Chapter

Development of Quantum Unit of Temperature Standard in Thermoelectric Research

Svyatoslav Yatsyshyn, Yuriy Bobalo, Tetiana Bubela, Bohdan Stadnyk and Mykola Mykyichuk

Abstract

The quantum standard of temperature based on the revealed quantum unit of the mentioned quantity is studied. It is recommended first to apply as an intrinsic standard. Such a standard does not need permanently recurring measurements against the realization of the SI unit to validate its accuracy. It may be considered as the intrinsic standard of temperature that could be embedded into cyber-physical systems (CPSs) ensuring their precision operation. The methodological base of involvement of the developed standard in the formation of the thermoelectric power of thermoelectric transducers as well as the generator is considered. The feasibility of a unified consideration of the nature of thermoelectric power within macro- and nanothermodynamics is shown. This approach is driven by the increasing use of nano elements based on 1D-, 2D- nanomaterials (nanowires and nanosheets, respectively) and nanostructured materials in technology, in particular, to improve the key parameters of thermoelectric generators and thermometers. In the first case, this is thermoelectric efficiency, and in the second case, the accuracy of thermometers, which is determined by the stability in a time of thermoelectric power.

Keywords: thermoelectricity, quantum standard of temperature, drift of thermo-EMF, elastic strain engineering, thermoelectric transducer

1. Introduction

Thermoelectricity, as it is evident from the papers of International Forum on Thermoelectricity, May 2017, Belfast, is continuously developing in two main areas:

- Thermoelectric phenomena and means for energy production. The main thing here is high parameters: thermoelectric quality factor *ZT* and similar coefficients;

- Thermoelectric phenomena and means for measuring temperature (thermoelectric thermometry). Here the main item seems to be the high stability of thermoelectric characteristics or rather their temperature dependence.

There is a certain gap in the physical mechanisms between these areas, as the goals of both areas are significantly different. Since the second area is more metrological; in our opinion, it is interesting to present its achievements in the perspective of further development of the first area, as more focused on renewable energy and efforts of thermoelectric materials science to improve its energy efficiency. In general, there are good reasons for this: a characteristic feature of modern scientific methodology is interdisciplinary research [1], able to update scientific and technological approaches of the considered thermoelectricity.

2. Promising scientific and technological approaches in thermoelectric materials science

2.1 Elastic strain engineering

Thus, the technology of elastic strain engineering was studied [2] and implemented [3] for multigate field-effect transistor (FET) production. Its cornerstones are the synthesis of nanostructures with inherent elastic effects; applying force and measuring the consequences of its action; study of energy dissipation mechanisms; predicting the results of these effects on specific physical properties (in this case, we are interested in thermo-electromotive force (thermo-EMF)).

Although mechanical failure is a consequence of deformation that should be avoided, elastic deformation can produce a positive effect on the properties of materials. The effect of elastic deformation becomes more obvious at small sizes, because micro/nanoscale materials and structures can withstand exceptionally high deformations until they fail [4]. Studies of elastically loaded nanowires have demonstrated [5] that they can withstand significant elastic deformations, and their bending modulus increases exponentially with decreasing nanowire diameter. At the same time, deformations modify the electronic structure of semiconductor nanowires, causing the metal–insulator transition at room temperature and effectively converting mechanical energy into electrical. Simultaneously, the basin properties substantially depend on the temperature [6] while production and operating of produced means.

2.2 Metrology and thermodynamics

To consider the physical phenomena that alter the main thermoelectric characteristics, we involve the thermodynamics of irreversible processes [7, 8]. The latter had proved its suitability for various fields of science and technology, as it had separated the set of different factors acting on the object (thermoelectric material) into several independent, in the first approximation, groups. First of all, the thermodynamics of massive objects have been developed. According to it, 6 degrees of freedom act on such objects that were the 6 thermodynamic forces and 6 thermodynamic flows. To determine each of them, a system of 6 algebraic equations with 6 unknowns has be solved [9].

In the early stages of the development of thermoelectric thermometry, the determining impact factors were the chemical factors (changes in the content of a components), as well as the corresponding principles of primary transducer's drift due to the composition of thermoelectrodes. Diffusion factors and the corresponding principles of instability (changes in temperature and duration of use) became decisive in the later stages of thermometry, i.e., for protected thermoelectric thermometers.

Mechanical factors and principles of instability have become significant in the further aggravation of the requirements for metrological and operational characteristics of thermometers.

2.2.1 Thermoelectric transducer's conversion functions and chemical impact factor

Thermo-EMF in chemically distributed thermoelectrodes ($grad_x\mu$) in the temperature field ($grad_xT$) is obtained by solving the equation of electric current transfer under the condition that J_e = 0:

$$\mathrm{U} = \int_x \alpha[T(x)]\nabla_x T dx + \frac{1}{e}\int_x \nabla_x \mu[T(x)]\,dx \tag{1}$$

Until recently, such thermo electrodes were considered as homogeneous and therefore their impact-function was neglected. That is the well-known equation of thermo-EMF produced in the long and thin thermoelectrode:

$$\mathrm{U} = \int_x \alpha[T(x)]\nabla_x T dx \tag{2}$$

2.2.2 Function of influence at thermo diffusion and functional-gradient thermoelectric materials

The solution of the heat transfer equations from 1273 to 273 K of Fe and Ni impurities with C content and heat transfer Q in molybdenum single crystal leads to the methodological component of the error ΔU_x:

$$\begin{aligned} U &= U_0 + \Delta U_X = \int_T \alpha(T)dT + \frac{QC}{e}\ln\frac{T_H}{T_C} \\ \Delta U_X &= \frac{Q_{Fe}C_{Fe} + Q_{Ni}C_{Ni}}{e}\ln\frac{T_H}{T_C} \end{aligned} \tag{3}$$

Here, the relative chemical function of influence was accessed as the ratio of this function ΔU_x to its value $U_0 : K_X\ (T, C, Q, \ldots) = \Delta U_X/U_0 = 0.0026$.

