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EFFECT OF STRUCTURE DEFECTS ON THE LATTICE THERMAL CONDUCTIVITY OF *Zn-Cd-Sb* THERMOELECTRIC MATERIALS

The paper is concerned with the effect of crystal structure defects, such as screw and edge dislocations, packing defects and grain boundaries on the lattice thermal conductivity of Zn-Cd-Sb system. Calculations are performed with regard to phonon-phonon scattering due to normal and umplapp processes, as well as phonon scattering by the above defects. Both sound velocity anisotropy and the Gruneisen tensor anisotropy are taken into account. To calculate phonon relaxation time, an approximation is used wherein this time, though anisotropic, depends on phonon frequency as a whole, rather than on its quasi-momentum components taken separately. The results of calculations show that at attainable densities, only screw and edge dislocations can have a tangible effect on the lattice thermal conductivity of single-crystal thermoelectric materials based on Zn-Cd-Sb in the temperature range of relevance for practical applications. In so doing, it was established that according to increase in phonon scattering efficiency, and, hence, the degree of its effect on the lattice thermal conductivity, the above defects are arranged in the following order: grain boundaries, screw dislocations, packing defects, edge dislocations. Bibl. 11, Fig. 3.
Key words: lattice thermal conductivity, phonon scattering, normal processes, umklapp processes, crystal structure defects, defect density, grain boundaries, screw dislocations, packing defects, edge dislocations.

Introduction

Reduction of the lattice thermal conductivity of thermoelectric materials is an important reserve for improving their thermoelectric figure of merit. This reserve is essential even for relatively low-resistivity materials, such as bismuth telluride and its alloys [1]. It is even more essential for high-resistivity materials, in particular, *Zn-Cd-Sb* alloys. For the purpose of using it, numerous attempts are made to control structure imperfection of these materials in order to increase the intensity of phonon scattering. In particular, polycrystalline materials are used instead of single-crystal materials. Moreover, the possibilities of creating amorphous or amorphized materials are considered, as well as materials that would be "phonon glasses" and also "electronic crystals" [2]. At the same time, *Zn-Cd-Sb* single-crystal materials are used to fabricate thermocouple and especially anisotropic thermoelements. Because of this, it makes sense to analyze the effect of various crystal structure defects on the lattice thermal conductivity of these materials. Such an analysis is the purpose of this article.

Analytical calculation of the lattice thermal conductivity of rhombic crystals with structure defects and discussion of its results

Said analysis will be performed by the example of component κ_{11} of this thermal conductivity. With regard to the effect of crystal structure defects, its analytical expression is given by:

$$\kappa_{11} = \frac{\rho h}{64\gamma_{11}^2\theta^3 k_B T_D^2}\int_0^1 \frac{x^4 \exp(x/\theta)dx}{\left(\exp(x/\theta)-1\right)^2}\left[\frac{\left(v_{1l}\right)^{8/3}\left(v_{2l}v_{3l}\right)^{2/3}}{x^4+\mu_{11}x+\Delta_{11dl}}+\frac{2\left(v_{1t}\right)^{8/3}\left(v_{2t}v_{3t}\right)^{2/3}}{x\left(3.125\theta^3+\mu_{11}\right)+\Delta_{11dt}}\right]. \quad (1)$$

In these formulae, ρ – single-crystal material density, v_1, v_2, v_3 – sound velocities along principal crystallographic directions, γ_{11} – component of the Gruneisen tensor, μ_{11} – component of umklapp coefficients tensor, T_D – caloric Debye temperature, $\theta = T / T_D$, Δ_{11dl} and Δ_{11dt} – relative contributions to probabilities of phonon scattering on structure defects, k_B – Boltzmann constant, h – Planck constant. Indexes *l, t* refer to longitudinal and transverse legs, components of the Gruneisen parameter tensors and umklapp coefficients are considered to be independent of phonon polarization.

We will now determine the values Δ_{dl} and Δ_{dt} for different types of defects, taking into account model expression [3] for relaxation time at normal phonon-phonon scattering processes, as well as model expressions [4] for the intensity of phonon scattering on some basic defects of crystalline structure. In doing so, as long as the above expressions are given for the case of a simple cubic lattice with one atom in a unit cell, we will generalize them, having conventionally substituted real unit cells of zinc and cadmium antimonides, as well as *Zn-Cd-Sb* ternary alloys, by equal-sized cubes. Performing this substitution, we will neglect the small difference between true angles of the unit cell and the right angles.

For instance, when phonons are scattered at grain boundaries, Δ_{11dl} and Δ_{11dt} are determined as follows:

$$\Delta_{11dl} = \frac{9\cdot 10^{-2}\rho\left(v_{1l}v_{2l}v_{3l}\right)^2 h^4 L}{256\pi^3 k_B T\left(k_B T_D\right)^4 \sqrt[3]{a_1 a_2 a_3}}, \quad (2)$$

$$\Delta_{11dt} = \frac{9\cdot 10^{-2}\rho\left(v_{1t}v_{2t}v_{3t}\right)^2 h^4 L}{256\pi^3 k_B T\left(k_B T_D\right)^4 \sqrt[3]{a_1 a_2 a_3}}. \quad (3)$$

In so doing, a_1, a_2, a_3 – lattice constants, L – dimensionless parameter characterizing the density of grain boundaries:

$$L = N_{gb}\sqrt[3]{a_1 a_2 a_3}, \quad (4)$$

where N_{gb} – the number of grain boundaries per unit length.

When phonons are scattered by screw dislocations, Δ_{11dl} and Δ_{11dt} are determined as follows:

$$\Delta_{11dl} = \frac{9\cdot 10^{-2}\rho h^3\left(v_{1l}v_{2l}v_{3l}\right)^{5/3} L}{64\pi^2 k_B T\left(k_B T_D\right)^3}x, \quad (5)$$

$$\Delta_{11dt} = \frac{9\cdot 10^{-2}\rho h^3\left(v_{1t}v_{2t}v_{3t}\right)^{5/3} L}{64\pi^2 k_B T\left(k_B T_D\right)^3}x. \quad (6)$$

In this case, the dimensionless parameter L characterizing dislocation density is found as:

$$L = N_{scr} b^2, \quad (7)$$

where N_{scr} – the number of screw dislocations per unit area, b – the Burgers vector.

