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Letter

Ballistic Thermoelectricity

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Abstract: The analysis of Local thermo-EMF in p-n junctions made it possible to reveal the phenomenological features of ballistic thermoelectricity. By the Curie Symmetry Principle, in polar structures of p-n junctions, the thickness of which is of the order of the electron mean free path, the contribution of ballistic effects to the formation of the total EMF is decisive. This ballistic contribution to thermo-EMF provides both high output voltages and high efficiency of DIRECT energy conversion.

***Keywords*:** phenomenology of kinetic phenomena, Curie's theorem, diffuse effects, potential barriers, ballistic transfer, Prigogine's local entropy production, DIRECT energy conversion efficiency

The study of composite disordered materials did not lead to the desired cardinal increase in the thermoelectric figure of merit [1], which prompted a deeper look into the nature of thermoelectric phenomena [2] and proceeded to the design of thermoelectrics based on semiconductor structures. This was the impetus for assessing the degree of reliability of the Basic Physical Models [3] and for their correction [4].

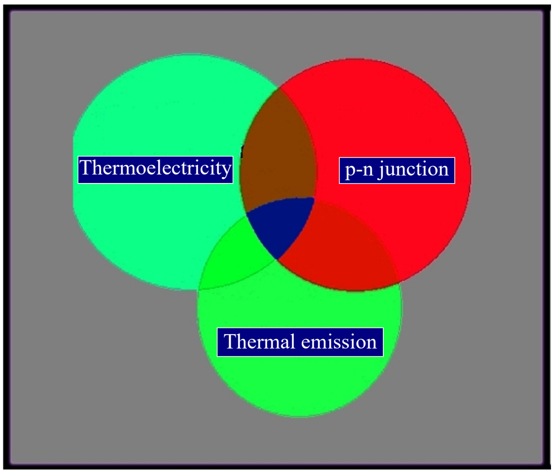


Figure1. Intersections of three local phenomenologies describing coupled effects

Nature is one. And its description according to Aristotle was originally the same. However, its fragmented description gives contradictory and mutually exclusive conclusions in the field of intersection of the established local phenomenologies of different phenomena. Thus, in the modern phenomenologies of Thermoelectricity, Thermionic Emission and The Theory of Semiconductor p-n junction, different pairs of these forces are used from three thermodynamic forces: temperature, concentration and electric (Figure 1).

Whereas taking into account all the thermodynamic forces and flows used in them (Figure 2) based on the invariants of the intersection of these local phenomenologies (blue segment in Figure 1), gives not only a rigorous, consistent description of each of the effects presented in Figure 1, but also the opportunity to expand the phenomenology, which made it possible to correct the Theory of semiconductor n-n junctions, which have long reached the NANO level [5].

E-T phenomenology	$J_E = L_{EE}F_E + L_{EN}F_N$
Thermoelectricity	$J_T = L_{ET}F_E + L_{TT}F_T$
E-N phenomenology	$J_E = L_{EE}F_E + L_{EN}F_N$
p-n junction	$J_N = L_{EN}F_E + L_{NN}F_N$
N-T phenomenology	$J_N = L_{NN}F_N + L_{NT}F_T$
Thermal emission	$J_T = L_{NT}F_N + L_{TT}F_T$

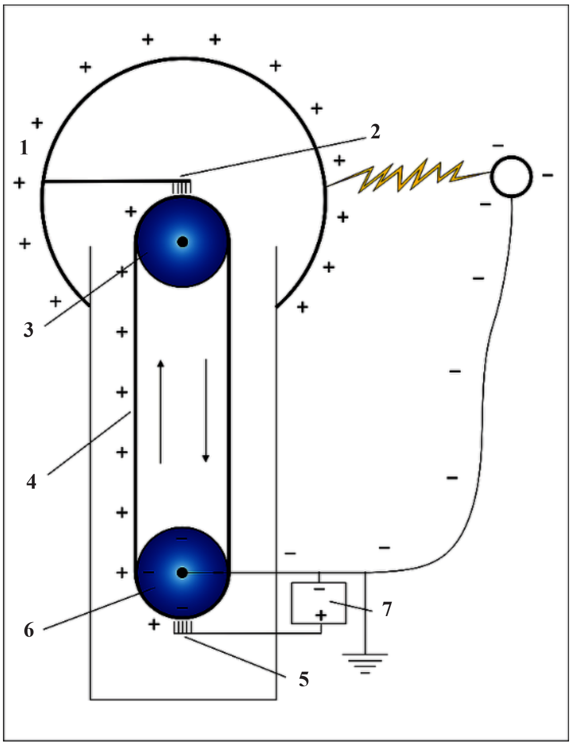
Figure 2. Three local phenomenologies of kinetic phenomena