2.2.3 Thermo-EMF and thermodynamics

The basic principles of the thermodynamic method in the phenomenological sense were created in the 1950–1960 on the basis of classical thermodynamics [7] and described in the thermodynamics of irreversible processes [8]. Statistical thermodynamics of nonequilibrium processes is broader as science. Its two parts (thermodynamic and electronic approaches) compose a single doctrine of the properties of material objects, which are manifested in their interactions. In linear thermodynamics, while the system is quite near the equilibrium, the thermodynamic flows J and the force X are conjugated by the relations of Onsager reciprocity:

$$J_i = \sum_j \beta_{ij}\,\mathrm{X}_j \ldots\ldots (i;j = 1\ldots l), \partial e\ \beta_{ij} = \beta_{ji}\ldots\ldots\ldots (i,j = 1\ldots l), \tag{4}$$

which are obtained by decomposition of a complex function $J = J(X_1; X_2; \dots X_6)$ in the Taylor series near the point $(X_1; X_2 \dots X_l) \to 0$:

$$J_I(X_1, \dots, X_6) = J_I(0) + \sum_J \frac{\partial J_I}{\partial X_J}\bigg|_{(0)} (X_J - 0) + \sum_j \sum_n \frac{\partial^2 J_I}{\partial X_j \partial X_n}\bigg|_{(0)} (X_J - 0)(X_n - 0) + \dots \tag{5}$$

The basis for considering the transfer processes in the linear approximation provided in conditions $J_I(0) \to 0$ and $X_1; X_2 \dots X_l \to 0$ are:

$$J_I(X_1, \dots, X_6) = J_I(0) + \sum_J \frac{\partial J_I}{\partial X_J}\bigg|_{(0)} (X_J - 0) = \sum_J \beta_{IJ} X_J \dots \dots (i; j = 1 \dots l) \tag{6}$$

are the results of the study of thermometric substance [10] at the significant, experimentally determined $gradT$ = 10^4 K/mm, above which the relationship of thermodynamic forces and flows becomes nonlinear. It is almost impossible to achieve such a significant gradient in industry.

In general, thermoelectric phenomena occur in the presence of thermal and electrical conductivity in a thermodynamic system. That is, in a rather long and thin conductor, which is in a temperature-distributed medium, as a result, thermo-EMF or a value equivalent to that described in connection with it. The corresponding two components of the equation relating to heat flow I_e and charge flow I_T are defined as:

$$I_e = k_1\left[q^2 E_l - eT\nabla\left(\frac{\mu}{T}\right)\right] - \frac{e}{T}k_2 \nabla T I_T = k_2\left[qE_l - T\nabla\left(\frac{\mu}{T}\right)\right] - \frac{1}{T}k_3 \nabla T \tag{7}$$

Here E_l is the electric field strength; $k_1; k_2; k_3$ are the kinetic coefficients. From here we can determine the thermo-EMF. As is known, the Seebeck effect consists of the occurrence of the potential difference between open ($I_e = 0$) thermoelectrodes in the cold zone:

$$k_1\left[q^2 E_l - eT\nabla\left(\frac{\mu}{T}\right)\right] - \frac{e}{T}k_2 \nabla T = 0; E_l = \frac{k_2 - k_1\mu}{ek_1 T}\nabla T = \alpha \nabla T, \tag{8}$$

here α is a Seebeck coefficient. In this case, thermoelectrodes are considered homogeneous, without a gradient of chemical potential ($\nabla\mu = 0$) along the length at which the temperature gradient ∇T is created. By integrating along the length of the thermocouple located in the temperature gradient zone, we obtain characteristic function or an integrated thermo-EMF of thermocouple:

$$U = \int_x E_l dx = \int_x \alpha_{th} \nabla T dx = \int_T \alpha_{th}(T) dT \tag{9}$$

Here α_{th} is the Seebeck coefficient of thermocouple. The integral, defined by the boundaries $T_1; T_2$ corresponding to the temperatures of reference and hot junctions, allows us to come to the basic laws of thermoelectric circuits.

Previously, we have developed the basics of the thermodynamic approach for estimating the drift of thermo-EMF of the thermocouple. Thermodynamic forces and flows were considered especially in the presence of deformation since due to manufacturing sensitive elements of thermoelectric transducers or the thermoelectric material the mechanical stress and strains can be significant in them. Under the

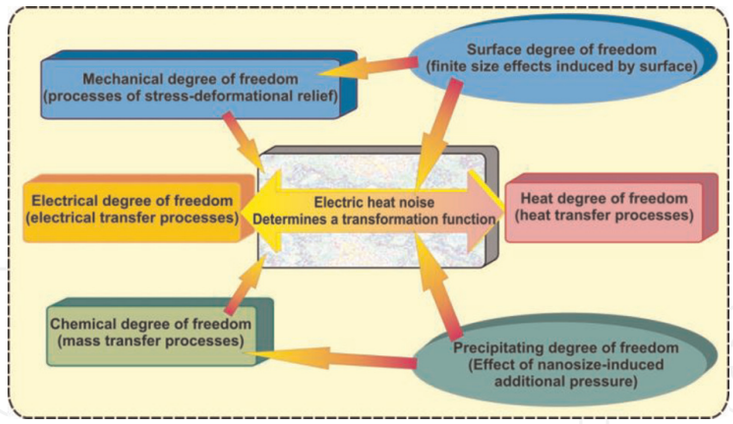

Figure 1.
Conversion function (transfer processes associated with electrical + chemical + heat degrees of freedom that are forming Seebeck coefficient) and influence function (transfer processes associated with the mechanical degree, responsible for drift of thermoelectrodes).

condition of an elastic continuum with dislocations, when $\frac{dU_{int}}{dt}$, the component $p\frac{dV}{dt}$ can be replaced by the product of strain $\hat{\varepsilon}$ and stress $\hat{\sigma}$ (tensors)

$$p\frac{dV}{dt} = \hat{\sigma}\frac{d\,\hat{\varepsilon}}{dt} \tag{10}$$

Phenomenological consideration of stressed thermo electrode shows an increase in Gibbs energy. Then in the basic equation of thermodynamics arises an additional thermodynamic force $X_J = \nabla\left(\frac{\sigma^2}{2E_U}\right) = \frac{\sigma}{E_U \nabla_x \sigma}$ due to this energy, here $\nabla_x \sigma$ is the divergence of mechanical stresses along thin cylindrical thermo electrode with coordinate x. The energy accumulated during deformation significantly affects the conversion function of the transducer by forming a mechanical function of influence (**Figure 1**).

