Chapter 13

William Thomson (Lord Kelvin) and thermoelectricity

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Abstract

Some information on the results of Thomson's scientific research in the field of thermoelectricity is given below. The experiments that preceded this research and served, together with his thermodynamic approach, to Thomson as a basis for discovery of the fundamental relations in thermoelectricity named after him are characterized. Discoveries of the Thomson thermoelectric effect and transversal thermo-EMF in anisotropic crystals are also considered. Practical applications of the regularities and phenomena in thermoelectricity discovered by Thomson are described together with the prospects of their further applications.

1 Introduction

William Thomson (Fig. 1) belonged to that rare type of a scientist who combined the qualities of a brilliant theoretician capable of applying mathematical instruments to physical phenomena description, a perspicacious physicist who deeply understood the essence of the surrounding world phenomena, a careful experimenter possessing accurate skills in laboratory investigations and a talented engineer who aptly applied physical laws to development and design of various apparatus useful for humanity and speeding up scientific and technical progress.

His knowledge and skills Thomson achieved from the brilliant minds of his time. It was his father who cultivated his love of mathematics. Later Laplace, Lagrange, Fourier, Liouville, Charles and Sturm became his teachers of mathematics. Renier was the one to teach him the secrets of the experiment. This marvelous experimenter performed measurements so accurate that their results have not lost significance up to now. Having used his experimental approaches together with development of those of his own, Thomson created the first ammeters and voltmeters, absolute electrometers and other numerous devices. Faraday, the great experimenter, influenced Thomson greatly. Thomson performed a series of brilliant applied works based on his discoveries, knowledge and experience.

Thermoelectricity did not belong to his main scientific priorities. Nevertheless, it was due to Thomson's research work that very important fundamental results for this interesting and constantly developing scientific trend were also obtained. The description of Thomson's fundamental contribution to thermoelectricity is given below.

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Figure 1: William Thomson (1824–1907).

2 On the events that preceded Thomson's discoveries in thermoelectricity

The equilibrium thermodynamics of the reversible processes created by Thomson served as a basis for his discoveries in thermoelectricity. Its application to the description of thermoelectric phenomena was one of the vivid results of the said theory [1–9].

Two thermoelectric effects were well known to Thomson.

2.1 The first thermoelectric effect: the Seebeck effect

Seebeck's discovery was really dramatic [10]. It was not the aim Seebeck set to find the way of direct heat conversion into electricity. He was enchanted by Oersted's experiments (Fig. 2) on the magnetic field induction under the influence of the electric current [11]. While varying them differently, Seebeck noticed that if the electric circuit consisted of two dissimilar materials (e.g. bismuth and copper) and if one of the combinations of these materials was subjected to heat, a magnetic field appeared inside such circuit that was registered by the deflection of the magnetic needle (Fig. 3). Seebeck called this effect **thermomagnetism**, as he really observed the transformation of heat into the magnetic field.

Seebeck reported on his discovery of thermomagnetism to Berlin Academy of Sciences in 1821. It was received with great enthusiasm. Seebeck's reports on thermomagnetism were printed in the Proceedings of the Royal Academy of Sciences in Berlin which were issued as late as 1825 [12].

The information on the Seebeck effect of thermomagnetism, though, was soon spread among scientists. It reached Oersted by the end of 1822.

Having repeated the Seebeck experiment, Oersted described it as the most wonderful discovery among the discoveries he had ever faced. And, as the electric current was the reason for

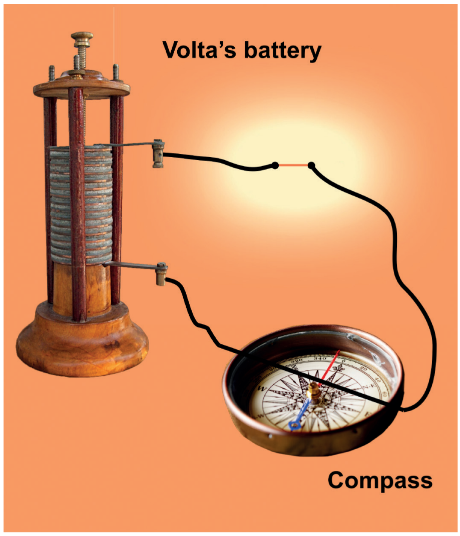

Figure 2: Occurrence of the magnetic field at the electric current flow in Oersted's experiment.

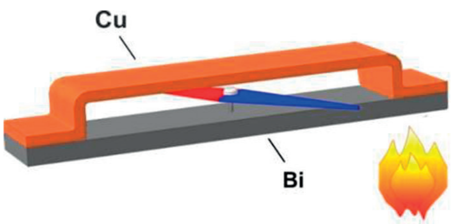

Figure 3: Schematic of the Seebeck's discovery of thermomagnetism.

magnetic field induction occurrence in Oersted's discovery, it was but natural to assume that the magnetic field in the Seebeck's experiment was excited by current as well (Fig. 4).

To prove his assumption, Oersted broke the circuit in Seebeck's experiment (Fig. 5) and connected a galvanometer which registered the electric current to the break.

In 1823, Oersted published the results obtained in the *Annales de Chimie et de Physique*. In the same year, he reported on his discoveries to the French Academy of Sciences [13].

He started his report with words: 'I have the honour to present to the Assembly the amazing experiments that helped Seebeck prove the possibility of obtaining electric current in the circuit consisting of solid conductors exceptionally by distorting temperature balance in them'. He suggested that this effect should be called *Thermoelectricity*.

It is evident that Oersted had not forgotten about Seebeck. Furthermore, he granted Seebeck with the priority in the discovery of thermoelectricity.

Such a name for the Seebeck effect was correct and so it found total support among scientists.

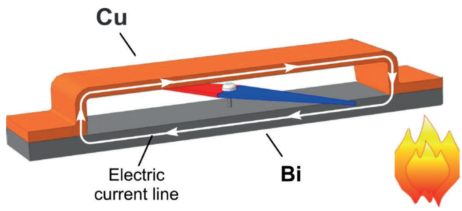

Figure 4: Idea of the current excitation in the Seebeck's experiment.

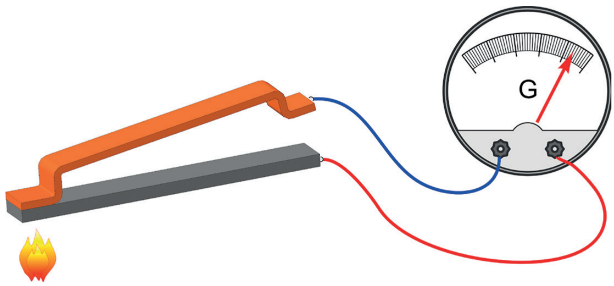

Figure 5: Oersted's experiment that verified the electric nature of the Seebeck effect.