When phonons are scattered by packing defects, Δ_{11dl} and Δ_{11dt} are determined as follows:

$$\Delta_{11dl} = \frac{0.21\rho h^2 \left(v_{1l}v_{2l}v_{3l}\right)^{4/3} \sqrt[3]{a_1a_2a_3}L}{64\pi k_B T \left(k_B T_D\right)^2} x^2 , \tag{8}$$

$$\Delta_{11dt} = \frac{0.21\rho h^2 \left(v_{1t}v_{2t}v_{3t}\right)^{4/3} \sqrt[3]{a_1a_2a_3}L}{64\pi k_B T \left(k_B T_D\right)^2} x^2 . \tag{9}$$

In this case, the dimensionless parameter L characterizing the density of packing defects is found as:

$$L = N_{sf} \sqrt[3]{a_1a_2a_3} , \tag{10}$$

where N_{sf} – the number of packing defects per unit length.

When phonons are scattered by edge dislocations, Δ_{11dl} and Δ_{11dt} are determined as follows:

$$\Delta_{11dl} = \frac{3\rho h v_{1l}v_{2l}v_{3l}\left(a_1a_2a_3\right)^{2/3} L}{32\gamma_{11}^2 k_B^2 T T_D} x^3 , \tag{12}$$

$$\Delta_{11dt} = \frac{3\rho h v_{1t}v_{2t}v_{3t}\left(a_1a_2a_3\right)^{2/3} L}{32\gamma_{11}^2 k_B^2 T T_D} x^3 . \tag{13}$$

In this case, the dimensional parameter L characterizing the density of edge dislocations is found as:

$$L = N_{ed}\left(a_1a_2a_3\right)^{2/3} , \tag{14}$$

where N_{ed} – the density of edge dislocations per unit length.

Dependences of component κ_{l11} on parameter L for various types of defects in *ZnSb* crystals at 293 K, *CdSb* crystals at 293 K and $Zn_{0.125}Cd_{0.875}Sb$ crystals at 300 K are shown in Figs. 1,2, respectively.

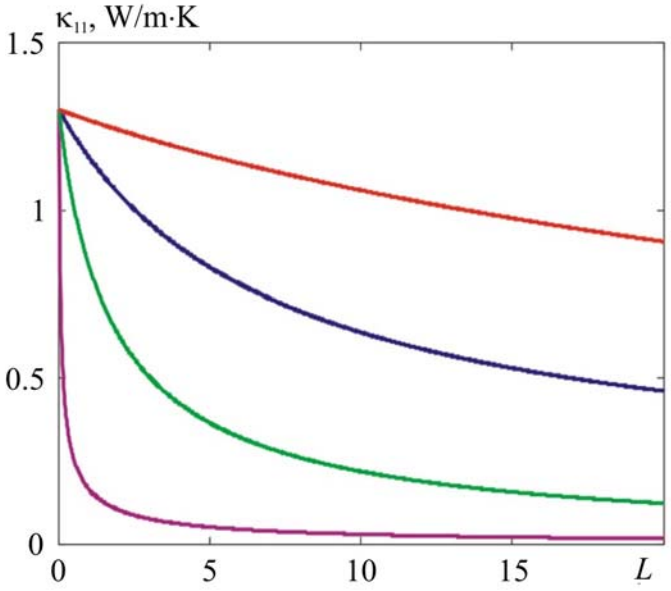

Fig.1. Dependence of the lattice thermal conductivity of ZnSb at 293K on parameter L at phonon scattering :1) at grain boundaries; 2) by screw dislocations; 3) by packing defects; 4) by edge dislocations.

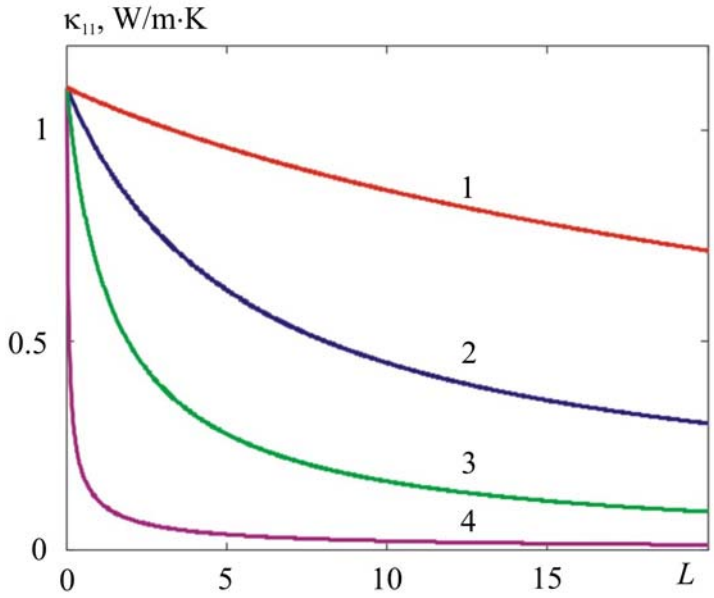

Fig.2. Dependence of the lattice thermal conductivity of $Zn_{0.125}$ $Cd_{0.875}$ Sb at 300K on parameter L at phonon scattering:1) at grain boundaries; 2) by screw dislocations; 3) by packing defects; 4) by edge dislocations

Numerical data for calculations are taken from [5 – 8]. From the figures it is seen that in all cases the lattice thermal conductivity of *Zn-Cd-Sb* thermoelectric materials is least effectively reduced by phonon scattering at grain boundaries, and most effectively – by edge dislocations. But in order for this decrease to be significant at room or higher temperatures, the defect densities must be very high. Thus, for instance, to reduce the lattice thermal conductivity by half as compared with a perfect single crystal due to scattering at the grain boundaries, it is necessary that their density exceed $6.63 \cdot 10^{10}$ m^{-1}. But such a high density of grain boundaries is impossible even in a polycrystalline material with grains whose dimensions are measured by nanometers. Nevertheless, in such materials the effective decrease in the lattice thermal conductivity is due to the comparability of the mean free paths of phonons with grain sizes. To halve the lattice thermal conductivity due to additional phonon scattering by screw dislocations, it is necessary that at their density equal, say, to 10^{15} m^{-2}, the corresponding Burgers vectors be of the order of 135 crystal lattice constants. This Burgers vector will be realized, if we take into account that the ratio of the elasticity limits of *Zn-Cd-Sb* alloys to their shear moduli is much less than 1/135 [9]. Thus, phonon scattering by screw dislocations can be an effective mechanism for reducing the lattice thermal conductivity of cadmium and zinc antimonides.

Therefore, the effective reduction of the lattice thermal conductivity of thermoelectric materials due to the additional phonon scattering by packing defects is impossible for the same reasons as due to their scattering at grain boundaries (if dimensional effects are not taken into account).