Under the conditions of electric current transfer in the deformed thermoelectric substance of the thermo electrode at sufficiently low temperatures in the absence of diffusion mass transfer and open thermocouple circuit, when $I_e \to 0$:

$$I_e = k_1\left[e^2 E_l - e\frac{\sigma}{mE_U}\nabla\sigma\right] - \frac{e}{T}k_2\nabla T = 0, \tag{11}$$

It becomes possible to compute the characteristic function U_0 in the form of its nominal value and mechanical impact-function ΔU_M:

$$U(T, \dots) = U_0(T) + \Delta U_M = \int_x \alpha[T(x)]\nabla_x T dx + \frac{1}{em}\int_x \frac{1}{E_U}\sigma\nabla_x\sigma[T(x)]dx, \tag{12}$$

here E_U is the material's modulus of elasticity.

3. Temperature measurement as a basis for thermoelectric research

3.1 Prerequisites

To characterize the substances of thermoelectric materials science in relation to their properties, regardless of their type, it is necessary to determine exactly the

temperature. In thermoelectric thermometry, the conversion function is determined by dependence of thermo-EMF on temperature. In thermoelectric energetics, the temperature significantly affects figure of merit ZT. Independently of the application, the accuracy of temperature measurement [9] becomes essential.

Currently within the world the overall process of transition to a radically higher level of metrology is stimulated by transferring the reference base to a quantum basis. Almost all standards of physical quantities, except temperature, have been replaced [11].

The need for a reproducible quantum standard of temperature was demonstrated by the works presented in [12]. Activities were related to the cardinal problem of thermometry: Committee on Data for Science and Technology has clarified the redefinition of the concept of "Temperature" [13]. It was proposed to replace temperature measurements with energy ones and thus avoid methodological error due to calibration of temperature measuring instruments at the triple point of water. A number of leading metrological centers that are Great Britain (NPL) [14], Germany, etc., have developed a new definition of the unit of temperature: Kelvin, K, is a unit of thermodynamic temperature; its size is determined by fixing the numerical value of Boltzmann constant equal to $1.38065\ldots \bullet 10^{-23}$. As a result, the size of the kelvin becomes independent of the material and is determined by the change in thermodynamic temperature, which leads to a change in thermal energy at $k_B T$ equal to $1.380\,65\ldots \bullet 10^{-23}\,J$. Then it remains to predetermine as accurately as possible the Boltzmann constant, which is realized in [15, 16]. The latter is isolated from other fundamental constants [17]. Therefore, while applying the proposed method as a basic, the obtained results of temperature measurement hold an additional error. It is due to the indirectness of the measurement, which becomes less accurate compared with direct measurement.

This error δT consists of the sum of 2 errors: $\delta E + \delta k_B$. Otherwise, the replacement of temperature measurements inevitably raises a number of difficulties in the field of low-energy measurements related to the sensitivity of devices, insufficient insulation [18, 19] and, most importantly, with establishing the unknown value of the quantum of energy. At the same time, all other standards of physical quantities of the SI system have already become quantum.

3.2 Quantum of temperature and its implementation

The quantum of temperature was first introduced within the system of Planck units in the form of temperature T_P, where it acts as a determining unit of the temperature scale: 0°C = 273.15 K = $1.9279 \bullet 10^{-30}\ T_P$ [16]. We have proved the existence of a quantum of temperature and also revealed the possibility of its use in the quantum temperature standard [20]. The latter is realized on the basis of the current quantum standards of electrical resistance R based on the inversely proportional value of the conductivity quantum ($R = 1/\sigma_Q$) [21] and the voltage standard U based on the array of Josephson junctions [22].

3.2.1 Thermoelectric method of measuring temperature

Independent of temperature, operating current of considered device passes through the material, that is, the superconducting carbon nano tube (CNT) [23], graphene [24], or other substance where the quantum Hall effect may be realized. The design of a CNTFET field-effect transistor with a CNT built into the base is used [25]. When the latter is selected with superconducting properties, such a transistor is

characterized by an electrical resistance of 25812.807557 ± 0.0040 Ω [26] caused exclusively by the resistive properties of supply contacts. While conducting current I through the CNT on such contacts, it arises a temperature jump ΔT:

$$\Delta T = \frac{2hI}{3k_B e} = \frac{2hN}{3k_B \Delta t}, K, \tag{13}$$

when limiting the number of electrons N per unit time to one electron, temperature increase is determined by the ratio of Planck and Boltzmann constants:

$$\Delta T\big|_{\substack{\Delta t \to 1s \\ N \to 1}} = \frac{2h}{3k_B}\left[\frac{K}{s}\right] \cdot 1[s.] = 3.199493\,42 \bullet 10^{-11}\ \mathrm{K} \tag{14}$$

Thus obtained in such a way, the usniversal value denominated by us [27] as the reduced quantum unit of temperature (RQIT) is independent of the different influence factors and kind of substance. The value of RQUT, being measured in relation to the units of the SI system, is characterized by uncertainty, which is determined by the sum of uncertainties of two constants: Planck constant h and Boltzmann constant k_B [28], which together form its total relative uncertainty equal to $59.2 \bullet 10^{-8}$. For temperature changes of $\sim 10^{-11}$ K due to single-electron relaxation, we must obtain measurable values sufficient to record temperature changes. This means that, first, the current through a carbon nanotube/semiconductor with a quantum Hall effect should be increased.

In this direction, studies conducted [29] found the following. The break of an electric circuit due to the CNT defect can occur when the temperature of the nanotube increases by several hundred degrees, caused, for instance, by the self-heating effect. The latter is less pronounced in semiconductor nanotubes compared with tubes with a metallic conductivity due to different heat dissipation mechanisms. Second, electronic phenomenon with a pronounced integration effect was proposed to register a weak temperature signal. That is the Seebeck effect based on elementary eddy currents [30], which correspond to the cooperative motion of electron groups.

3.2.2 Implementation of the quantum temperature standard

Designing the temperature standard based on the temperature quantum has become possible with unique standards of physical units, including the electrical resistance standard (based on the conductivity quantum inversion) and the electric voltage standard (based on the Josephson junction array) together with the frequency standard. While powering the device from the electric voltage standard, it is possible to pass a certain number of electrons through the electrical resistance standard of nominal value equal to the Klitzing constant $R = h/e^2 = 25812.807\ldots\ \Omega$). In the considered temperature standard based on the CNTFET [27], the source and drain are made from nickel and copper, which together form a thermocouple through a CNT performing the function of hot quasi-junction of linear dimension ~0.02 μm; characteristic function of the mentioned thermocouple is known or predetermined.