Despite this, Seebeck did not acknowledge the evident results of Oersted's experiments. In his book *Semiconductor thermoelements*' Ioffe writes the following: 'Seebeck not only refused to accept such natural explanation of his discovery but fought vigorously against it within several years accusing representatives of the theory of thermoelectric currents of being fascinated with the 'fashion' due to Oersted's discovery' [14].

Ioffe suggested that such Seebeck's behavior was caused by his wish to explain the nature of the magnetic field of the Earth with a help of his effect of thermomagnetism.

All the same, it became generally accepted to define the Seebeck effect as thermoelectromotive force that appears at the free ends of the broken electric circuit that consists of two dissimilar materials A and B, provided the place of their connection is heated and free ends are kept under the steady temperature (Fig. 6).

Oersted had a good understanding of the possibility of practical application of the Seebeck effect for the creation of sources of electricity. In 1824, together with Fourier, he fabricated the first thermoelectric generator which, due to its reliability and stability, was further used in a great number of important experimental researches.

Such thermoelectric source of electricity was employed by Ohm. He obtained rather precise results on the connection between the electric voltage, current and resistance of the electric circuit due to the exceptional stability of the source (Fig. 7). These experimental results served as a base for discovery by Ohm of his law in 1826 [15].

Peltier also used a thermoelectric power source for his experiments. The said experiments led to the discovery of still another thermoelectric effect named after Peltier.

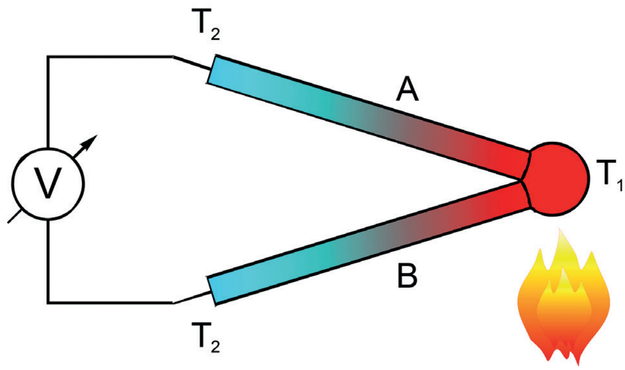

Figure 6: Seebeck effect.

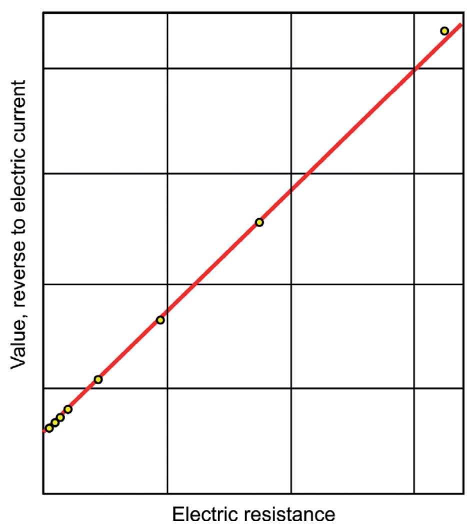

Figure 7: Results of Ohm's experiments on the linear dependence between the electric resistance and current. Experimental results are marked with circles.

2.2 Second thermoelectric effect: the Peltier effect

Peltier, a watchmaker from Paris, started self-education at the age of 30 and became attracted by electric measurements that were in trend in those days. He started with the measurements of bismuth and antimony conductivities for which purpose he cast the 0.5 mm diameter rods, 45 mm long. These rods played an important role in the discovery of his famous effect by Peltier.

Peltier also tried to check one of the theories of emergence of heat while the electric current passes through the conductor. For this purpose, he used rods sending current through them and measuring the level of their heating with the help of a thermocouple (Fig. 8). It was a French physicist Becquerel who suggested temperature measuring with the help of thermocouple in 1826. Peltier found out that in the central part of the rod, as it was expected, the temperature was nearly the same and higher than the ambient temperature. But, to his surprise, he discovered that the temperature on one end of the rod turned out to be higher than that on the opposite.

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Temperature abnormalities were observed at the place of dissimilar materials junctions. That was nothing but the Peltier effect [16].

At first, the Peltier's discovery was treated with suspicion because the temperature abnormalities were quite small and Peltier's reputation as a researcher was not high enough.

More explicit data were given by the so called Peltier thermal cross (Fig. 9) that consisted of the said two bars (bismuth and antimony) connected with each other in the middle. Electric current was sent through two nearest ends of the bars while two other parts of the bars formed a thermocouple for measurement of the temperature at the place of their connection. When the current was sent one way, the junction became heated; at the reverse direction, it became cooled. Even this experiment could not persuade skeptics in the existence of the Peltier effect. It was Lentz (1838) who put the end to these arguments by having successfully frozen water with the help of bismuth–antimony alloy.

The events enumerated above demonstrate a very uncertain situation regarding thermoelectric effects that existed by the time Thomson started his research into thermoelectricity. The experimental data, especially those of the Peltier effect, were, in general, of the qualitative character, unlike, for instance, rather precise Ohm's researches, which led him to the discovery of his law.

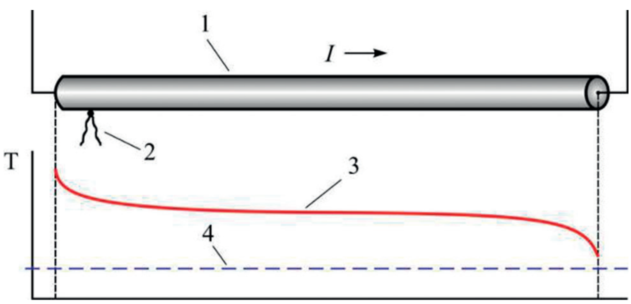

Figure 8: Peltier's experiment schematic. 1 – Bi or Sb rod, 2 – thermocouple for temperature measurement, 3 – temperature along the rod, 4 – ambient temperature.

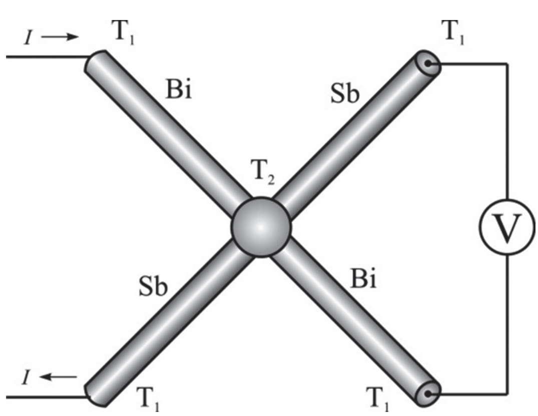

Figure 9: Peltier thermal cross.

There existed absolutely no qualitative or quantitative connections between the Seebeck and Peltier effects. A theory was absent that might have been able to describe them.