Finally, in order to halve the lattice thermal conductivity due to additional scattering by edge dislocations, it is necessary that their density at the lowest possible value of the Burgers vector, which in the framework of the approach used is $\sqrt[3]{a_1 a_2 a_3}$, exceed $1.44 \cdot 10^{17}$ m^{-2}. On the one hand, the largest dislocation density detectable by the electron microscope is approximately 10^{16} m^{-2} [9]. On the other hand, the value of the Burgers vector can substantially exceed and, as a rule, exceeds its lowest possible value. And the density of edge dislocations necessary for effective reduction of the lattice thermal conductivity, other things being equal, decreases in inverse proportion to the square of the length of the Burgers vector, and, therefore, is quite attainable. Thus, additional scattering of phonons

by edge dislocations can also serve as an effective mechanism for lowering the lattice thermal conductivity of thermoelectric materials based on *Zn-Cd-Sb*.

It should be noted, however, that if the change in the lattice thermal conductivity of $Zn_xCd_{1-x}Sb$ alloys due to a change in their composition could be explained only by the accumulation or "healing" of structural defects, this thermal conductivity would have to be a monotonic function of x, varying from the thermal conductivity of *CdSb* at $x = 0$ to the thermal conductivity of *ZnSb* at $x = 1$. However, the experimental data [10, 11] indicate that such monotony does not occur. Thus, for instance, in [10] it is shown that alloys have the lowest thermal conductivity at room temperature, for which the values of x are equal to 0.35 and 0.45 (the thermal conductivities of these alloys are 1 and 1.2 W/(m·K), respectively). In this case, the electrical conductivities of these alloys are by no means the least possible. Therefore, a decisive role in the formation of a relationship between the thermal conductivity and the composition of these alloys is played by the lattice component of thermal conductivity, especially the part which is caused by phonon-phonon scattering with umklapp. The data of [10] are to a certain extent confirmed by the data of [11]. In this paper it is shown that alloys of composition $Zn_{0.4}Cd_{0.6}Sb$ and $Zn_{0.6}Cd_{0.4}Sb$ possess the lowest thermal conductivity among the five investigated alloys. Their thermal conductivity is the same, and approximately equal to 0.712 W/(m·K), which is 28 % lower than that of zinc and cadmium antimonides. Therefore, a change in the thermal conductivity of $Zn_xCd_{1-x}Sb$ alloys with a change in their compositions is mainly due to a change in the unit cell of crystal lattice leading to a variation in the values of tensor components of umklapp coefficients. The discrepancies between the data of [10] and [11] can be explained by the fact that in the former case the materials studied were polycrystalline substances obtained by casting into an earth mold, and in the latter case - single crystals grown by the zone melting method with the use of zone levelling. In the former case, owing to the higher concentration of charge carriers, the electrical conductivity and, consequently, the total thermal conductivity of the alloys turned out to be larger, and the fraction of the lattice component in it – smaller. Therefore, in the latter case the symmetry of the values of tensor components of umklapp coefficients with respect to $Zn_{0.5}Cd_{0.5}Sb$ composition was more clearly manifested.

Conclusion

1. Analytical expressions are obtained that describe the effect of structure defects on the lattice thermal conductivity of *Zn-Cd-Sb* alloys.
2. It is established that, at attainable densities, structure defects that can significantly reduce the lattice thermal conductivity of *Zn-Cd-Sb* alloys are edge and screw dislocations. At the same time, the effective reduction of the lattice thermal conductivity in going from single crystals to polycrystalline thermoelectric materials is possible mainly due to size effects caused by the comparability of the crystallite sizes with the phonon mean free paths in a single crystal.
3. It is shown that the behavior of the thermal conductivity of *Zn-Cd-Sb* single-crystal materials, depending on the composition in the temperature range of relevance for practical applications, is due not to the accumulation or "healing" of structural defects, but to the restructuring of the crystal lattice, which leads to significant changes in the values of tensor components of umklapp coefficients.

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ВПЛИВ ДЕФЕКТІВ СТРУКТУРИ НА ГРАТКОВУ ТЕПЛОПРОВІДНІСТЬ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ *Zn-Cd-Sb*

Розглянуто вплив дефектів кристалічної структури, таких, як гвинтові та крайові дислокації, дефекти впакування й межі зерен на граткову теплопровідність системи Zn-Cd-Sb. У процесі розрахунків враховано розсіювання фононів одного на одному, обумовлене як нормальними процесами, так і процесами перекидання, а також розсіювання фононів на зазначених дефектах. Враховані як анізотропія швидкості звуку, так і анізотропія тензору Грюнайзена. Для розрахунків часу релаксації фононів використовується наближення, у якому цей час хоча й анизотропно, але залежить від частоти фонона в цілому, а не від складових його квазіімпульсу окремо. Результати розрахунків свідчать про те, що за досяжних щільностей відчутний вплив на граткову теплопровідність монокристалічних термоелектричних матеріалів на основі Zn-Cd-Sb в актуальній для практичного застосування області температур можуть справляти лише гвинтові й крайові дислокації. При цьому встановлено, що за зростанням ефективності розсіювання фононів, і, отже, ступеня впливу на граткову теплопровідність, згадані вище дефекти розташовуються в наступному порядку: межі зерен, гвинтові дислокації, дефекти впакування, крайові дислокації. Бібл. 11, рис. 3.

Ключові слова: граткова теплопровідність, розсіювання фононів, нормальні процеси, процеси перекидання, дефекти кристалічної структури, щільність дефектів, межі зерен, гвинтові дислокації, дефекти впакування, крайові дислокації.

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ВЛИЯНИЕ ДЕФЕКТОВ СТРУКТУРЫ НА РЕШЕТОЧНУЮ ТЕПЛОПРОВОДНОСТЬ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ НА ОСНОВЕ Zn-Cd-Sb

Рассмотрено влияние дефектов кристаллической структуры, таких как винтовые и краевые дислокации, дефекты упаковки и границы зерен на решеточную теплопроводность системы Zn-Cd-Sb. В процессе расчетов учтено рассеяние фононов друг на друге, обусловленное как нормальными процессами, так и процессами переброса, а также рассеяние фононов на указанных дефектах. Учтены как анизотропия скорости звука, так и анизотропия тензора Грюнайзена. Для расчета времени релаксации фононов используется приближение, в котором это время хотя и анизотропно, но зависит от частоты фонона в целом, а не от составляющих его квазиимпульса по отдельности. Результаты расчетов свидетельствуют о том, что при достижимых плотностях ощутимое влияние на решеточную теплопроводность монокристаллических термоэлектрических материалов на основе Zn-Cd-Sb в актуальной для практического применения области температур могут оказать только винтовые и краевые дислокации. При этом установлено, что по возрастанию эффективности рассеяния фононов, и, следовательно, степени влияния на решеточную теплопроводность, упомянутые выше дефекты располагаются в следующем порядке: границы зерен, винтовые дислокации, дефекты упаковки, краевые дислокации. Библ. 11, рис. 3.