As a result, we provide ability to measure the temperature jump on the sensitive element of the standard by thermoelectric method with the minimal methodic error (or with the minimal uncertainty) while controlling the current passing through the CNT. The mode of operation of the device is pulsed. It is powered by a sequence of

short ($\sim 10^{-2}$ s) pulses. At the first stage, while supplying, a temperature jump is created. At the second stage (the absence of current), a temperature increase is measured with help of a thermocouple. Specifically, at $I = 10^8$ e/s $\approx 6.24 \bullet 10^{-10}$ A, the temperature jump of $3.2 \bullet 10^{-3}$ K is achieved, which is to be measured. For K-type thermocouple ($\alpha \sim 41$ μV/K), the measured value is 0.14 μV, and for semiconductor thermocouple, it can be up to 1.4 μV. Pre-established uncertainty $\sim 59.2 \bullet 10^{-8}$ permits to suggest that the temperature jump is determined with absolute uncertainty $\sim 1.9 \bullet 10^{-9}$ K.

Subsequent transfer of the set value of the temperature jump from the quantum standard to the reference thermocouple of the first category is carried out by placing its hot junction close to CNT of the temperature standard. If their readouts differ, which may be due to heat loss and other processes, a correction factor should be introduced. The latter may be particularly suitable for studying the thermodynamic processes occurring in the considered standard. That is, this coefficient can be useful for studying not only the processes in thermocouple, but also to clarify the thermodynamic basis of thermoelectricity.

3.2.3 Macro- and nanoproperties related to temperature quantization as the main physical quantity of the SI system

Let us try to link the possibility of temperature quantization with the manifestation of the properties of the bulk level [31]. Naturally, to define it, we use the phenomenon of thermoelectricity, where nanoeffects in the form of a series of elementary eddy currents are involved in the formation of macro characteristics—thermo-EMF [32] due to which we are able to record the small changes in temperature with minimal methodological errors.

4. Development of thermoelectric research and verification of thermoelectricity

4.1 Classical thermodynamics and thermoelectricity

Within Thomson's thermodynamic theory, the Peltier heat is converted into electrical energy with the maximum possible efficiency of the Carnot cycle. Hence, there was obtained the first thermoelectric Thomson ratio ($\pi = \alpha T$), which connects the coefficients of two thermoelectric phenomena: Peltier and Seebeck. The second Thomson thermoelectric ratio ($\tau_A - \tau_B = T d\alpha/dT$), based on the consideration of the heat energy balance in the thermoelectric circuit, has justified the appearance of Thomson coefficients of each of the two thermoelectrodes (τ_A; τ_B) in the considered thermoelectric circuit as well as firstly predicted thermoelectric effect, contrary to the experimentally proven Peltier and Seebeck effects. In 1853, Thomson verified his own prediction that is the thermodynamic theory of thermoelectricity by recording Thomson's heat with thermometers. In 1867, F. Le Roy had repeated this experiment, replacing thermometers with thermocouples, and confirmed the results of Thomson [33].

With the quantum standard of temperature at our disposal, such studies should be repeated, especially since they relate to nanoscale effects as being performed on nanoobjects (CNT is considered below). Since Thomson consciously realized his discovery of the thermoelectric effect within classical thermodynamics in the absence of irreversibility, and the drift of thermo-EMF is due to irreversible factors

(thermodynamics of irreversible processes), then it seems quite interest to conduct research using the quantum standard of temperature.

4.2 Enhancement of the methodology for studying Peltier and Thomson coefficients

To study the Peltier and Thomson coefficients at the nanolevel, with help of the quantum voltage standard, we propose a CNTFET structure in which the source and drain are made of dissimilar materials *A* and *B* composing the hot junction of quasi-thermocouple. Then it becomes possible to calibrate this particular thermocouple and proceed the experiments.

By slightly changing the structure of CNTFET and making the source and drain from the same material, we can study the low-temperature effect of phonon drag on thermo-EMF. After all, it occurs according to [34] at the smallest diameters (1.0 … 10 nm), which corresponds to the diameter of the CNT of the conductive material in the area of its contact with another bulk.

However, of particular interest are studies of the deviations of the temperature changes of the quantum standard, measured by the additional reference thermocouple, from the predicted values. Otherwise, their dependence on a number of influencing factors helps to identify the peculiarities of the formation of not only thermo-EMF at the micro and nano levels and also to clarify the ambiguous statistical and thermodynamic interpretation of temperature in nanotechnology [35].

Here the approach connected with studying of mechanical stresses impact on thermo-EMF can be interesting. Although mechanical failure is a consequence of deformation that should be avoided, elastic deformation can provide a positive effect on the substance properties. Since this effect becomes more obvious while diminishing, micro/nanoscale materials and structures can withstand exceptionally high elastic deformations until the failure [36].

4.3 Elastic strains engineering and thermoelectric studies

The elastic strains engineering is able significantly improve the defining characteristics of the created standard. The effect of elastic deformation becomes more apparent at small sizes, since micro/nanoscale materials and structures can withstand exceptionally high elastic deformations before failure. Studies of elastically loaded nanotubes have shown the following: (1) Nanotubes can support significant elastic deformations, and their bending modulus increases exponentially as the nanotube diameter decreases; (2) the strains modify the electronic structure of semiconductor nano/micro probes, causing the transition of the metal–insulator at room temperature and effectively converting mechanical energy into electrical energy. The plastic deformation is absent in the nanoscale due to the proximity of the interface surfaces to the location of possible packaging defects (dislocations, nanopores, and nanowires). As a consequence, there is only elastic deformation. The latter have three linear deformation components and three torsional deformation components. Linear deformation is with + and -. Torsional deformations are left and right. In other words, there are 12 types of deformations that can be calculated and reproduced on the one hand and used for dosed and reproducible effects on thermo-EMF while measuring the temperature in the vicinity of CNT attachments. This is the content of the engineering of elastic strains for nanoscale objects of proposed *I-T* converting element, which can be represented as in particular as thermocouple with thermoelectrodes.