That is why the foundation of the thermoelectric effect theory on such a shaky basis demanded from Thomson not only thorough understanding of the essence of thermoelectric phenomena but also enigmatic intuition of the scientist, facing the choice of major factors and neglecting of minor ones in order to describe processes which occur in a thermoelectric circuit.

3 Fundamental thermoelectric Thomson relations

Thermoelectricity was one of the first areas of physics where Thomson applied thermodynamics of equilibrium processes developed by him. Thomson's main guiding idea was the assumption that thermoelectric phenomena are reversible and so might be described with the help of methods of equilibrium thermodynamics of reversible processes.

3.1 First thermoelectric Thomson relation

Thomson used a physical model of a thermoelectric circuit (Fig. 10) which consisted of two conductors whose junctions where kept under absolute temperatures T and $T + dT$. Thermo-EMF αdT appearing in the circuit carries the electric charge q through the conductors. Here, α is the Seebeck coefficient for the pair of metals. When thermoelectric current passes through this circuit, Peltier heat πq is emitted at one junction and absorbed at the cold one $(\pi + d\pi)q$, π being the Peltier coefficient. According to the second law of thermodynamics, Peltier heat πq is converted into electric energy $q\alpha dT$ with the maximum possible within the Thomson thermodynamic theory efficiency of the Carnot cycle $\frac{dT}{T}$

$$q\alpha dT = \frac{dT}{T}\pi\alpha. \tag{1}$$

Hence, the first Thomson thermoelectric relation appears [5] that combines the coefficients of two thermoelectric phenomena, that is,those of Seebeck and Peltier:

$$\pi = \alpha T. \tag{2}$$

3.2 Second Thomson thermoelectric relation

Thomson also considered that to preserve heat balance in the thermoelectric circuit, there should be another distributed thermoelectric effect that leads to either heat emission or heat absorption in the bulk of semiconductor with the current provided the temperature balance is violated there (Fig. 11). Therefore, in each of conductors A and B that form a thermoelectric circuit heat $\tau_a qdT$ and $\tau_b qdT$ should be either emitted or absorbed; where τ_a, τ_b here are the Thomson coefficients of materials. The law of energy conservation for a thermoelectric circuit has then the form of

$$\alpha qdT - \left(\pi + d\pi\right)q + \pi q + \tau_a qdT - \tau_b qdT = 0, \tag{3}$$

where the first component is electric energy, the second and third are Peltier heat at junctions, the fourth and the fifth are Thomson heat in conductors A and B.

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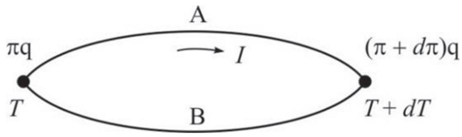

Figure 10: Thomson's thermoelectric circuit.

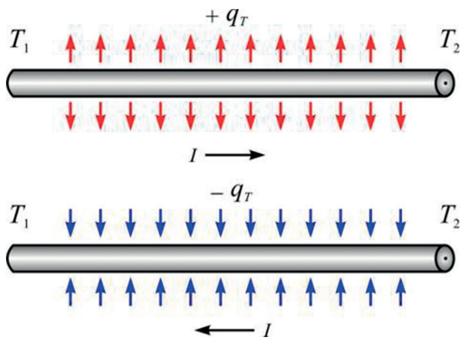

Figure 11: Thermoelectric Thomson effect.

Reducing the last equation by q and termwise dividing it by dT, as well as using from expression (1)

$$\frac{d\pi}{dT} = \frac{d\alpha}{dT}T + \alpha$$

it was obtained that

$$\tau_a - \tau_b = T\frac{d\alpha}{dT}. \tag{4}$$

The formula (4) is the second Thomson relation and the effect of Thomson heat occurrence is called the thermoelectric Thomson effect [1,5].

These results were published by Thomson in his work 'On a Mechanical Theory of Thermoelectric Currents' in December 1851. They gave start to the creation of the phenomenological theory of thermoelectricity.

This was the first case of theoretically predicted thermoelectric effect unlike the Seebeck and Peltier effects which were, by common knowledge, discovered by chance.

4 Experimental verification of Thomson thermoelectric effect

Having received the first and the second relations for thermoelectricity, Thomson was well aware of the fact that they were based on the hypothesis which he formulated as follows: 'The electromotive forces produced by inequalities of temperature in a circuit of different metals, and the thermal effects of electric currents circulating in it, are subject to the laws which would follow from the general principles of the dynamical theory of heat if there were no conduction of heat from one part of the circuit to another' [5].

Thomson saw no ways to prove his hypothesis by theoretical means so the crucial role here he gave to the experiment: 'In adopting this hypothesis, it must be distinctly understood that it is only a hypothesis, and that, however probable it may appear, experimental evidence in the special phenomena of thermoelectricity is quite necessary to prove it' [5].

Such experimental verification would be well grounded on the base of the reliably discovered and measured Thomson effect.

Therefore, Thomson started active search for his effect. First experiments gave no positive results as well as the following ones with no positive effect.

It was only at the end of November 1853 that Thomson reached the desirable target [6]. Considering the reasons for previous failures, an experimental setup was created where, to improve heat exchange, the layered samples of metal stripes were used instead of bars. They went through three containers with water (Fig. 12). The middle container was filled with hot water, and the outside ones - with cold. Water temperature was registered with thermometers. Such a setup enabled creation of temperature gradients of different direction along the conductor. When electric current was sent through it, such conditions led to emission and, correspondingly, absorption of the Thomson heat which was registered with the thermometers. When the current was reversed, the change in temperatures exactly corresponded to the predicted properties of the Thomson effect. This meant success. The prediction of Thomson thermodynamic theory of thermoelectricity was verified.

For a long time, the researchers failed to repeat Thomson's experiment. It was only in 1867 that the French physicist F. Le Roux [17] got indisputable proofs of the existence of the Thomson effect. It is interesting to notice that the main advantage in his experiment was the use of thermocouples instead of gas thermometers for temperature measurements.

5 On the effect of thermodynamic reversibility on Thomson relation

As stated above, Thomson was well aware that he had obtained his discoveries in thermoelectricity with the use of insufficiently reliable assumptions of the absence of the influence of irreversible effects connected with the Joule heat emission and heat transfer with the thermocouple thermal conductivity. Heat exchange with the environment was totally neglected [5].

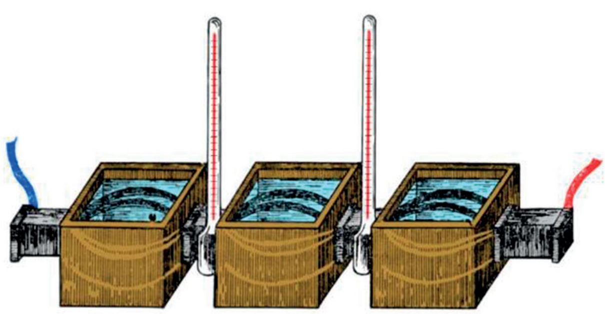

Figure 12: Experimental setup where Thomson observed his thermoelectric effect.

