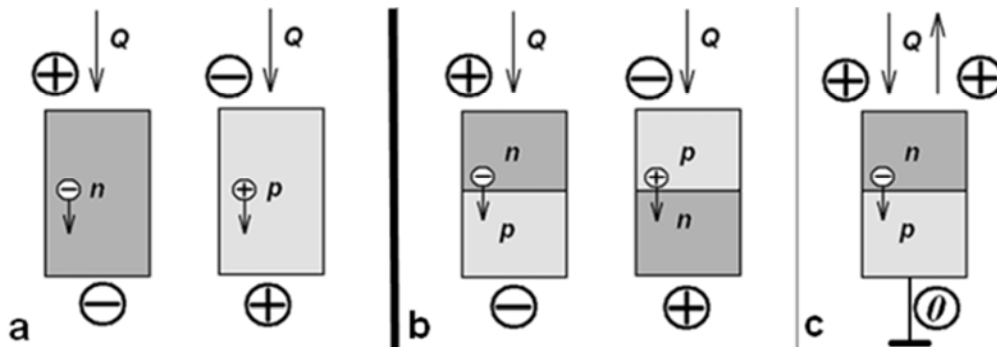
Figure 1. The qualitative picture emergence of an EMF when the heat flow Q passes through a sample: A - diffuse Seebeck in homogeneous samples with different conductivity types, b and c - local thermo-EMF at the p-n junction.

Figure 1c shows the qualitative difference between the macroscopic Seebeck effect and the local thermo-EMF: if we fix-zero the bottom contact (grounding) of the p-n junction and make an inversion of the direction of the heat flow, then we get the EMF of the same sign, not the opposite one, as in the macroscopic thermoelectrics.

Rough, but, nevertheless, the parametrical description of photoeffect used even in practice [22] consists in use speculatively received on the basis of diffusion equation of the IVC of the ideal diode with the additive which is linearly depending on light flow

$$J_E = J_0(e^{\frac{eU}{kT}} - 1) - P \cdot J_{Ph} \qquad (36)$$

where U - the voltage at the p-n junction, and P - its current sensitivity of effect.

Such obviously not phenomenological approach gives, as shown in fig. 2, the shift of the IVC down the axis of current and emergence of positive photo-EMF and is used as noted, in practice for calculation of the working point of photo diodes.

Analogously to the parametric bias of the IVC of the current downward to the light, one can also describe the parametric displacement of the IVC, only upwards, under the action of the heat flux, which leads to the generation of giant local thermo-EMF in the p-n junction.

This approved, but rough model needs to refine both the I-V characteristic and the selected parameter. This is confirmed by the control measurements of the I-V characteristics in the photoelectric effect. This is demonstrated in Figure 2a and nonphysical infinite values of local thermo-EMF. In fact, this model only correctly explains the sign of the effect.
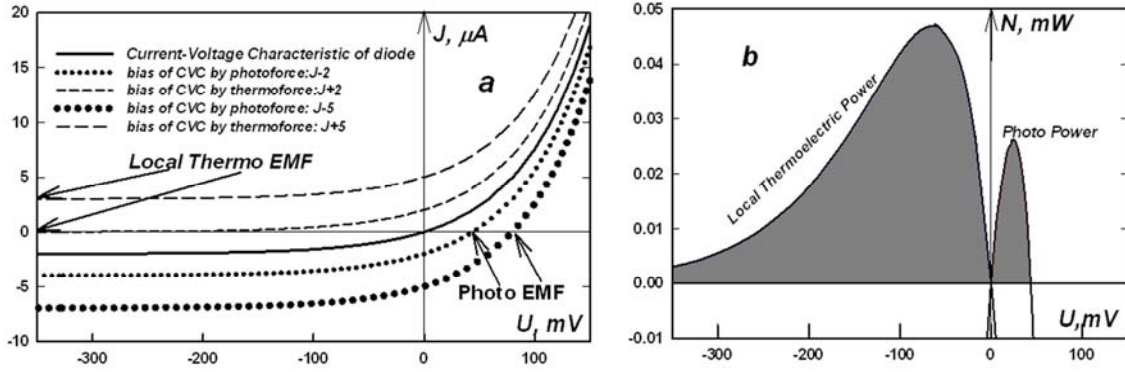
Figure 2. *Bias of the IVC on current for the ideal diode by the photo flow and the heat flow in diametrically opposite directions (a) and generated by the bias of the IVC of the ideal diode in these quadrants power (filled with gray colors in Figure 2b).*