The extended phenomenology made it possible to make a rigorous description of these effects on the NANO scale as well. At the same time, it became obvious why the increase in the efficiency of thermoelectric energy conversion based on the Seebeck and Peltier effectors [6-8] has reached saturation for almost half a century, both for generators and refrigerators. And all further improvement in the operation of thermoelectric devices was reduced to purely structural improvements of these devices [9].

As was shown earlier in a number of experimental and theoretical works, the efficiency limitation of thermoelectric devices that has arisen for a long time is inherent in the diffuse nature of the Seebeck and Peltier effects used by them [10, 11, 2]. Therefore, thermoelectric conversion, originally declared as DIRECT, in fact, using the effects arising from the friction of electrons on the crystal lattice of thermoelectric material, strictly speaking, is not such and corresponds to INDIRECT energy conversion [12, 13].

This “indirectness” now determines the fundamentally low CRC of thermoelectric conversion, since such a “direct” conversion, as shown earlier, is in principle analogous to the production of electricity in a Van der Graff generator. When combing, we move not only the surface layer of the comb electrified due to friction, but also the comb itself, and the whole hand, so in the Van der Graff generator (Figure 3) most of the energy is spent on the mechanical operation of the device, and only a small part of it is converted into electrical energy.

And, similarly to the Van der Graff generator, diffuse, thermoelectric energy conversion is INDIRECT, because the main part of the flow of the body or electric current wastes kinetic energy in vain. And accordingly, even ideally, it has a low, almost long-achieved efficiency.



1 - spherical electric screen
2, 5 - contacts
3, 6 - rollers
7 - high-voltage air ionizer

Figure 3. Van der Graff generator

In addition, high electron concentrations are required for optimal diffuse thermoelectrics. So the entire Seebeck effect is determined only by a small difference in the average energy of electrons in the flow (in Figure 4 just above the bottom of the conduction band) and their Fermi level of "standing" (electrons in Figure 4 just below the bottom of the conduction band), related to the average thermal energy, which is 25 meV for room temperature (see the formula in Figure 4). In this case, the diffuse thermo-EMF, equal to this small difference between the average Fermi energy and the energy in the flow μ, is at the optimum only 200 μV/deg.

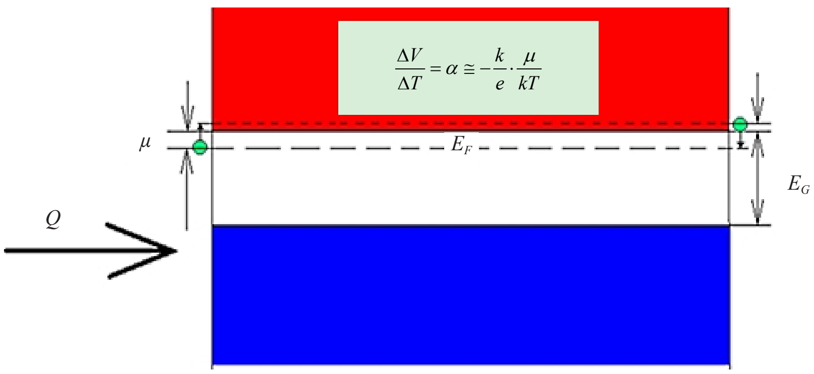


Figure 4. Scheme of generation in a semiconductor diffuse thermo-EMF of Seebeck

Local thermo-EMF s arise at potential barriers of the order of the height of the potential barrier EG, i.e. about V/

deg. So additional current-to-voltage converters are not required at all.