Such assumptions might have been approximately valid for the Joule heat only provided the currents were small. Actually, due to the quadratic dependence of the Joule heat on the current, its value at small currents might have appeared to be considerably smaller than that of the Peltier heat.

Thomson's theory was severely criticized by Boltzmann. He pointed out that the Joule heat irreversibility may really be neglected when currents are small. Though, irreversibility caused by heat transfer due to the thermal conductivity through the thermocouple from one junction to another should be considered because both this heat and the Thomson effect are proportional to temperature gradients in the first power.

But more correct descriptions of thermoelectric effects based on the irreversible processes thermodynamics [18–25, etc.] gave results not differing from those discovered by Thomson earlier. Therefore, **The first Thomson relation is always true**.

6 Generalization of Thomson relations pursuant to thermodynamics of irreversible processes

Relations (2) and (4) were obtained in a more general form for the cases of anisotropic medium in the magnetic field. In accordance with the thermodynamic theory of irreversible processes, formulae (2) and (4) were obtained in the form of

$$T\alpha_{km}\left(\vec{B}\right) = \Pi_{mk}\left(-\vec{B}\right), \tag{5}$$

$$\tau_{T,ik}(\vec{B}) = T\frac{\partial \alpha_{ki}(-\vec{B})}{\partial T}, \tag{6}$$

whereas a particular case for anisotropic medium, the relations obtained by Thomson follow from.

From the first and second Thomson relations for anisotropic medium there appears the interrelation between three tensors of thermoelectric coefficients

$$\hat{\tau} + \hat{\alpha} - \frac{\partial \hat{\Pi}}{\partial T} = 0. \tag{7}$$

These fundamental relations allow, for example, easy calculation of Peltier coefficients, provided the Seebeck coefficients are known for the given temperature, or determination of the Thomson coefficients provided the Seebeck coefficients and their temperature dependencies are known.

Moreover, they ensure a deeper understanding of the physical nature of thermoelectric effects. Thus, by combining (5) and (6) for an anisotropic medium we have

$$\tau_{T,ik} = \frac{\partial \Pi_{ik}}{\partial T} - \alpha_{ik}. \tag{8}$$

As seen from the formula (8), two mechanisms participate in the formation of the Thomson heat. First, the existence of the temperature gradient leads to appearing of the thermoelectric field proportional to α_{ik}. Charges, while moving in this field, perform either positive or negative (depending on the current direction) work, thus leading to either emission or absorption of the heat. Second, changes in the Peltier coefficient $\partial\Pi_{ik}/\partial T$ in the non-isothermal medium stipulate the inhomogeneity of the media (even homogeneous in the isothermic conditions) thus leading to the Peltier effect along this homogeneity.

With the use of the relation (5) it may be shown that the isothermic Nernst-Ettingshausen coefficient is connected with the adiabatic Ettingshausen coefficient through the relation

$$TQ_i^{\perp} = P_E \kappa_{11}, \tag{9}$$

which is called the Bridgman relation and is a corollary of the application of the first Thomson relation (5) to gyrotropic medium.

7 First Thomson relation novel form

It is well known that the connection between electric field intensity vector **E**, current density **j** and resistivity ρ is defined from the Ohm law

$$\mathrm{E} = \rho \mathbf{j}, \tag{10}$$

whereas the relation between temperature gradient ∇T, heat flux vector **q** and thermal conductivity coefficient κ is given by the Fourier law

$$\mathbf{q} = -\kappa \nabla T. \tag{11}$$

These equations are valid when either electric or thermal processes occur in the medium. Therefore, these equations are not suitable for simultaneous thermoelectric processes description.

Generalization of eqns (10) and (11) for a thermoelectric medium were found [22,23,26] on the basis of the irreversible processes thermodynamics, in the form of

$$j_i = \sigma_{ik} E_k - \sigma_{ik} \alpha_{km} \frac{\partial T}{\partial x_m}, \tag{12}$$

$$q_i = \Pi_{lk} j_k - \kappa_{lm} \frac{\partial T}{\partial x_m}. \tag{13}$$

Here E_k is the electric field intensity component, j_k is the electric current density vector component, q_i is the heat flux density vector component, σ_{ik} is the electric conductivity tensor component, α_{im} is the thermo-EMF tensor component, κ_{im} is the thermal conductivity tensor component, Π_{ik} is the Peltier coefficient tensor component, indices i, k, l, m pass the meanings 1, 2, 3. Equations (12) and (13) are called generalized Ohm and Fourier laws, respectively. They are well known and applied to solution of various thermoelectric problems.

In [27], the condition of the correctness of the system of eqns (12) and (13) was determined by Luste. The system contains six non-uniform linear equations related to six quantities, namely three components of the electric field E_i and three components of the temperature gradient $\partial T/\partial x$. Such a system is known to have a unique solution provided its determinant does not equal to zero:

$$\begin{vmatrix} \rho_{11} & \rho_{12} & \rho_{13} & \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \rho_{21} & \rho_{22} & \rho_{23} & \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \rho_{31} & \rho_{32} & \rho_{33} & \alpha_{31} & \alpha_{32} & \alpha_{33} \\ \Pi_{11} & \Pi_{12} & \Pi_{13} & -\kappa_{11} & -\kappa_{12} & -\kappa_{13} \\ \Pi_{21} & \Pi_{22} & \Pi_{23} & -\kappa_{21} & -\kappa_{22} & -\kappa_{23} \\ \Pi_{31} & \Pi_{32} & \Pi_{33} & -\kappa_{31} & -\kappa_{32} & -\kappa_{33} \end{vmatrix} \neq 0 \tag{14}$$

Condition (14) may be presented in the dimensionless form

$$Z^* T \neq -1, \tag{15}$$

where

$$Z^* T = \frac{\Pi^* \alpha^*}{\rho^* \kappa^*}, \tag{16}$$

$$\Pi^* = \vec{\tau}_0(\breve{\Pi}\vec{j}_0), \tag{17}$$

$$\alpha^* = \vec{\tau}_0\left(\breve{\alpha}\vec{j}_0\right), \tag{18}$$

$$\rho^* = \vec{j}_0(\breve{\rho}\vec{j}_0), \tag{19}$$

$$\kappa^* = \vec{\tau}_0(\breve{\kappa}\vec{\tau}_0), \tag{20}$$

where $\vec{\tau}_0, \vec{j}_0$ are unit temperature gradient and electric current density vectors.

In expressions (15) and (16), the product Z^*T is of special interest. This product usually appears when thermoelectric energy conversion is described in the expressions for the efficiency, where

$$ZT = \frac{\alpha^2}{\kappa\rho}T \tag{21}$$

is the most significant parameter of the thermoelectric material quality on which thermoelectric energy conversion efficiency depends.