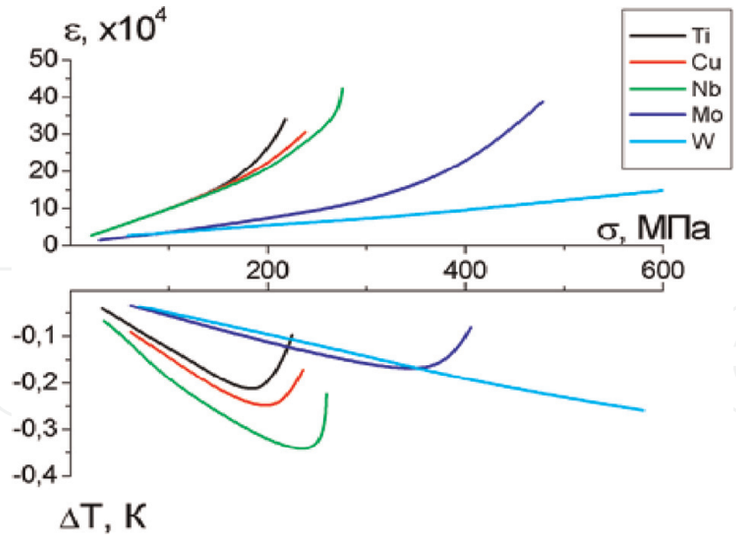

Figure 2.
Influence of elastic deformation on temperature change of pure metals of bulk specimens.

We have studied the influence of elastic deformation (within the limits of up to 1%) on thermo-EMF of different bulk metals and revealed that impact is reversible (**Figure 2**):

Here E_u is Young's module. In particular, for nickel-based alloys, changes in the influence function and the Young's modulus correlate with the coefficient K = 0.598.

The stresses were assessed for the needed current 1 nA passing through superconducting CNT and dissipating in places of CNT attachment, providing the temperature jump ~1.0 K. When the temperature coefficients of linear expansion of the electrode materials (Ni; Cu) are respectively $13 \cdot 10^{-6}$ K^{-1} and $16.5 \cdot 10^{-6}$ K^{-1}, then, at a temperature jump, there arise the thermo structural mechanical stresses. They are caused by the differences of their expansions to the silicon substrate ($5 \cdot 10^{-6}$ K^{-1}) on which they are fixed. This can lead to an additional uncertainty, which should be taken into account especially for the temperature standard.

4.4 Thermoelectric thermometry and nanothermodynamics

Due to elastic strain engineering, nanostructured materials according to [37] can acquire outstanding opportunities to adjust the physical and chemical properties by changing the field of distributed six-dimensional elastic deformations. For example, in thermoelectric energetics where high efficiency is required, these problems have been mastered designing the generators in 3–4-dimensional space where spiral shapes of thermocouples and thermocouples with directed porosity were invented [38], etc. The same applies to thermoelectric materials.

Thermoelectric thermometry traditionally considers almost all problems in the one-dimensional approximation, which, however, is substantiated by usage of long and thin cylindrical thermoelectrodes. The appearance of functional gradient thermocouples [39] adds one or two more dimensions to solving the drift problems of thermoelectric thermometers. Functionally gradient thermocouples are realized on the basis of thermoelectric materials with smoothly distributed properties (or with a gradient of chemical potential along the electrodes), on which a temperature gradient is imposed during operation. Thus, their conversion function becomes more accurate. Recently, [40] developed an original technology to obtain one-step functionally

graded materials fabrication using ultra-large temperature gradients, which may be valuable in the considered issue.

4.5 Nanothermodynamic aspects of updating thermoelectricity

No less important is the study of the correctness of extending macroscopic thermodynamics and statistical physics to nanoscale objects composed of so few atoms that they cannot be described thermodynamically. First of all, this applies to the concept of "temperature" [35]. To transfer the provisions of thermodynamics to nanoscales, it is necessary to understand the unique properties of nanosystems.

4.5.1 Consideration of the action of surface tension force

Maintaining an understanding of metrological approaches to the essence of processes within a thermosensitive substance, we have expanded the range of thermometric methods for studying the role of surface tension gradient as the major thermodynamic force in nanothermodynamics. In particular, we have conducted studies of solid- and liquid-phase sensitive elements while reducing their size in the micro- and nanoarea [41].

In the macroworld, the readouts of a liquid-in-glass thermometer (height of the liquid column Δh), the inner diameter d of which is significant, are described with temperature by the equation: $\Delta h = cd\Delta T$, mm (here c is a constant). As it can be seen, the sensitivity of the thermometer decreases with tube's inner diameter diminishing. The effect of surface tension force is manifested by bending of the meniscus, which leads to the readout error. In the liquid-in-nanotube thermometer is dominated the transfer processes associated with the surface degree of freedom, as the behavior of the liquid in the thin capillary is determined by the effect of wetting dependent on the surface tension force. The temperature dependence of this force is described for different liquids so that the data are embedded in the curve:

$$\sigma V^{2/3} = k(T_c - 6 - T) \tag{16}$$

Here $k = 2.1 \times 10^{-7}$ J/K mole$^{-2/3}$ is an Eötvös constant; T_C is the characteristic temperature, which in the case of water is equal to 547 K: then the coefficient of surface tension is zero. The Eötvös rule and the Schild equation determine the dependence of the surface tension of the liquid on temperature, and the surface tension coefficient itself is a linear function of temperature. If plot this function, you get the line intersecting the X axis at the characteristic temperature. Equation of calibration characteristics of liquid-in-nanotube thermometer was solved considering the transfer systems for thermosensitive substance with mechanical and surface degrees of freedom, since such thermometer measures the temperature in volume with the insignificant temperature gradient:

$$I_m = -L_{11}\nabla V - L_{12}\nabla M., I_s = -L_{21}\nabla V - L_{22}\nabla M \tag{17}$$

here $I_m; I_s$ are the liquid transfer flows due to changes in volume and surface tension respectively; L_{ij} are the transfer coefficients. The first Eq. (17) describes the mechanical flow as the flow of displacement of a liquid column under the action of thermodynamic forces due to the gradient of its volume and the gradient of its surface area. The second equation concerns the flow of transfer of the surface degree of

freedom that's the flow of alteration in the size of the column under the action of the described thermodynamic forces.

Hence the equation of the calibration characteristic of the liquid-in-nanotube thermometer takes the form (**Figure 3**):

$$\Delta h = b(T_c - 6 - T)/d \tag{18}$$

Here b is a constant.