Ключевые слова: решеточная теплопроводность, рассеяние фононов, нормальные процессы, процессы переброса, дефекты кристаллической структуры, плотность дефектов, границы зерен, винтовые дислокации, дефекты упаковки, краевые дислокации, плотность дефектов.

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MODELS OF CHEMICAL BONDING IN Bi_2Te_3

A complex approach has been developed for calculating the electronic structure parameters of hybrid orbitals corresponding to nonequivalent interatomic distances in low-symmetry bismuth telluride crystals. On the basis of quantum mechanical and quantum statistical approaches, calculations of the Fermi energy, effective charges, effective radii, as well as redistribution of electron density and dissociation energy of nonequivalent hybrid orbitals (NHO) are performed. The obtained results can be used in the development of technological modes for the production of new materials based on bismuth tellurides, which have high sensitivity, stability, and characteristics identity, especially necessary for thermal converters of metrological application. Bibl. 11, Fig. 3, Table 1.
Key words: chemical bond, force and energy characteristics, Fermi energy, effective charges, effective radii, dissociation energy, nonequivalent hybrid orbitals.

Introduction

Bismuth telluride is considered to be the best investigated of thermoelectric materials.

It has high thermoelectric parameters; due to doping, it can be obtained both – and p-type. Moreover, bismuth telluride is easiest to prepare in the form of sufficiently perfect single crystals. However, despite the multi-year studies of its physicochemical properties, a number of key points have not been clarified yet. The issues of chemical bonding remain open, and the theoretical comprehension of numerous empirical dependences is connected with the revision of the system of established views on the problem of interatomic interaction, i.e. with the emergence of qualitatively new, non-standard concepts, which are not always the result of the development of existing theories, and often deny some of them [1].

In this connection, predicting the physicochemical properties of materials based on bismuth and tellurium by theoretical analysis of their electronic structure is a relevant task of thermoelectric materials science.

The need for complex studies is caused by the fact that various phenomenological approaches are based on fitting a certain interpretation model to the results of experimental studies and do not allow one to unite numerous empirical relationships with the aim of searching for technological modes for obtaining materials with predicted properties.

Therefore, in the present paper, the task was set as follows: on the basis of quantum mechanical and quantum statistical approaches, to develop a complex method for calculating the parameters of the electronic structure of the materials under investigation in order to further apply the results obtained in solving technological problems.

Quantum statistic models of the electronic structure of *Bi* and *Te*

To solve this problem, it is necessary first of all to establish the correlation between the energy parameters of the initial components (bismuth and tellurium) and the energy of formation (destruction) of chemical bonds in bismuth telluride crystals. To do this, in the approximation of the electron gas model in a metal, it was necessary to find the maximum energy E_F of electron when the electron gas in question is in the ground state.

This model of the atom is based on two ideas: one borrowed from quantum mechanics, the other from quantum statistics.

We will start from the quantum mechanical part of our problem. According to standard initial assumptions in quantum mechanics, the energy of electrons in a metal having the shape of a cube of size L is determined by formula [2]:

$$E = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right), \tag{1}$$

where n_1, n_2, n_3 natural integers.

Since in the examined metal we must distribute a very large number of electrons, it is necessary to use the methods of quantum statistics. Let n be the distance from the origin to the point, then

$$n_1^2 + n_2^2 + n_3^2 = n^2, \tag{2}$$

and we can write that the number of points of the first octant, with integer-valued coordinates enclosed between spheres of radius n and $n + dn$, is:

$$\frac{1}{8} 4\pi n^2 dn = \frac{\pi}{2} n^2 dn \tag{3}$$

"Placing" in each of these points two electrons with the opposite spin orientation (by virtue of the Pauli principle), we get that between n and $n + dn$ there are $\pi n2dn$ electrons. Considering further that the energy (1) depends only on n can be written:

$$E = \frac{\hbar^2 \pi^2}{2mL^2} n^2, \quad dE = \frac{\hbar^2 \pi^2}{mL^2} ndn \tag{4}$$

The number of electrons whose energies are between the values of E and $E + dE$, we find the formula:

$$dN = \pi n^2 dn = \sqrt{2m}\, \frac{mL^3}{\pi^2 \hbar^3} \sqrt{E}\, dE \tag{5}$$

The maximum energy of electron, when the electron gas is in the ground state, is determined by the total number of electrons N:

$$N = \sqrt{2m}\, \frac{mL^3}{\pi^2 \hbar^3} \int_0^{E_F} \sqrt{E}\; dE \tag{6}$$

If we introduce into consideration the density

$$W = \frac{N}{L^3} \tag{7}$$

then we obtain formulas that do not include the volume of the metal under consideration:

$$W = \frac{1}{3\pi^2}\left(\frac{2mE_F}{\hbar^2}\right)^{3/2} \tag{8}$$

or

$$E_F = \frac{\hbar^2}{2m}\left(3\pi^2 W\right)^{2/3} \tag{9}$$

As long as $W = \rho / m$, where m is the mass of one atom of metal under consideration, formula (8) yields numerical values of maximum electron energy, which is called the Fermi energy of electron gas.

With the help of (8) the Fermi energy of bismuth and tellurium was calculated,

$$E_F^{Bi} = 2.71241\,\text{eV}, \tag{10}$$

$$E_F^{Te} = 3.47835\,\text{eV} \tag{11}$$

and were further used in the consideration of processes of formation of chemical bonds in bismuth telluride crystals, analysis of the diagram of states, phase transitions and polymorphous transformations.

Quantum chemical models of the electronic structure of Bi_2Te_3

The present paper contributes to further studies of quantum chemical models started in [3] and their application to solving the problems of formation of atomic interaction in A^{V}–B^{VI} crystals. According to [4], the dependences $tg\alpha = \Delta \lg R_u / \Delta n$ turned out to be the most useful when searching for the solution of the problem of the relationship of effective radii Ru with the number of electrons n on the orbitals of atoms. Interrelation of the slopes of rectilinear dependences of logarithm R_u on n excludes the possibility of arbitrary change in the composed quantities. A good agreement of the complex of experimental data is given by the system of equations [4]:

$$\lg R_{uA}^{x} = \lg R_{uA}^{0} - x tg\alpha_A, \tag{12}$$

$$\lg R_{uB}^{-x} = \lg R_{uB}^{0} + x tg\alpha_B, \tag{13}$$

$$\alpha_1 = R_{uA}^{x} + R_{uB}^{-x} \tag{14}$$

where $R^{0}_{uA(B)}$ is the radius of atom in the unexcited state, and x is valence. The system of equations (12 – 14) is written on the assumption that the absolute values of the charges of the interacting atoms are equal. In this case, the complex process of rearranging the electronic shells of interacting atoms is reduced to the transfer of electrons from the orbitals of one to the orbital of the other. Therefore, additional criteria are needed that allow the crystal chemical system of equations (12 – 14) to be translated into the language of quantum chemistry. According to [3], for this purpose it is necessary to analyze the dependence of the interatomic distances on the effective charges: $d_1 = f(z_{ef})$. The change in the z_{ef} values of atoms should be done in such a way as to assure the equality of density of states at the boundaries of corresponding ions: removal of electrons ($+\Delta q$) or their localization ($-\Delta q$) in this bond direction equally changes the values of charges that this pair of atoms had at $d_1 = d_{min}$, $z_{efA(B)} = z_{minA(B)} + \Delta q/2$.