Actually, in an isotropic medium kinetic coefficients $\breve{\rho}, \breve{\sigma}, \breve{\alpha}, \breve{\Pi}, \breve{\kappa}$ are scalars and hence, if the first Thomson relation is used, we obtain from (21) for an isotropic medium $Z^*T = ZT$.

But ZT and Z^*T were not obtained from the energy description of thermoelectric energy conversion. Therefore, this parameter has a wider meaning. It determines the compatibility of the Ohm and Fourier generalized laws at which the said laws describe thermoelectric phenomena simultaneously. Hence, when Z^*T is used, the conditions under which thermoelectric phenomena occur can be defined.

Let us give a more detailed attention to the said conditions.

Suppose we generalize the first Thomson thermoelectric relation for the case of free anisotropic media in the magnetic field. For this purpose, we need to compare the generalized coefficient Π^* with the product α^*T:

$$\Pi^* = \tau_0\left(\hat{\Pi}\, j_0\right),$$

$$\alpha^* T = T\tau_0(\hat{\alpha}\, j_0) = \Pi^* \delta, \tag{22}$$

where

$$\delta = \frac{\alpha^*\left(\vec{B}\right)}{\alpha^*\left(-\vec{B}\right)}. \tag{23}$$

Having taken into consideration (4), the dimensionless parameter δ may be presented in the form

$$\delta\left(j_0, \tau_0, B\right) = \frac{j_0 \hat{\alpha}(B)\tau_0}{j_0 \hat{\alpha}\left(-B\right)\tau_0}, \tag{24}$$

From which it is evident that this parameter in the absence of the magnetic field becomes

$$\delta\left(\vec{j}_0, \vec{\tau}_0, 0\right) = 1. \tag{25}$$

In the presence of the magnetic field, (23) may become the value different from (Fig. 1) for that case only, if

$$\hat{\alpha}\left(B\right) \neq \hat{\alpha}\left(-B\right). \tag{26}$$

The said becomes possible provided a change in the Seebeck coefficient takes place when the direction of the magnetic field becomes reverse. It does not occur in the majority of materials, though, hence

$$\hat{\alpha}\left(B\right)=\hat{\alpha}\left(-B\right) \text{ and } \delta = 1 \tag{27}$$

But, for some low symmetry crystals, a so-called commutation effect [14] was observed when the change in the magnetic field direction at the absolute value of the field intensity preservation leads to a significant change of the Seebeck coefficient. As it was shown in reference [28], on the basis of the thermodynamic theory, the parameter δ should satisfy the condition

$$-1 < \delta \leq 1, \tag{28}$$

and generalized thermal efficiency $Z^{*}T$ may lay within the limits of

$$-1 < Z^{*}T < \infty. \tag{29}$$

The last equation also answers the question that was a subject of a lively discussion within many years, namely on the so-called 'theoretical limit' of $Z^{*}T$ thermal efficiency of thermoelectric materials. It follows from the said equation that the upper positive limit for $Z^{*}T$ does not exist and from the standpoint of thermodynamics generalized thermal efficiency may be arbitrary large. In the same time, in the crystals where commutation effect is possible, that generalized thermal efficiency $Z^{*}T$ might be even negative, not exceeding the figure of one in absolute value, though.

From eqns (22) and (23), considering thermodynamic limits for δ, it is evident that

$$\prod^{*} \geq \alpha^{*}T\ . \tag{30}$$

The above expression is the generalization of the first Thomson relation. It was first formulated by Luste.

For an isotropic medium only the relation (30) has the form of a strict equality (2), but for a general case, when the magnetic field is present in the crystals with low symmetry, it has a form of inequality.

Consequently, the application of irreversible processes thermodynamics to description of Thomson relations for more complicated anisotropic and gyrotropic media results in the development of the thermoelectricity thermodynamic theory as well as to the disclosure of new regularities whose physical meaning should be still understood.

8 On practical applications of Thomson relations

Apart from theoretical value, Thomson relations have practical applications. In energy applications (thermoelectric generators or coolers), though, the Thomson effect is rather small as compared to the effects of electric power generation, the Peltier effect, heat transfer along the legs of thermocouples and the Joule heat, and equals some percent of their value only. That is why the Thomson effect is usually neglected at energy devices design.

There are places, however, where it should not be neglected and those are measuring technique in the first place.

The Thomson effect should be considered at precise measurements of the thermoelectric energy converters, generator modules parameters (Fig. 13).

Properties of modules are determined at the application of various operating modes: open electric circuit, maximum efficiency, maximum power, etc. Here, the Thomson effect $\pm Q_T$ is considered in the heat and energy balances equation:

$$Q_0 = Q_\kappa - \frac{1}{2}Q_I + Q_\Pi \pm Q_T + Q_E + Q_A \tag{31}$$

where Q_0 is the heat power supplied to the module, Q_κ is the heat transferred due to the legs thermal conductivity, Q_I is the Joule heat, Q_Π is the Peltier heat, Q_T is the Thomson heat, $+Q_E$ is the external circuit electric power, and Q_A are the heat losses due to deviations from adiabaticity. The error in the definition of modules parameters where the Thomson effect is considered is lessened down to 1.5–3%.

Application of the first Thomson relation at the precise measuring of thermoelectric materials properties is also of great help [29] (Fig. 14). To measure the thermo-EMF coefficient, electric current is sent through the sample under measurements in the direction at which the junction

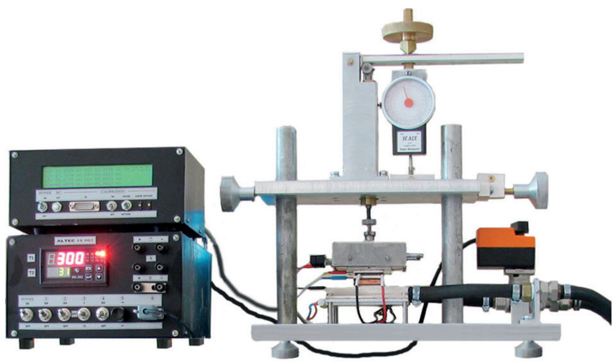

Figure 13: Equipment Altec-10002 for precise measurements of the generator module parameters with the Thomson effect considered [30].

Figure 14: Schematic and appearance of the automated measuring setup for the material thermoelectric properties determination. 1 – thermostat, 2 – thermocouples, 3 – current leads, 4 –reference heater, 5 – sample.

adjoining the reference heater is cooled. After that current I is sent through the reference heater with resistance R, heat release here compensating for the Peltier effect. Such a compensation is more precisely defined by the absence of thermo-EMF in the sample.

In such a case

$$Q_{\Pi} = I^2 R\,, \tag{32}$$

and in accordance with the first Thomson relation

$$\alpha = \frac{I^2 R}{T}\,. \tag{33}$$

Of still more importance is consideration of the Thomson effect at the development of standards of alternating current and voltage. For this purpose, thermoelectric converters of the alternating current into direct one are used, which consist of an electric heater 1 and a thermal couple 2 [31].