4.5.2 Consideration of the action of specific energy in the formation of the precipitations of the second phase in the matrix

Nanothermodynamics [8] involves the introduction of an additional degree of freedom in the basic equation of thermodynamics. This is γdV (V is the volume of precipitations) due to the loss of specific energy γ while precipitating the second phase in the matrix of the original substance. Issue has been carried out for contact supercooled thin layer of substance at the stage of final sintering of the compressed powder by studying the grains interaction through abovementioned layer. An informative characteristic of the supersaturated phase state was the contact supercooling, which was defined as the difference between the equilibrium temperature of the liquid phase of a given composition with a solid phase at the planar interface and the equilibrium temperature of a crystal with a given surface curvature with the same liquid phase. Supercooling (up to 10 K) of a number of materials was revealed, as a result of which a significant ($\sim$ 10 K/cm) temperature gradient have arisen [42].

4.5.3 Consideration of additional source of occurrence of eddy currents

In the classical thermal conductivity, it is believed that the only cause of heat flow in solids is a nonzero temperature gradient. However, the thermal deformation ε of the bulk in the case of intense heat flow leads to the so-called coherence effect, which consists of the interaction of deformation and temperature fields. Evaluation of the effect impact was performed on glass and steel samples, characterizing by the same values of thermal conductivity a_T. The glasses are characterized by the coherence parameter $\frac{\varepsilon'}{a_T T'} << 400$; for steel, a similar parameter is much lower ($\frac{\varepsilon'}{a_T T'} \sim 20$). This means that for ceramics (nanostructured materials), slight changes in temperature lead to significant consequences of the deformation impact.

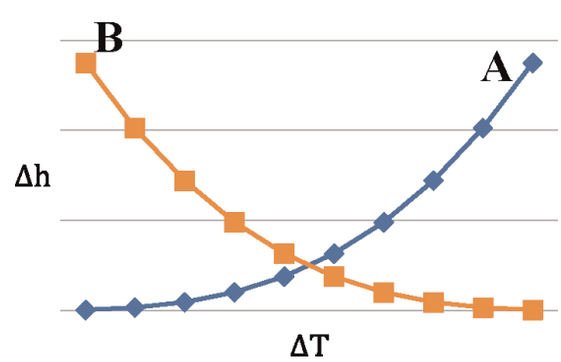

Figure 3.
Calibration characteristic of the liquid-in-glass thermometer (A) and the liquid-in-nanotube thermometer (B).

5. Generation of eddy currents in extreme cases

5.1 Absence of a temperature gradient applied to the thermoelectric material

At one case of thermoelectric material appliance, we can consider the lack of an appreciable temperature gradient imposed on it. Nevertheless, eddy thermoelectric currents can occur and act, because in accordance with the fluctuation-dissipative principles of thermodynamics in the substance, there are fluctuations in thermodynamic parameters, including temperature. Such oscillations are inevitably manifested by eddy thermoelectric currents. The latter lead to the appearance of charge fluctuations on the surface, which can be identified by passive noise spectroscopy [43].

5.2 Significant rate of temperature change in the thermoelectric material

In a substance annealed at the certain temperature and moved to an environment of a higher temperature, due to the formation of dislocation ensembles there are mechanical stresses that can accumulate internal energy. This leads to a change in the noise characteristics, explained by the involvement of the mechanism of energy accumulation-scattering on local quasi-defects of tensile vacancy origin in their interaction with phonons. When current is passed or without it, phonons are generated, accumulated in quasi-defects and then relax in a reversible or irreversible manner, resulting in 1/f or thermal noise [44], respectively. As a result, local eddy thermoelectric currents may occur.

The Raman method makes it possible to study the electron–phonon interaction. The wave number of the optical phonon of the Stokes component significantly depends on the temperature [45]. For example, for monocrystalline silicon, this dependence in the range 300–400 K is linear: $\nu_0(cm^{-1}) = 0.025\Delta T$, here ΔT is the change in temperature of the single crystal. As the temperature increases, the wavelength of the scattered light approaches the wavelength of the laser. This is due to the

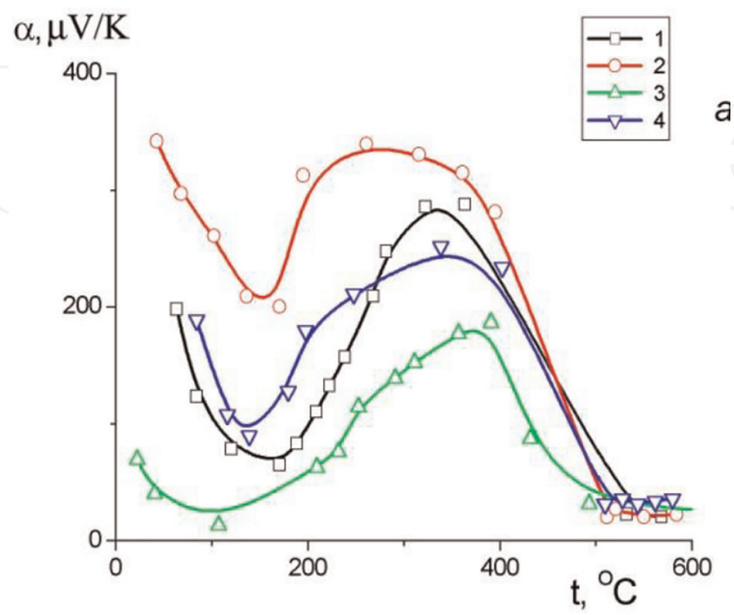

Figure 4.
Seebeck coefficients α of tellurium doped with 1.1% (1) and 1.5% (2) zinc and 1.1% (3) and 1.5% (4) of gallium.

elimination of the tensile action of micro stresses in the tested substance by increasing the mobility of vacancies. Therefore, at pre-melting temperatures, the effect of impurities on thermo-EMF becomes almost the same, as it is evidenced by the behavior of tellurium doped with zinc and gallium while melting above 400°C (**Figure 4**).

6. Conclusion

Progress in thermoelectric energetics is determined by the advances in materials science and is based, on the one hand, on the achievements of nanotechnology as a source of implementation of significant technological trends and, on the other hand, on the achievements of Metrology 4.0 as part of Industry 4.0 [46], which provides the foundation pillars for emerging quantum technologies in the branch of temperature measurements as the main controlled parameter of production and usage of thermoelectric facilities, devices, transducers, and sensitive elements.