With this approach, the system (12) – (14) takes on the form:

$$d_1 = R_{uA}^{zA} + R_{uB}^{zB} \tag{15}$$

$$\lg R_{uA}^{zA} = \lg R_{uA}^{0} - \left(z_{\min A} + \frac{\Delta q}{2} \right) tg\alpha_A \tag{16}$$

$$\lg R_{uB}^{zB} = \lg R_{uB}^{0} - \left(z_{\min B} + \frac{\Delta q}{2} \right) tg\alpha_B \tag{17}$$

It is noteworthy that the function $d_1 = f(z_{ef})$ in the approximation ($x_A = -x_B$) is correct only for $d_1 = d_{min}$, but it is sufficient for the system (15 – 17) to be solved at known d_1. This is the basis for the use of nonequivalent hybrid orbitals (NHO) to describe the interatomic interaction in the present paper.

Quantum mechanical models of interatomic interaction and dissociation energies of NHO

To derive semi-empirical dependences that can be used to calculate bond energies between homogeneous atoms in dimensional molecular and crystalline groups is one of important problems in the theory of materials science. The use of NHO to study the interaction in compounds that differ in stoichiometry, structure, chemical bond type, and physical and chemical properties allows us to proceed to the solution of prediction problems in materials science. Taking into account the above remarks, in this paper it became possible to describe the dependence of NHO bond energies on the lengths and electron configurations of interacting atoms in a single general expression:

$$D_{A-B}^{(i)} = \frac{C_1 (R_{uA}^{0} + R_{uB}^{0})}{(tg\alpha_A + tg\alpha_B)} \left(\frac{C_2 d_i}{d_i^2 - R_{uA}^{(i)} R_{uB}^{(i)}} - \frac{1}{d_i} \right), \tag{18}$$

where R^0_{uA}, d_i, $tg\alpha_A$ are coefficients of equations (12 – 14); C_1 is coefficient that reflects the relation between dimensional and energy characteristics and has energy dimension (eV); C_2 reflects the type of crystalline structure and quantitative relation between coefficients $tg\alpha_{Bi}$, $tg\alpha_{Te}$ and quantities (R_{uBi}/R_{uTe}). In contrast to [3] and [4], in the present paper the construction of formula (18) is carried out taking into account the fact that the similarity numbers must be dimensionless quantities. Therefore, the coefficient C_2 in formula (18) is a dimensionless quantity and, in the solution of the self-consistent variational problem, is chosen in the first approximation to be equal to unity.

Effective charges and effective radii of atoms of the nonequivalent chemical bonds in Bi_2Te_3 crystals

The chemical bonding of Bi_2Te_3 was widely discussed in the literature [1]. But despite this, until now its nature cannot be considered definitively established.

Crystallographic data on Bi_2Te_3 compound were first published by Lange [5]. He described the structure of Bi_2Te_3 as rhombohedral with a spatial group $D^5_{3d}(R_{3m})$ and parameters $a_R = 10.43$ Å, $\alpha_R = 24°8'$.

More accurate measurements on the well annealed powders of stoichiometric composition were performed in [6]. In so doing, one should note the work [7], where it was shown that in the non-annealed powders the intensity of some reflexes is weakened, and some of them even disappear. To obtain reliable data, annealing at $T \approx 550$ °C is necessary.

One should also pay attention to the *Bi-Te* diagram of state [8]. This is a typical diagram of systems forming a chemical compound. The lines of the liquidus and solidus intersect at the maximum point (congruent point, at which the compositions of the melt and the solid phase coincide). Diagrams of this type have two features that are important for the technology.

One of them is that the initial components can dissolve in the chemical compound, and another feature of the diagrams considered is the displacement of the maximum less than the liquidus with respect

to the stoichiometric composition. In this case, during crystallization of the stoichiometric melt, the solid phase is enriched by a component toward which the maximum shifts. A solid phase of the stoichiometric composition can be obtained by crystallization under equilibrium conditions of a melt with an excess of another component or by rapid cooling of the stoichiometric melt and homogenizing annealing.

How can we explain the fact that the initial components can dissolve in a chemical compound and what is the role of annealing in technological processes from the standpoint of available information on the chemical bond?

According to the available information [1], the Bi_2Te_3 structure can be represented as a set of complex layers - quintets perpendicular to the symmetry axis of the third order. Due to the presence of a layered structure, Bi_2Te_3 easily accumulates along the (0001) planes in a hexagonal cell. The Te atoms in the Bi_2Te_3 lattice have two essentially different places $Te^{(1)}$ and $Te^{(2)}$. *Bi*, accordingly, has three $Te^{(2)}$ and three $Te^{(1)}$ neighbours. The lengths of bonds between them are given in the table.

Unfortunately, there is still no experimental data on the distribution of electrons over bonds within the quintet.

To solve the problem, it was necessary to first determine the maximum energy of the electron gas in the ground state (the Fermi energy) and compare it with the energy of thermal motion (kT = 0.048 eV at 500 K).Therefore, thermal excitation can only slightly change the distribution of electrons over energies.

Table

Effective charges, effective radii and dissociation energies of nonequivalent hybrid orbitals in Bi_2Te_3 crystals

φ_j / $R_u, \Delta q, D_j$	φ_1 (Te_1-Te_2)	φ_2 (*Bi*-*Bi*)	φ_3 (*Bi*- Te_1)	φ_4 (*Bi*- Te_2)	φ_5 (*Bi*-*Bi*)	φ_6 (Te_1-Te_1)
$d_j^{\exp}$(Å)	–	–	3.12	3.22	–	3.57
d_j^{theor}(Å)	2.88	3.1	3.12	3.22	3.5	3.57
R_U^{Bi}(Å)	–	1.55	1.847	1.906	1.75	–
R_U^{Te}(Å)	1.439	–	1.273	1.314	–	1.785
R_U^{Bi} / R_U^{Te}	–	–	1.4509	1.4505	–	–
Δq bond φ_j	0.49	0.32	0.2	0.05	-0.45	-0.625
D_j (eV)	2.393	2.577	2.27	2.198	2.283	1.929

At the same time, it can affect considerably the mode of motion of individual NHO: with a rise in temperature, there is increase in the amplitude of vibrations of atoms along NHO, and this, in turn, leads to the appearance of precession-rotational motion of individual NHO as a whole and results both in polymorphous transformations and phase transitions.