Primarily, the required AC current $I_{\approx}$ is sent through the heater, thermo-EMF $E_{\approx}$ being fixed (Fig. 15). Then, direct current with a value providing EMF of the thermocouple equal to $E_{\approx} = E_{=}$ is sent through the heater. For this case, $I_{=}$ should be equal to the required value of the alternating current $I_{\approx}$. Since $I_{=}$ can be determined with the error of $10^{-4} - 10^{-6}$ percentage, the precision of reproduction of the alternating current unit will be totally dependent on the precision of a thermoelectric converter. The Thomson effect becomes here the main error that distorts the identity of temperature distribution in the heater when both direct and alternating current are sent through it. For this reason, a thermocouple is heated to different temperatures $I_{=} - I_{=} = \Delta T$ at equal functioning values of alternating and direct currents that results in the error of their comparison up to 5–8 percentage.

To reduce the said error, a thermopile is installed along the heater (Fig. 16) which helps minimize the Thomson effect operation error [31]. Application of such thermoelectric converters implements reproduction of the alternating current and voltage units with the accuracy up to 10^{-4} percentage. They are used for national standards and facilities for alternating currents measurements (Fig. 17). Film thermoelectric AC converters were developed in USA (NIST), Germany (PTB/IPHT), Korea (KRISS) [33,34], etc.

9. Thomson transversal EMF: anisotropic thermoelements

In his paper [35], Thomson scrutinized thermoelectric phenomena in crystalline media. For the uniaxial crystals case, he introduced the Seebeck thermo-EMF coefficients α_1 and α_2 along

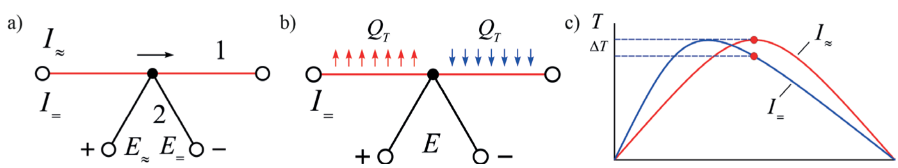

Figure 15: Schematic of the elemental thermoelectric AC converter (a), the Thomson effect Q_T (b) and symmetry distortion in temperature distribution in the heater (c) due to the Thomson effect.

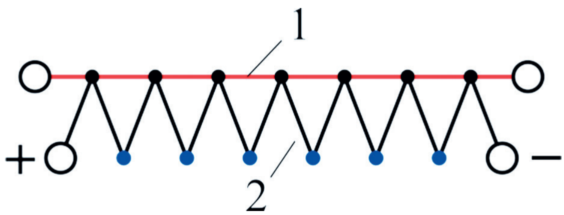

Figure 16: Schematic of the multiple-unit thermoelectric AC converter.

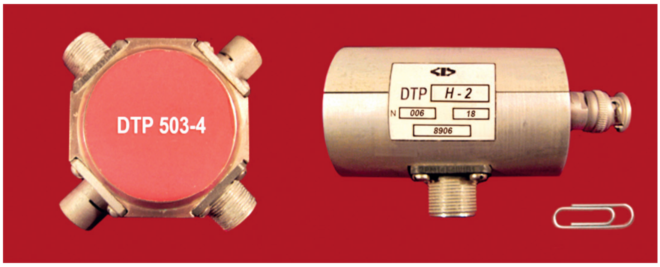

Figure 17: Thermoelectric converters of current (a) and voltage (b) for AC metrology [32].

crystallographic axes x_1 and x_2, which could have been different, $\alpha_{11} \neq \alpha_{22}$. Therefore, such crystals possess thermo-EMF anisotropy. If a rectangular sample is cut from this material (Fig. 18) at the angle φ to crystallographic axis x_1 and temperature gradient is established along the sample ∇T, thermo-EMF coefficient along this direction will be described by the formula

$$\alpha_{\parallel} = \alpha_{11}\cos^2\varphi + \alpha_{22}\sin^2\varphi. \tag{34}$$

Of principal importance here is the discovery of the Seebeck transversal effect by Thomson; the said effect occurring perpendicularly to the temperature gradient in an anisotropic material. Its value was calculated by Thomson in the form of

$$\alpha_{\perp} = \left(\alpha_{11} - \alpha_{22}\right)\sin\varphi\cos\varphi. \tag{35}$$

Somewhat later, Borelius [36], guided by the Thomson thermo-EMF transversal coefficient, wrote the value of the transversal thermo-EMF in the obvious form

$$E_{\perp} = \left(\alpha_{11} - \alpha_{22}\right)\sin\varphi\cos\varphi\frac{a}{b}\left(T_1 - T_2\right). \tag{36}$$

The fact that the value of thermoelectromotive forces transversal to the temperature gradient becomes dependent on the samples a and b geometry, is noteworthy.

In fact, it meant that, relying on the Thomson transversal thermo-EMF, it is possible to develop a thermoelectric energy converter (Fig. 19), different in essence from conventional thermocouples. It is traditionally called an anisotropic thermoelement.

Such a thermoelement has a set of attractive properties.

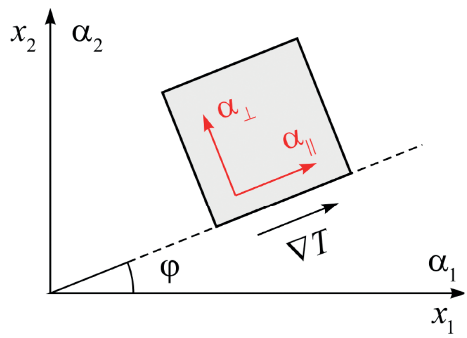

Figure 18: Conditions for the longitudal $\alpha_{\|}$ and the transversal $\alpha_{\perp}$ thermo-EMF coefficients occurrence.

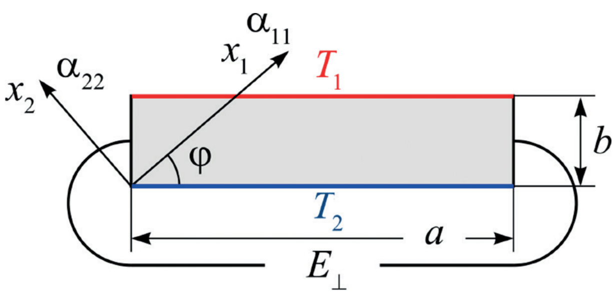

Figure 19: Schematic of an anisotropic thermoelement based on the Thomson transversal thermo-EMF.

First, unlike thermocouples, it may be fabricated from one material, thus excluding commutation problems, accompanying thermopiles.

Second, different from thermocouples, the value of the developed thermo-EMF depends on the sample geometry. The bigger the relation a/b, the higher the developed voltage.

Third, such a thermoelement is extremely manufacturable: once a rectangular sample with the anisotropic thermo-EMF is cut from the crystalline material, the electricity generator is ready.