However, the local thermo-EMF s arising on the microcontacts were previously classified as anomalous due to the inconsistency of the diffuse theory and due to the poor reproducibility of the experimental results [14]. As shown in previous works, the diffuse theory is simply not applicable to them, and the Richardson-Langmuir restrictions on ballistic currents in the initial section of the current-voltage characteristic (CVC) contained an error of several orders of magnitude. A rigorous calculation of the spatial transition of electrons gives their total flux much larger than the linear approximation between zero voltage and kT [15]. In fact, the entire electron flow is compressed at the lowest allowed energy level above the barrier [16], which corresponds to the absence of scattering at barrier thicknesses less than the electron mean free path. Taken together, this leads to the fact that in the output generator resistance of the Local thermo-EMF, at small thicknesses of potential barriers, it becomes much less than their galvanic resistance.

The p-n junction created by microelectronics is an ideal contact [17, 18], on which Local thermo-EMFs are reliably recorded, perfectly reproduced and summed (amplified) in semiconductor structures. Their experimental studies in structures based on silicon carbide, silicon and gallium nitride [19, 20] made it possible to expand the phenomenology of both thermoelectricity with thermal emission and the description of the operation of the p-n junction itself.

The use of potential barriers for modifying a semiconductor has been carried out previously. For example, "quantum dots" in gallium arsenide or polytypes in silicon carbide were used. They were used, among other things, in thermoelectrics, creating quasicrystals with a lattice of concentration solitons for the mobility threshold of current carriers [21, 22]. But the result was just a new effective medium, a modified semiconductor - either the width of its band gap was changed, as in different silicon carbide polytypes or in samples of silicon carbide nanopowder sintered with metal, or the concentration of carriers in the allowed band, as in gallium arsenide and in higher manganese silicide. But the diffuse thermoelectric figure of merit remained the same. There was no new mechanism for influencing it - and for the modified effective medium, the old mechanisms were preserved.

The beginning of the use of ballistic effects in thermoelectricity was set a long time ago in his pioneering work "Vacuum thermoelement" by one of my mentors in his youth Andrei Ivanovich Anselm [23]. In fact, he proposed to use the first vacuum diodes as thermogenerators. But in practice, these diodes were not vacuum, but plasma, and their characteristic (macroscopic) dimensions did not ensure the prevalence of ballistic effects over diffuse ones. In addition, it was purely empirically concluded that it is more efficient to use an asymmetric potential barrier, creating it due to the different work functions of the cathode and anode materials [24]. Paradoxical as it may seem, but in a semiconductor diode the mean free path of quasi-free electrons can be more easily achieved less than the thickness of the potential barrier than in a "vacuum" diode for "free" electrons in the plasma gap. The creation of semiconductor structures with a series of potential barriers less than the mean free path of electrons, each at the achieved technological level, is easier to implement than for a "vacuum" diode.

At the same time, a fundamental point was revealed in fundamentally polar n-n junctions, which is fully consistent with the Curie theorem. Asymmetric potential barriers provide an additional opportunity for the realization of ballistic effects in a semiconductor. To some extent, this also manifests itself in the well-known asymmetry of the branches of the current-voltage characteristic (CVC) of a semiconductor diode when they are shifted in current by a light or heat flux:

$$\Delta J_{Th/Ph} = k_{Th/Ph} \cdot O_{Th/Ph} \qquad (1)$$

Where $O_{Th/Ph}$ is the energy flow through the p-n junction, and $k_{Th/Ph}$ is the current coupling coefficient in the p-n junction from the flow of heat or light (for light - the quantum yield at a given wavelength of light. That is, there is a current-voltage characteristic shift similar to the shift in the photo effect, but of the opposite sign EMF. But the current shift of the current by an additional flow leads to generator effects in quadrants (Figure 5), But the shift of the current-voltage characteristic by an additional flow leads to generator effects in the quadrants (Figure 5, left).

The bias of the non-linear I-V characteristic, as shown in Figure 5, gives rise to a voltage whose polarity is determined by the polarity of the p-n junction, while the polarity of the small diffuse Seebeck thermo-EMF is completely determined by the direction of the heat flow.

In the generator quadrants, as in any battery, the current and voltage are in antiphase (Figure 5, on the right).

The experiments confirmed the qualitative picture of the I-V characteristic displacement by a constant, stabilized heat flux, but somewhat distorted by the Thermo-Electronic resonance arising in the p-n junction (Figure 6), which will be considered in detail in the next work.