In connection with this, the next stage of the research in this paper was the calculation of the interatomic distances in Bi_2Te_3 for the nearest neighbors. Using the technique developed in [9 – 10] and

applied in [11], in this paper we calculated the interatomic distances $d^{(1)}_{Te_1-Te_2}$, $d^{(2)}(Bi-Bi)$, $d^{(3)}(Bi-Te^{(1)})$, $d^{(4)}(Bi-Te^{(2)})$, $d^{(5)}(Bi-Bi)$, $d^{(6)}(Te^{(1)}-Te^{(1)})$.

Calculation data are also given in the table (alongside with the experimental data [1]).

To establish the dependence of the effective charges on the interatomic distances, it was necessary to write a system of equations (15) – (17) for each i-th NHO, and then, by solving the inverse problem by the already known interatomic distances $d_i (1 \le i \le 6)$, to find R_{uBi}, R_{uTe}, Δq.

Calculation data are given in the table. The necessary R_x, $\mathrm{tg}\alpha_{Bi}$ and $\mathrm{tg}\alpha_{Te}$ for generation of equation systems (15) – (17) were found by the procedure [4]. As a result of the calculations, the following numerical values were obtained: R^o_{Bi} = 1.63 Å; R^o_{Te} = 1.57 Å; $\mathrm{tg}\alpha_{Bi}$ = 0.068; $\mathrm{tg}\alpha_{Te}$ = 0.076.

For the purpose of correct using the formalism of NHO method, in this paper we constructed the diagram $d_i = f(x)$/ Fig. 1 shows the dependence of the interatomic distances d_i of $\varphi_i(Bi_x\text{-}Te_{-x})$ bonds (in angstroms) on the effective charges x in the range $4 \le x \le 4$. As follows from the above results, the minimum on this dependence is realized at $d_{\min}$ = 3.2 Å, exceeding the real interatomic distances d_1; d_2; d_3 given in the table. All this necessitated recalculation of the effective charges Δq for each bond.

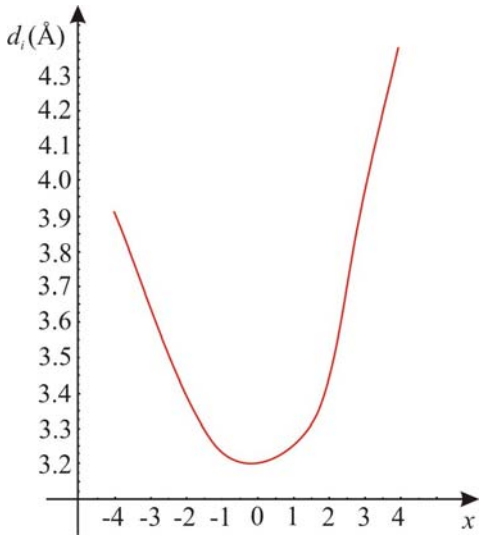

Fig. 1. Dependence of interatomic distances d_i on the effective charges x of BiTe bond $\varphi_i(Bi_xTe_{-x})$

Then, with regard to the above remarks, R_u^{Bi}, R_u^{Te} and Δq were calculated for the nonequivalent hybrid orbitals $1 \le i \le 6$.

Thus, as a result of taking into account the quantum mechanical and quantum statistic interpretation of the empirical material in a uniform quantitative method for calculating the parameters of the electronic structure, in this paper it became possible to describe the dependence of the NHO bond energies on the lengths and electron configurations of Bi_2Te_3 atoms by one general expression. As a result of the calculations, according to (18), the numerical values of the NHO bond energies in Bi_2Te_3 crystals were obtained.

The results of calculations of effective radii R_u^{Bi}, R_u^{Te}, redistribution of electron density Δq_i, dissociation energy D_i are given in the table. With a view to expand the possibilities of using formula (18) for solving the tasks of polymorphous transformations, phase transitions, conditions of thermal treatment of resulting materials, this paper presents the dependences of dissociation energies on the atomic energy characteristics (reflected in coefficient c_1), Fig. 2, and parameters of similarity numbers (reflected in coefficient c_2), Fig. 3.

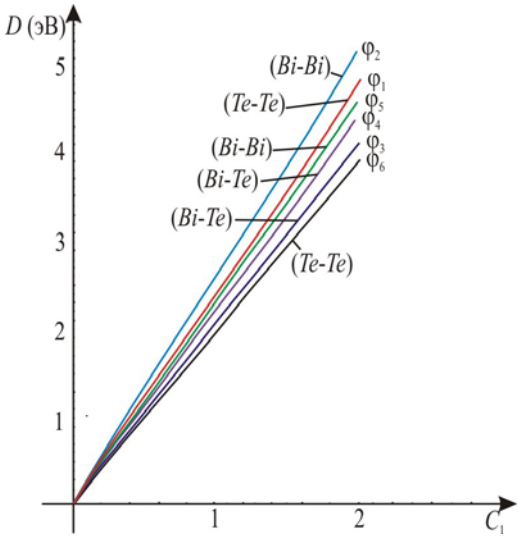

Fig. 2. Dependence of the NHO dissociation energy on the atomic energy characteristics C_1

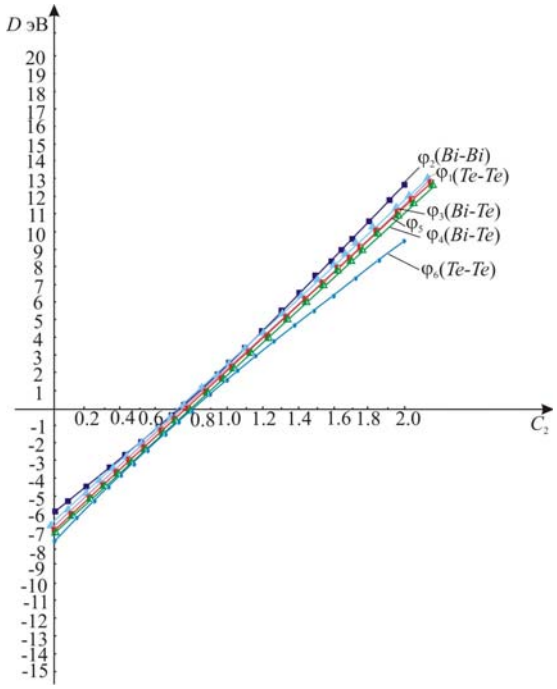

Fig. 3. Dependence of the NHO dissociation energy on parameters of similarity numbers C_2

Analysis of these dependences allows establishing the relationship between the physicochemical properties of the resulting material and the choice of initial components and technological methods for the synthesis of new thermoelectric materials based on bismuth telluride.