It can be accelerated by the introduction of the quantum temperature standard (here the quantum temperature unit is expressed by the ratio of the Boltzmann and the Planck constants), not only as metrological instrument for ensuring the exactness and precision of temperature measurements, and as a tool for studying the spectrum of thermoelectric phenomena by using CNTFET as the kernel construction element, corresponding in the measuring cycle to a nanosized thermocouple. Involvement of the developed elastic strain engineering technology for the manufacture of multigate field-effect transistors gives possibility to improve the efficiency of thermoelectric materials.

Evaluating the achievements of W. Thomson (Lord Kelvin) in thermoelectricity, built on classical thermodynamics, while providing the quantum temperature standard operated on elements based on the thermodynamics of irreversible processes, we gain the ability to study in more detail the reserves of thermoelectricity and to clarify the validity of the basic laws of thermoelectricity for the nanoworld.

Since nanothermodynamics involves the consideration of additional for classical thermodynamics degrees of freedom due to the action of surface tension forces and mechanical stresses, it is possible to modify the thermoelectric properties of materials by forming multidimensional distributed fields of elastic stresses, which can be implemented nowadays. At the same time, nanothermodynamics should develop both in the direction of thermodynamic formalism (introduction of additional surface degree of freedom), which describes the increasingly important role of surface tension forces while reducing the qualificative size of systems to nanodimensions, and in the direction of consideration of elastic stresses in nanoobjects, able to lead to the appearance of anticipations of the second phase. Action of these factors is manifested through thermo-EMF, as a characteristic integrated over the volume of thermoelectric material.

The emergence, study, and subsequent usage of specific mechanisms of eddy thermoelectric currents in thermoelectricity cannot be ruled out. This may be the effect of coherence inherent in nanostructured materials, in which the minimal changes in temperature lead to the associated deformation aftereffect. That is, the influence of deformation on the major thermoelectric parameters has to be meticulously studied. In the future, it is necessary to develop the fundamental principles of generating the eddy thermoelectric currents in the absence/presence of significant temperature gradients imposed on the material. These currents exist in the thermoelectric substance in any case according to the fluctuation-dissipative principles of thermodynamics.

To update the thermoelectricity, the next aspect of the involvement of nanothermodynamics can be considered. That is a justification for the qualified elimination of correlation effects, for which is recommended based on the thermodynamic approach: (a) to select and evaluate independent factors influencing the studied objects; (b) to optimize the number of measurements while providing the necessary metrological characteristics; c) to process the obtained data on the basis of a proper understanding of nanostructured effects as well as substantiating that the detected "artifacts" are not created in the measuring system itself. While studying the measuring instrument as the major unit of the whole system, we have to be sure in its reliability especially concerning the developed thermocouples. It is expedient here to consider thermocouples with built-in self-testing [47]. Moreover, it is recommended by [48] to perform such temperature measurement system basing on thermocouple with controlled temperature field.

Author details

Svyatoslav Yatsyshyn*, Yuriy Bobalo, Tetiana Bubela, Bohdan Stadnyk and Mykola Mykyichuk
Lviv Polytechnic National University, Ukraine

*Address all correspondence to: sviatoslav.p.yatsyshyn@lpnu.ua

References

[1] Ohta M, Jood P, Murata M, et al. An integrated approach to thermoelectrics: Combining phonon dynamics, nanoengineering, novel materials development, module fabrication, and metrology. Advanced Energy Materials. 2018;**9**(23):1801304. DOI: 10.1002/aenm.201801304

[2] Xu N. Elastic Strain Engineering Effectiveness of Strain Solutions for Next-Generation MOSFETs. Berkeley: University of California; 2012

[3] Li J, Shan Z, Ma E. Elastic strain engineering for unprecedented materials properties. MRS Bulletin. 2014;**39**(2): 108-114

[4] Taloni A, Vodret M, Costantini G, Zapperi S. Size effects on the fracture of microscale and nanoscale materials. Na ture Reviews Materials. 2018;**3**:7. DOI: 10.1038/s41578-018-0029-4

[5] Boukai AI, Bunimovich Y, Tahir-Kheli J. Nature. 2008;**451**(7175):168-71. DOI: 10.1038/nature06458

[6] Bernhard IF. Technische Temperaturmessung. In: Physikalische und meßtechnische grundlagen, sensoren und Meßverfahren. Meßfehler: Springer, 2012

[7] Glansdorf P, Prigogine I. Thermodynamic Theory of Structure, Stability and Fluctuations. New York: Wiley; 1971

[8] Geckeler KE, Nishide H, editors. Advanced nanomaterials. John Wiley & Sons; 2009

[9] Yatsyshyn S, Stadnyk B. Accuracy and metrological reliability enhancing of thermoelectric transducers. Sensors and Transducers. 2010;**123**(12):69-75

[10] Ternan J. Thermal drift of thermocouples due to inhomogeneous changes in composition. Journal of Applied Physics. 1984;**55**(1):199-209

[11] de Podesta M. The definition of the Kelvin in the New SI: Its rationale, implementation and implications. In: Proceeding of XIII International Symposium on Temperature and Thermal Measurements in Industry and Science (TEMPMECO 2016); Zakopane, Polska, 26.06-01.07. 2016. p. 12

[12] Yatsyshyn S, Stadnyk B, Ya L, Buniak L. Handbook of Thermometry and Nanothermometry. Barcelona: IFSA Publishing; 2015

[13] Fischer J. International Temperature Scale and New Definition of Kelvin, Meeting on Fundamental Physical Constants, Eltville, 4; 2015

[14] Mills Ia, Quinn T, Mohr P, Taylor B, Williams E. The new SI: Units and fundamental constants, Royal Society Discussing Meeting. 2011

[15] Benz S, Pollarolo A, Qu J, Rogalla H, Urano C, Tew W, et al. An electronic measurement of the Boltzmann constant. Metrologia. 2011;**48**(142):23

[16] Pitre L, Risegari L, Sparasci F, Plimmer MD, Giuliano A. Determination of the Boltzmann constant from the speed of sound in helium gas at the triple point of water. In: Metrologia., 2015;**52**(5):S263. DOI:10.1088/0026-1394/52/5/S263

[17] Lipinsky L, Szmyrka-Grzebyk A. Proposals for new definition of the kelvin. Metrology and Measurement System. 2008;**15**(2):227-234

[18] Hohmann M, Breitkreutz P, Schalles M, Fröhlich T. Calibration of heat flux sensors with small heat fluxes. In: Proceedings of the 58 Internationales Wissenschaftliches Kolloquium: "In Shaping the Future by Engineering". Ilmenau, Germany: Technische Universität; 08-12 Sept. 2014. p. 29

[19] Lindeman M. Microcalorimetry and transition-edge sensor. [Thesis UCRL-LR-142199]; US Department of Energy, Laurence Liverpool National Laboratory; 2000

[20] Yatsyshyn S, et al. Yatsyshyn S, Stadnyk B, editors. Pat. UA № 115601. The method of receiving the temperature quantum on the basis of fundamental constants of the matter and creation of the temperature standard for its realization; 2017 (In Ukr.)