The patent for the thermoelectric electricity source based on the Thomson transversal EMF was received in 1964 [37,38].

The efficiency of such a thermoelement is determined from the expression [39].

$$\eta = \frac{1}{4} Z_A \eta_K \bar{T}, \tag{37}$$

where

$$Z_A = \frac{(\alpha_{11} - \alpha_{22})^2 \sigma}{\kappa}. \tag{38}$$

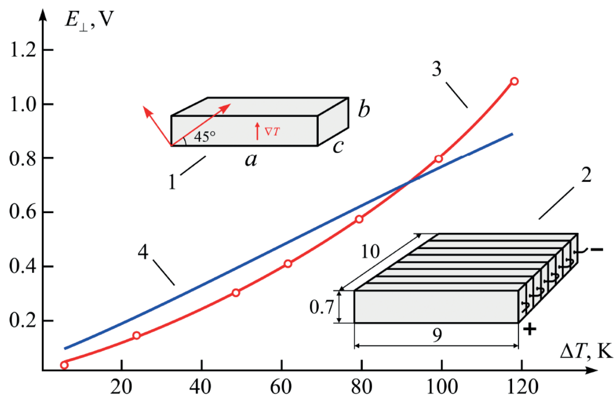

Figure 20: Results of testing of a thermoelectric generator of anisotropic elements. 1 – basic thermoelement, 2 – thermopile of anisotropic thermoelements, 3 – thermopile electric voltage $E_{\perp}$, 4 – calculated values $E_{\perp}$, ΔT – temperature difference on upper and lower surfaces of the battery.

In these expressions η_K is the Carnot efficiency, $\overline{T}$ is an average temperature, σ and κ are electric and thermal conductivities of the material, respectively. The expression Z_A characterizes thermoelectric material figure of merit and bears the same meaning as the Ioffe criterion for thermocouple elements.

The first thermoelectric generator based on the Thomson transversal EMF was fabricated and examined by the author of the present work in 1964 [40].

For experiments single crystals of CdSb with the thermo-EMF anisotropy $\alpha_{22} - \alpha_{33} = 150$ μV/K were used. Eight anisotropic thermoelements with the dimensions $a = 9$ mm, $b = 7$ mm, $c = 7$ mm , whose edge a was oriented along the crystallographic axis < 100 > at the angle of 45° to the direction of the temperature gradient were cut from such material (Fig. 20). With the said orientation (see Formula 36) the value $E_{\perp}$ reaches its maximum. Thermoelements were connected in series into a thermopile and placed between the flat heater and the cooler with a help of thin electrical insulation. CdSb low thermal conductivity (≈ $2{\cdot}10^{-2}$ W/cm·K) allowed easy obtaining of sufficiently big temperature differences. At $T_1 = 23$°C and $T_2 = 140$°C, a transversal thermo-EMF 1.1 V was obtained.

The above results gave a convincing corroboration of the existence of the Thomson transversal thermo-EMF, as well as the correctness of the Borelius's formula together with the possibility of developing of thermoelectric electricity sources based on the transversal thermo-EMF.

As follows from (38), thermo-EMF anisotropy has the most significant effect on a thermoelectric material figure of merit. Unlike electric conductivity σ and thermal conductivity κ that always occur in electroconductive materials, thermo-EMF anisotropy $\Delta\alpha$ is quite a rare phenomenon. The reason for this is that for $\Delta\alpha$ to occur specific conditions are required. The following mechanisms should be present for thermo-EMF anisotropy occurrence:

(1) Existing of several scattering mechanisms in the presence of one type of carriers (either electrons or holes).

(2) Photon-electron drag effect.

(3) Simultaneous existence of several carrier types in the presence of a single anisotropic scattering mechanism.

The analysis has shown that for the first case the thermo-EMF anisotropy is insignificant and, thus, of no practical interest. For the second case, though, the growth of the thermo-EMF anisotropy is accompanied by the growth of thermal conductivity, neither of the said resulting in the figure of merit Z_A of the material but insignificant improvement. Of most prospective character is the third mechanism. In particular, when two types of carriers, electrons and holes, are present, maximum values of the thermo-EMF anisotropy are obtained if at least one of the conditions below is satisfied:

$$\begin{aligned} K_p / K_n &\gg 1, \\ K_n / K_p &\gg 1, \end{aligned} \tag{39}$$

where $K_n = \dfrac{\sigma_{22}^n}{\sigma_{11}^n}$; $K_p = \dfrac{\sigma_{22}^p}{\sigma_{11}^p}$; σ_{11}^n and σ_{22}^n are electronic constituents of the biaxial semiconductor electric conductivity tensor components, whereas σ_{11}^p and σ_{22}^p are their hole constituents.

Maximum thermo-EMF anisotropy values are obtained in the mixed conductivity area by introducing a donor impurity provided hole mobility u_p is larger than electron mobility u_n, or that of acceptor impurity, if $u_p < u_n$.

The above results were confirmed empirically for the CdSb anisotropic material, doped with impurity (Fig. 21). The highest known values for the thermo-EMF anisotropy $\Delta\alpha$ were obtained together with the corresponding increase in Z_A.

And still, figure of merit Z_A absolute values remain low enough. This explains the limited application of anisotropic thermoelements as generators. Search for the high-efficient anisotropic materials belongs to the future.

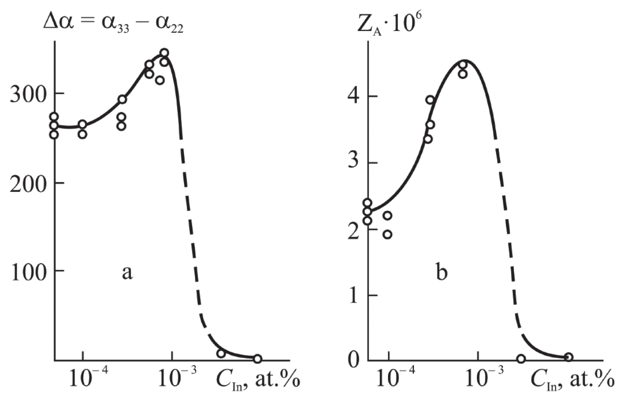

Figure 21: Dependencies of thermo-EMF anisotropy $\Delta\alpha$ (a) and thermoelectric figure of merit (b) of CdSb single crystals in concentration at 330 K.

The existing thermo-EMF anisotropy high values together with the possibility of increasing the anisotropic thermoelements electromotive forces by simple increase in a/b ratio makes them more and more attractive for the application of susceptible sensors. The increase in anisotropic thermoelements response time by means of their thickness lessening also serves their further promotion.

Notwithstanding the attractive features of anisotropic thermoelements, they have not yet enjoyed wide practical application as thermogenerators because the materials with high values of the anisotropic figure of merit Z_A have not been found yet. The solution belongs to the future.