Discussion of the results

Analysis of the results obtained showed that the dependences presented in this study can be used not only for calculating the binding energies of individual NHO in Bi_2Te_3 crystals, but also for developing technological modes for the production of new materials of Bi_2Te_3system with a predicted set of properties. The results obtained in this paper agree with the results of studying state diagrams of

stable and metastable equilibrium presented in [1], specify the possibilities of phase transitions and polymorphous transformations in the formation of physico-chemical properties of produced materials.

Conclusion

1. On the basis of a complex approach, a technique has been developed for applying the formalism of nonequivalent hybrid orbitals to calculate the interatomic interaction in Bi_2Te_3 crystals.
2. Calculations were performed of electron density redistribution on NHO, accompanied by electron drift to other directions of interatomic interaction, i.e. it becomes donor ($+\Delta q$) or acceptor ($-\Delta q$).
3. Taking into account the quantum-mechanical and quantum-static interpretation of empirical material, a method was developed and calculations of the dissociation energy of nonequivalent chemical bonds in Bi_2Te_3 crystals were performed.
4. The results obtained in the paper are consistent with the features of *Bi-Te* diagram of states and can be used in the development of technological modes for synthesis of new materials based on Bi_2Te_3.

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МОДЕЛІ ХІМІЧНОГО ЗВ'ЯЗКУ Bi_2Te_3

Розроблено комплексний підхід для розрахунків параметрів електронної будови гібридних орбіталей, що відповідають нееквівалентним міжатомним відстаням у низькосиметричних кристалах телуридів вісмуту. На основі квантовомеханічного й квантовостатистичного підходів проведені розрахунки енергії Фермі, ефективних зарядів, ефективних радіусів, а також перерозподілу електронної густини та енергії дисоціації нееквівалентних гібридних орбіталей (НГО). Отримані результати можуть бути використані при розробці технологічних режимів одержання нових матеріалів на основі телуридів вісмуту, що володіють високою чутливістю, стабільністю та ідентичністю характеристик, особливо необхідних для термоперетворювачів метрологічного призначення. Бібл. 11, Рис. 3, Табл. 1.
Ключові слова: хімічний зв'язок, силові й енергетичні характеристики, енергія Фермі, ефективні заряди, ефективні радіуси, енергія дисоціації, нееквівалентні гібридні орбіталі.

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МОДЕЛИ ХИМИЧЕСКОЙ СВЯЗИ Bi_2Te_3

Разработан комплексный подход для расчетов параметров электронного строения гибридных орбиталей, соответствующих неэквивалентным межатомным расстояниям в низкосимметричных кристаллах теллуридов висмута. На основе квантовомиханического и квантовостатистического подходов проведены расчеты энергии Ферми, эффективных зарядов, эффективных радиусов, а также перераспределения электронной плотности и энергии диссоциации неэквивалентных гибридных орбиталей (НГО). Полученные результаты могут быть использованы при разработке технологических режимов получения новых

материалов на основе теллуридов висмута, обладающих высокой чувствительностью, стабильностью и идентичностью характеристик, особенно необходимых для термопреобразователей метрологического назначения. Библ.11, Рис. 3, Табл. 1.

Ключевые слова: химической связи, силовые и энергетические характеристики, энергия Ферми, эффективные заряды, эффективные радиусы, энергия диссоциации, неэквивалентные гибридные орбитали.

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A NEW d^2/d^0 TYPE TETRAGONAL THERMOELECTRIC MATERIAL *HfSiSb*, A HALF-HEUSLER COMPOUND: A FP-LAPW METHOD

We have studied the electronic and thermoelectric properties of HfSiSb using first principle Density Functional Theory (DFT) within a Full Potential Linearized Augmented Plane Wave method (FP-LAPW). The electronic structure is a key in determining the thermoelectric properties. A most common generalized gradient approximation (GGA) is taken into consideration for electron exchange. The thermoelectric properties like Seebeck coefficient, electronic thermal conductivity and electrical conductivity are calculated. In addition, we have also included a lattice thermal conductivity (κ_p) to obtain the total thermal conductivity. The presence of total thermal conductivity gives us an exact understanding of material thermodynamics and its efficiency (ZT). HfSiSb possesses a tetragonal structure, the thermoelectric parameters are calculated along perpendicular and parallel direction. The low value of lattice thermal conductivity (below 10 W/Km) and sharp variation of ZT in the range (300 – 400) K predicts that this system is a potential thermoelectric material at room temperature. Bible 15, Fig. 5, Table 1.
Key words: band structure, Seebeck coefficient, thermal conductivity.

Introduction

Thermoelectric materials can convert waste heat into electrical power and thus have attracted great attention because it can lead to sustainable energy management [1]. In recent years, several materials have been studied to search for efficient thermoelectric materials. Among these several compounds, some of the compounds that were extensively investigated were Heusler compounds, derivative of HH compound, skutterudites, Zintl compounds, $Ca_3Co_4O_9$ etc. [2 – 5]. The best materials for thermoelectric devices were found to be alloys of bismuth, antimony and tellurium. [6]. However, the efficiency of thermoelectric materials is still limited for practical purposes. Highly efficient thermoelectric materials are therefore in urgent demand. The efficiency of a thermoelectric material is defined by its figure of merit *ZT*, which is expressed as $ZT = S2\sigma/\kappa \cdot T$ where *S* is the Seebeck coefficient, σ the electrical conductivity and κ the thermal conductivity. It is known that κ comprises two parts, $\kappa = \kappa_b + \kappa_p$ where κ_b and κ_p are respectively the electronic and phononic contribution to thermal conductivity.

In this work, we have investigated the electronic and thermoelectric properties of ternary antimonide *HfSiSb* for its potential use as thermoelectric material. Dashjav and Kleinke have investigated the crystal structure and electronic properties of *Ge* based ternary antimonide *HfGeSb* and found it to be a thermoelectric material with a tetragonal structure [8]. *HfSiSb* is a hypothetical compound with an assumption that this compound has the same structure as the *Ge* based compound. Recent structural studies on *HfSiSb* showed it to be mechanically stable [9]. No systematic research

has been reported on the electronic and thermoelectric properties of *HfSiSb* till date, and thus we have made a detailed investigation on these properties for this compound. The density of states (DOS), electronic band structure and the thermoelectric figure of merit *ZT* of this compound have been discussed in detail for the first time.