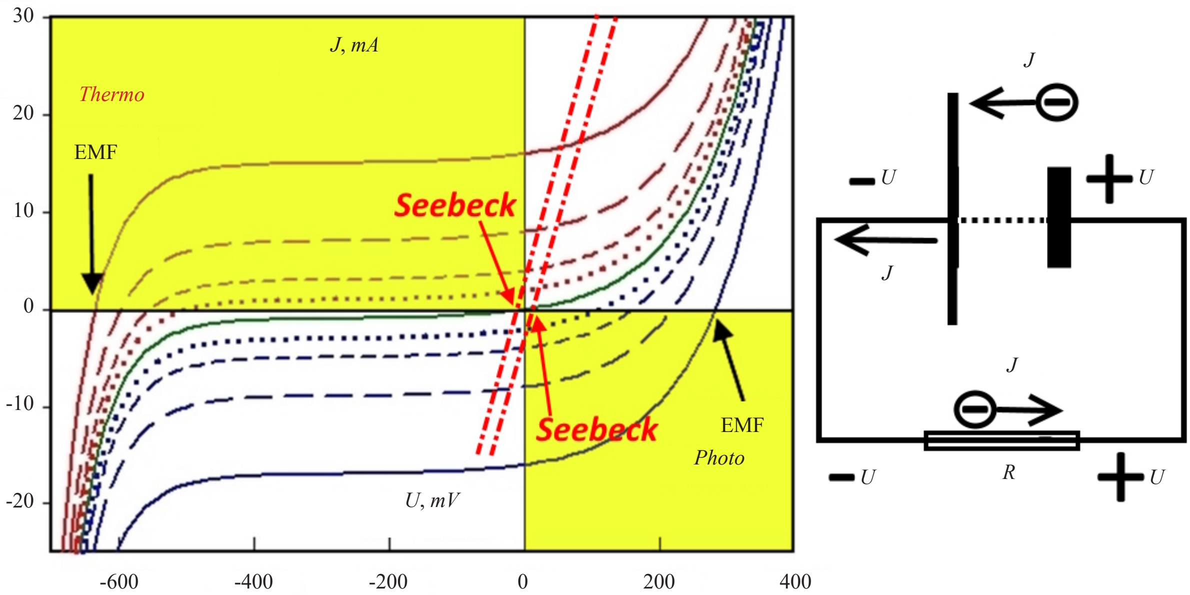


Figure 5. Estimated current-voltage characteristic displacements of an ideal p-n junction (green line) by equivalent (in terms of power) flows: thermal (brown curves) and light (blue curves), with a 2-fold increase in flows. The yellow color indicates the generation quadrants, where the current and voltage, as in a conventional battery (shown on the right), are in antiphase. The red dash-dotted lines show the diffuse CVC corresponding to the nonpolar Seebeck and Ohm's law