[21] Giesbers A, Rietveld G, Houtzager E, et al. Quantum resistance metrology in graphene. Applied Physics Letters. 2008; **93**:222109-1-3. DOI: 10.1063/1.3043426

[22] A Practical Josephson Voltage Standard at One Volt. Available from: http://www.lee.eng.uerj.br/downloads/graduacao/medidas_eletricasJosephsonJunction.pdf

[23] Schneider B, Etaki S, van der Zant H, Steele G. Coupling carbon nanotube mechanics to a superconducting circuit. Scientific Reports. 2012;**2**:599

[24] Novoselov K et al. Room-temperature quantum hall effect in graphene. Science. 2007;**315**(5817):1379

[25] Sahoo R, Mishra R. Simulations of carbon nanotube field effect transistors. International Journal of Electronic Engineering Research. 2009;**1**(2):117-125

[26] The NIST Reference on Constants, Units, and Uncertainty, CODATA Internationally Recommended 2014 Values on Fundamental Physical Constants. Available from: http://physics.nist.gov/cuu/Constants/index.html

[27] Stadnyk B, Yatsyshyn S. Metrological array of cyber-physical systems. Part 15. Approach to the creation of temperature standard on the basis of fundamental physical constants. Sensors and Transducers. 2016;**199**(4):62-66

[28] Yatsyshyn S, at al. Yatsyshyn S, Stadnyk B, editors. Cyber-physical systems. Metrological Issues. Barcelona: IFSA, International Frequency Sensor Association; 2016. p. 336

[29] Ouyang Y, Guo J. Heat dissipation in carbon nanotube transistors. Applied Physics Letters. 2006;**89**(18):183122. DOI: 10.1063/1.2382734

[30] Luste O, Kuz' R. Computer control of Eddy thermoelectric current. Thermoelectricity. 2004;**2**:11-19

[31] Stadnyk B, Yatsyshyn S. Quantum standard of temperature and possible thermoelectric studies on its basis. Journal of Thermoelectricity. 2017;**2**: 84-96

[32] AL. Chapt 13. William Thomson (Lord Kelvin) and thermoelectricity. In: Collins M, Dougal R, Koenig C, Ruddock I, editors. Kelvin, Thermodynamics and the Natural World. WIT Press; 2015. pp. 337-362

[33] Anatychuk L. Thermoelectricity. In: Thermoelectric Convertors of Energy. Vol. 2. Kyiv-Chernivtsi: Institute of Thermoelectricity; 2003

[34] Baranskii P, Gaidar G. Theory of anisotropy of electron phonon drag thermo EMF in n-Ge. Journal of Thermoelectricity. 2012;**2**:28-37

[35] Yatsyshyn S, Stadnyk B, Ya L. Research in nanothermometry. Part 1. Temperature of micro- and nanosized objects. Sensors and Transducers. 2012; **140**(5):1-7

[36] Penga X, Zhoua L, Lib X, Taob X, Xua G. Strain study of gold nanomaterials as HR-TEM calibration standard. Elsevier, Micron. 2015;**79**: 46-52

[37] Elastic strain engineering for unprecedented materials properties. In: MRS Bulletin. Li J, Shan Z, Ma E. Vol. 39 (2). 2014: p. 56. Available from: http://www.mrs.org/bulletin

[38] Goldsmid H. Porous thermoelectric materials. Materials. 2009;**2**:903-910. DOI: 10.3390/ma2030903

[39] Kuznetsov VL. Functionally Graded Materials for Thermoelectric Applications. In: Rowe DM (Ed.). Thermoelectrics Handbook: Macro to Nano (1st ed.). CRC Press; 2006. DOI: 10.1201/9781420038903

[40] Sweidan F, JinRyu H. One-step functionally graded materials fabrication using ultra-large temperature gradients obtained through finite element analysis of field-assisted sintering technique. Materials and Design. 2020;**192**:108714, Elsevier. DOI: 10.1016/j.matdes.2020.1087

[41] Yatsyshyn S, Stadnyk B, Melnyk K, Skoropad P, Baitsar R. Nanothermodynamics and nanometrology. In: Cyber-Physical Systems and Metrology 4.0. Barcelona: IFSA Publishing; 2021. pp. 105-157

[42] Ivanova A, Fuksov V, Gerasimov S, Pohodun A. Evolution of the inner liquid–solid interface during metal freezing. International Journal of Thermophysics. 2017;**38**:2. DOI: 10.1007/s10765-016-2168-4

[43] Bobalo Y, Kolodiy Z, Yatsyshyn S, Stadnyk B. Development of noise measurements. Part 3. Passive method of electronic elements quality characterization. Sensors and Transducers. 2013;**152**(5):164-168

[44] Stadnyk B, Yatsyshyn S, Ya. L, Datsiuk M. Development of noise measurements. Part 8. Nanometrology and nanothermodynamics as its scientific basis. Sensors and Transducers. 2013;**160**(12):25-34

[45] Stadnyk B, Yatsyshyn S, Seheda O. Research in nanothermometry. Part 6: Metrology of Raman thermometer with universal calibration artifacts. Sensors and Transducers. 2012;**142**(7):1-9

[46] Dreyfus PA, Psarommatis F, May G, Kiritsis D. Virtual metrology as an approach for product quality estimation in industry 4.0: A systematic review and integrative conceptual framework. International Journal of Production Research. 2022;**60**(2):742-776. DOI: 10.1080/00207543.2021.1976433

[47] Jun S, Kochan O, Kochan R. Thermocouples with built-in self-testing. International Journal of Thermophysics. 2016;**37**(4):1-9

[48] Kochan O, Kochan R, Bojko O, Chyrka M. Temperature measurement system based on thermocouple with controlled temperature field. In: Proceedings of Fourth IEEE Workshop on Intelligent Data Acquisition and Advanced Computing Systems: Technology and Applications. IEEE; 2007. pp. 47-50