But for the photoelectric effect, the real VAC is closer to the power shift, and for the thermoelectric effect they are generally close to the phenomenological introduction of an additional temperature force. But since the appearance of local thermo-EMF (which exceed the diffuse thermoelectric power by orders of magnitude) occurs against the background of a nonlinear IVC, the temperature force appears in a rough approximation by the parameter to the initial I-V characteristic. In this case, the IVC is displaced by electric force δF_k (voltage U), which at the initial, linear portion of the I-V characteristic can be described by the equation

$$\delta F_E = -\left[\frac{L_{ET}}{L_{EE}} F_T + \frac{L_{EN}}{L_{EE}} \delta F_N \left(F_T \right) \right] \qquad (37)$$

which shows, at record in the traditional form, the difference of local thermo-EMF from those determined by only the Seebeck coefficient S.

$$\frac{\delta E \cdot d}{\delta T} = \frac{U(\delta T)}{\delta T} = S + R \cdot \frac{\delta N}{\delta T} \qquad (38)$$

where d is the thickness of the p-n junction, and R the electro-diffusion coefficient for the total concentration of electrons and holes.

Apparently from the received expression two members have change of electric force δF_k: depends (linearly) not only on the small coefficient of Seebeck $\frac{L_{ET}}{L_{EE}} \sim S$ standing with the temperature force F_T, but also on additive to concentration force $\delta F_N \left(F_T \right)$ arising because of the unbalance of the giant drift and concentration flow in p-n junction.

But a rigorous analysis of the "three-phase" solutions within the extended E-N-T phenomenology is rather cumbersome and will be presented in the next paper. Now I only note that it is the "three-phase" that, in principle, gives an explanation to thermoelectric waves in anisotropic crystals [23] and detected in p-n junctions by the Gaussian resonance [4], and that it was the examination of kinetic processes in

the extended E-N-T phenomenology that made it possible to detect and correct the solutions presented in this paper within the framework of particular phenomenology. Just as the general approach gives a correct description of the Unified Nature, and the looping on particulars this Nature Picture often destroys [24].

4. Conclusion

In this paper, an elementary scrupulous analysis of the special case of thermoelectric effects was carried out, but on the basis of general principles. Such a heavy-handed approach made it possible to solve a two-pronged problem.

On the one hand, to specify the principles, to be exact to tell, compliance to the used principles of the "measured" parameters, on the other hand, to receive some estimates of theoretical limits of the number of parameters. At the same time it was received that, on the one hand, macroscopic approach in thermoelectricity sputtered out since to extract electricity by means of friction of electrons about the crystal grid not really differs from getting of electricity from the hairbrush at the combing. Macroscopic thermoelectricity eliminated the "indirectness" associated with the movement of rubbing macroscopic bodies, such as in the Van de Graaf generator. But macroscopic thermoelectricity also uses friction, the friction of the flow of electrons (macroscopic - electric current) about the crystal lattice (macroscopic - the crystal). And just as in the Van de Graaf generator, macroscopic thermoelectricity converts only part of the energy of the flow, a part taken up by friction. And only this part is converted "directly". That is why thermoelectric refrigerators have many times smaller refrigerating coefficient, than compression refrigerators. That is why the internal combustion engine has efficiency, three times higher than the maximum achieved for thermoelectric generators.

On the other hand, this heavy-weight approach showed the existence of previously unaccounted effects, which in high-contrast media give high voltages, which agrees with the large values of local thermo-EMF found. Moreover, it is the local thermo- EMF that "directly" converts the main part of flow energy of electrons, and friction for them, as well as for the macroscopic thermal machines mentioned above,

determines only energy losses. At the same time, the fact that the effective temperature of the electrons can be higher than the lattice temperature, will additionally increase the efficiency by increasing the Carnot coefficient.

In purely theoretical the plan, the carried-out analysis shows that transition to orthogonal coordinates eliminates contradictions between adjacent sections of physics: specifically between thermoelectricity, thermionic emission and p-n junction theory.

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