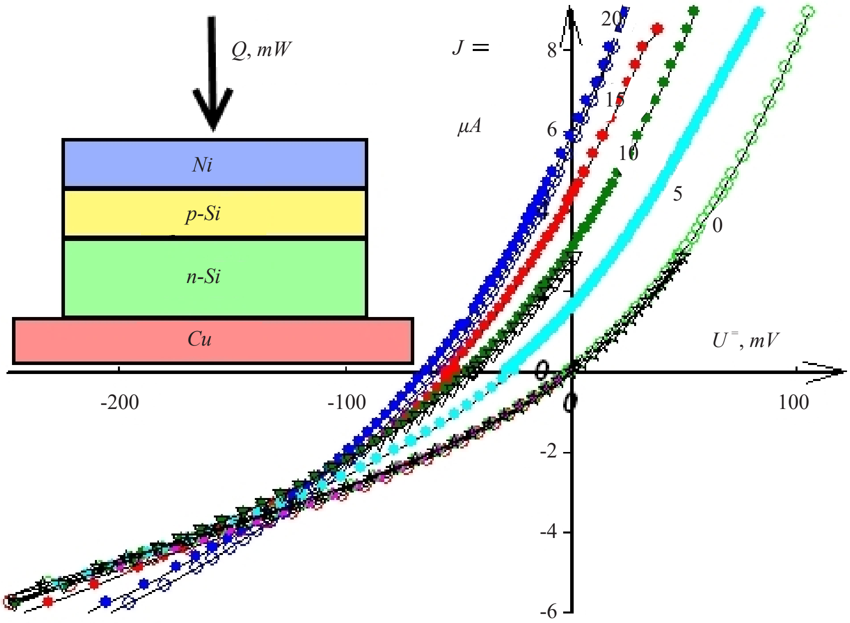


Figure 6. Experimental I-V characteristics of a p-n junction with stabilized different heat fluxes through it have a singular point, which is associated with Thermo-Electronic Resonance

And here, in conclusion, we only note that on asymmetric potential barriers, under the action of a temperature force due to ballistic effects and the production of Prigogine's local entropy, a "Maxwell demon" is actually formed, but not thermostatic, but thermodynamic - leading to a stationary difference in local temperatures at the boundaries of the barrier in the stream.

The emerging Local thermo-EMFs in a constant flow, as already noted, have the opposite sign of the photo-emf, and when using variable flows, the thermo- and photo-signals are antiphases. Moreover, as shown in the dependence of the amplitude of the Local thermo-EMF on the power of the flow (Figure 7), with an increase in the modulation frequency, they sharply increase in amplitude in the initial section of the power characteristic, and their dynamic range increases.

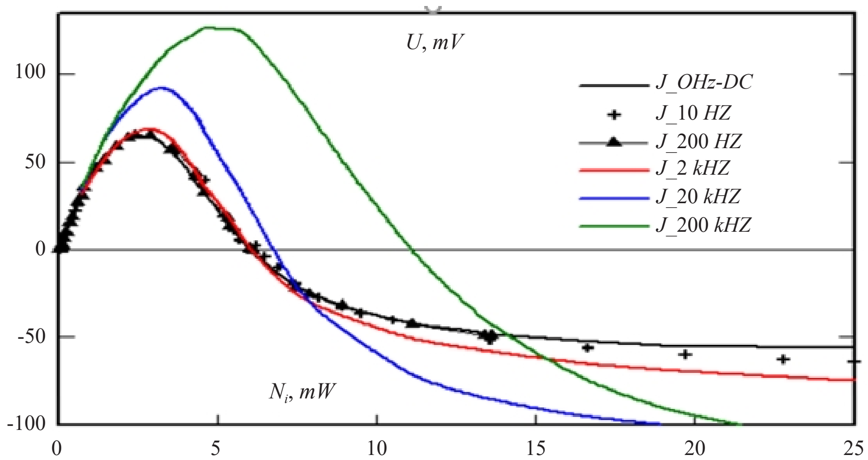


Figure 7. The dependence of the amplitude of Local thermo-EMF on the power of the heat flux and the frequency of its modulation

The limitations of the dynamic range shown in Figure 7 directly follow from the sharp increase shown in Figure 5 with subsequent saturation of the Local thermo-EMF when the I-V characteristic is shifted by the current by the heat flux. An additional limitation of the dynamic range of signal amplitudes with a subsequent change in their sign is associated, as shown by precision direct measurements using the contact DC method (Figure 8, left), with the contribution of the diffuse EMF of a thick silicon substrate to the integral thermo-EMF, and the modulated heat flux (Figure 7) - with its imposition on the passage of the temperature front through the p-n junction in a massive silicon substrate, on the Local thermo-EMF of the p-n junction itself.

In Figure 8 on the left: 1 - C-oriented pyrocrystal BN, 2 - centering thrust, 3 - cathode from a copper foil, 4 - Si-plates with a p-n-junction (as an illustration the vertical size of a layer with inverse conductivity is increased), 5 - massive copper anode-radiators, 6 - control thermocouples, 7 - thermal screen., 8 - optical and electrical screen, 9 - light-emitting diode (LED).

Taking into account the identified features of Local thermo-EMF modifies the traditional Theory of Electronics into Thermo-Photo-Electronics [25, 26].

The presented work is part of a book, the writing of which prompted/initiated the awakened interest of the industry in the Thermo-Electronics I have been developing for about 30 years. Although it is a passed stage for me and distracted me from solving more Global Issues [25, 26].