However, anisotropic thermoelements are finding a wider application in measuring technology. Potentiality of increase in thermoelectric sensors sensitivity by simple increase of the relation a/b makes them more and more attractive. Moreover, the speed of such devices rises with the decrease of the anisotropic thermoelement thickness.

That is why such sensitive and high-performance elements have found application as laser radiation receivers for power energy and energy distribution determination, especially in the high-power technological lasers (Fig. 22). Anisotropic thermoelements are of great use when applied in various heat-flux sensors for remote temperature measurements in different industrial processes.

Of special interest are thermoelements based on the Thomson anisotropic thermo-EMF made in the form of flat rectangular spirals cut from one single crystal [41,42]. Each turn of the spiral (Fig. 23) is nothing but four anisotropic elements connected in series. Electric voltage on the ends of the spiral occurs when the inner cavity of the spiral is heated whereas its outer surfaces are kept under the set temperature. Electric voltage here increases in proportion to the number of spiral turns. For instance, a spiral made of CdSb with the volume of 1 cm^3 at the temperature difference 50 K develops electric voltage as high as about 1000 V!

Such spiral structures possess exceptionally high sensitivity and register heat fluxes that approach the level of inner thermal noises. As commutation junctions are practically absent in such spirals, it excludes the influence of contact noises, thus favoring obtaining of ultimate sensitivity.

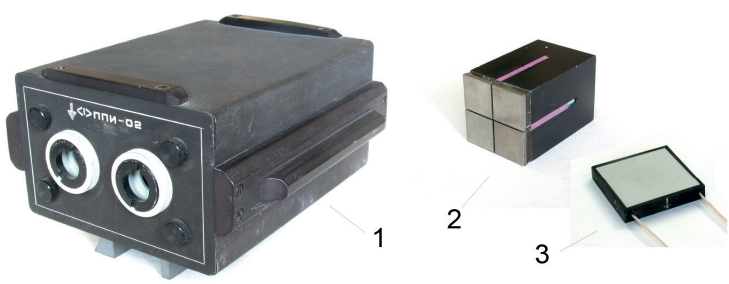

Figure 22: Devices with anisotropic thermoelements for radiation registering designed and developed in the Institute of Thermoelectricity: 1 – absolute differential receiver for continuous laser radiation power measurements, 2 – basic matrix for power laser CO_2 measurements, 3 – laser emission sensor with the sensitivity of 3 V/W.

The study of the properties of heat flux sensors made from such spirals was given special attention to. For this purpose, the information and energy theory of thermoelectric measuring systems [41] was applied, where the specific informativity equaling to the number of information bits, produced by a sensor per unit of time, was used as a sensor universal parameter.

Such an approach enabled creation of the methods of computer simulation of measuring devices with the said sensors to reach ultimate sensitivity. For example, with such approaches employed, superinformative microcalorimeters with ultimate values of sensitivity and high performance were developed (Fig. 24). Their application allows solution of both practical and scientific problems, which could not be realized with the help of conventional measuring equipment.

Thus, they help in determining of the expected lifetime of lithium chemical electricity sources, those sources being used in the devices of high importance, where their premature failure is inadmissible. The information on heat products of the microorganisms for the determination of the optimal dosage of antibiotics was obtained with such microcalorimeters. Characteristic dependencies of microorganisms' heat generation were found that could help in their identifi-

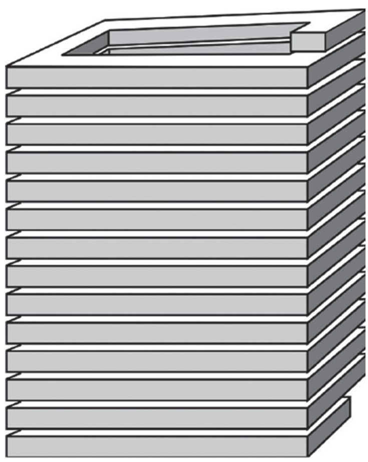

Figure 23: Anisotropic thermoelement of spiral shape.

Figure 24: Ultrasensitive fast-acting differential microcalorimeter (10^{-8} W), containing spiral anisotropic thermoelements, using the Thomson transversal thermo-EMF (1986) [43].

cation. Oscillating processes of their vital heat production important for search of mechanisms of microorganisms' informational exchange were discovered.

An important fact should be noted here that the increase in the energy needs of a human being is about 4% per year. The need in information at the same time rises as high as 100% every 2 years. Therefore, the increase in information becomes more important for humanity progress than energetics (Fig. 25).

The significance of informational systems becomes vital in such conditions. The role of measuring devices with thermoelectric sensors also increases.

It would be appropriate to remind here that it was Mendeleev, a metrologist by profession, who affirmed that, if the resolution of measuring devices is improved by one order, it would be a good premise for new discoveries in natural sciences.

Information and energy analysis shows that application of thermoelectric sensors, the ones with the Thomson's transversal thermo-EMF included will enable improvement of informativity of a set of important measuring devices ten- to hundredfold (Fig. 26). That is why, a transversal thermoelectric effect discovered by Thomson remains highly in demand in the present and will remain as such in the future.

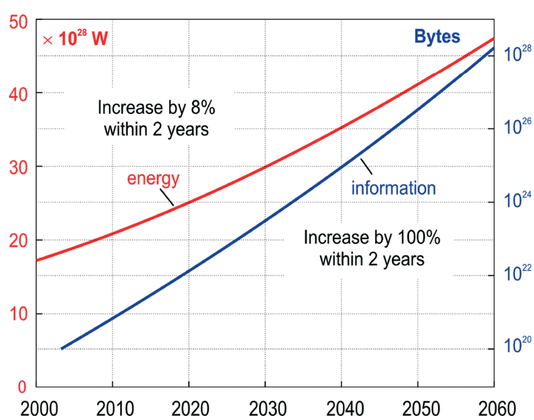

Figure 25: Comparison of prospects of energy and information consumption.

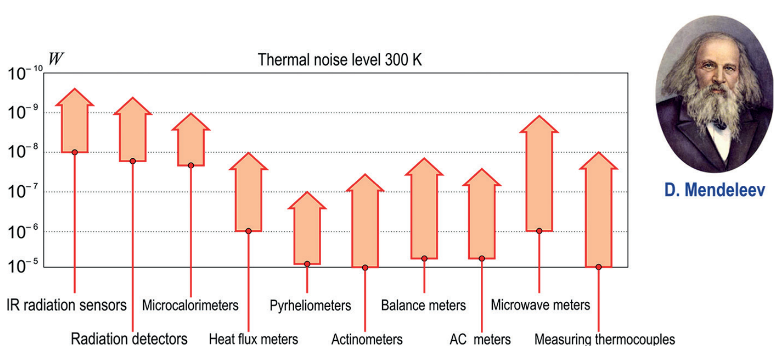

Figure 26: Prospects of development of measuring technology based on thermoelectric sensors application.

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