But in the formulation and solution of the noted Fundamental Problems, a significant methodological role was played by the phenomenological study carried out in this work. Work on the book on Thermo-Electronics continues, although the priority is the combing of the Theory of Relativity I started.

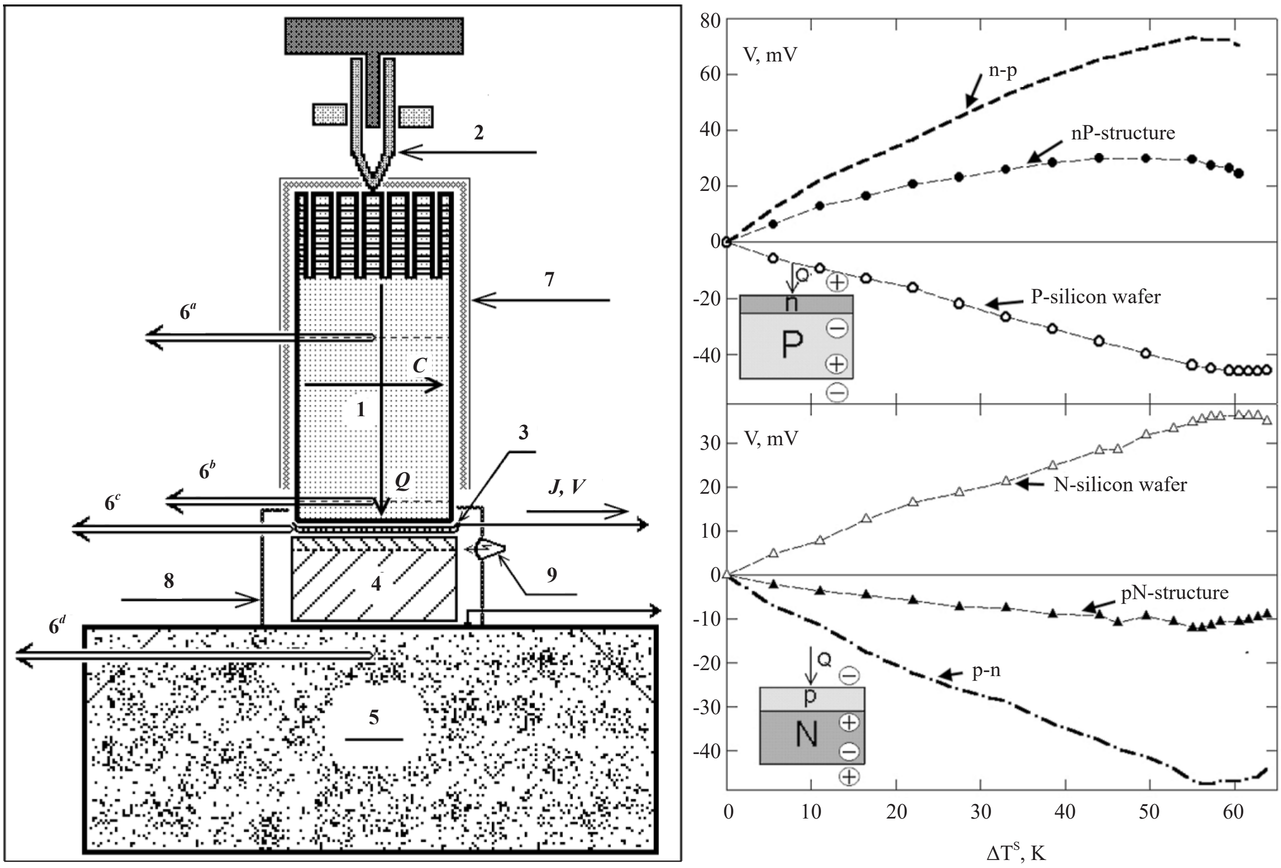


Figure 8. Experimental setup (left) used for measurements in silicon samples with and without a layer with inverse conductivity and without it longitudinal (parallel to the heat flow) Local thermo-EMF and the results of precision measurements of these samples (right), where the difference between the integrated EMF of the structure and the EMF of the silicon substrate gives gigantic integral values of the local thermo-EMF of the p-n junctions themselves

Conflict of interest

The author declares that there is no conflict of interest.

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