Crystal structure and computational method

Crystal structure

HfSiSb is a hypothetical compound and it is assumed that it crystallizes in the *ZrSiS*-type structure. *HfSiSb* has tetragonal structure with the space group P4/nmm. Its unit cell consists of six atoms occupying three two-fold positions: *Hf* on 2*c* (1/4, 1/4, *z*1), *Si* on 2*a* (3/4, 1/4, 0) and *Sb* on 2*c* (1/4, 1/4, *z*2) [9]. The following figure shows the crystal structure of ternary antimonide *HfSiSb* and its atomic position is shown in Fig. 1.

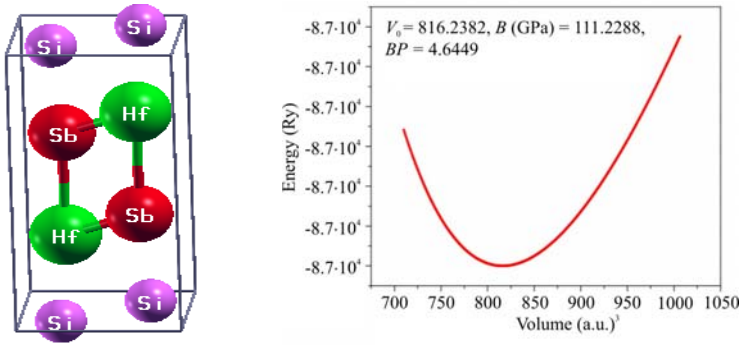


Fig. 1. Crystal structure of ternary antimonide HfSiSb.

Computational details

We have performed the first principle calculations based upon the density functional theory (DFT) using the WIEN2k code [10]. The total energy was calculated using the generalized gradient approximation (GGA) [11] and linearized augmented plane wave method (LAPW) [12]. The electronic and thermoelectric properties were calculated using the full potential linearized augmented plane wave method (FP-LAPW) [13] as implemented in the code WIEN2k. The cut off energy to define the valence and the core state separation was chosen as -6 Ry. We had set $R_{MT}{\cdot}K_{\max} = 7$ and used 10,000 *k*-points with 28 × 28 × 12 *k*-point mesh in the first Brillouin zone, which resulted in the generation of 1893 no. of plane waves in the irreducible part of the Brillouin zone. For self-consistence calculation, the convergence criterion for charge was set to 10^{-3} e^- and that for energy was set to 10^{-5} Ry. The semi-core states were treated ignoring the spin orbit coupling i.e. it was treated semi-relativistically.

To calculate the transport properties, we used the program code BoltzTraP [14] based on the Boltzmann semi-classical transport equation. The Fermi energy at zero temperature ($T = 0$K) was taken as chemical potential (μ) in the transport calculation.

Results

The lattice constant taken from the previous theoretical study given by Ref. [9] was used to perform the volume optimization. In order to determine the equilibrium lattice constant, bulk modulus, its pressure derivative etc., and the total energy *vs*. the changed volumes were fitted using Murnaghan's equation of state [15]. Fig. 2 shows the volume optimization curve and the comparison of the calculated lattice constant, bulk modulus etc. with that of the available on are presented in Table 1. The change in the parameters is given by Δ. Our calculated value of the bulk modulus is

111.2288 GPa, its pressure derivative is 4.6449 and the optimized lattice constants are, a = 3.746 Å and c = 8.618 Å.

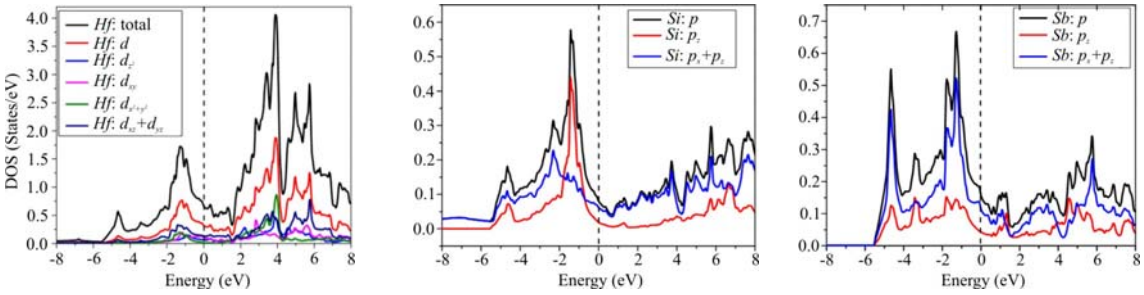
Table 1

Calculated equilibrium lattice parameters, bulk modulus (B) and its pressure derivative (B') of bulk modulus along with the available theoretical data

	a (Å)	c (Å)	B (GPa)	B'
Our result	3.746	8.618	111.23	4.645
Ref [9]	3.740	8.603	114.07	4.389
Difference (Δ)	0.006	0.015	2.84	0.256

Density of states (DOS)

To study the electronic properties optimal lattice constants $a = b$ = 3.746 Å and c = 8.618 Å were used. Fig. 3 gives the total DOS plot of *HfSiSb*. It shows that the maximum contribution to the total DOS is due to the *Hf* atoms (~ 4.2 eV), the *Si* and the *Sb* atom both has very low contribution of less than 1 eV. Since *Hf* has the highest contribution, therefore the sharp peaks in DOS are mainly due to the *d*-state electron in the semi-core and valence region (Fig. 4a). A closer look on the Fig. 4b and 4c shows that the *Si* contributes the least to the total DOS which is ~ 0.6 eV, whereas *Sb* has a contribution of ~ 0.7 eV. The contribution in *Si* and *Sb* is due to the *p*-state electron in the valence region.



a) *b)* *c)*

Fig. 2. (a) partial DOS of Hf (b) partial DOS of Si (c) partial DOS of Sb.

Band structure

Fig. 3 gives the band structure of *HfSiSb*. The band structure shows metallic nature of *HfSiSb*, with more dense bands in the conduction region than in the valence region.

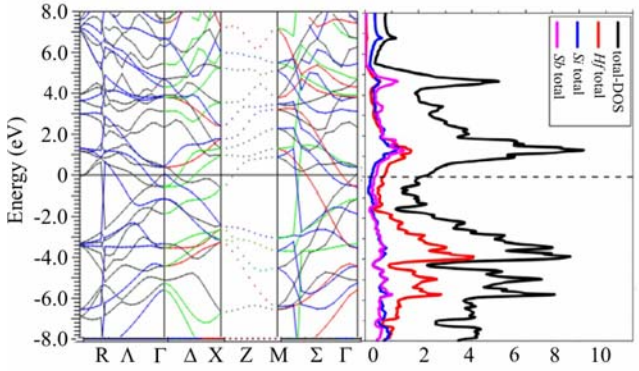


Fig. 3. Band structure of HfSiSb

The greater number of bands in the conduction region is due to the 3-*d* state of *Hf* atoms. In valence region also, dense bands are observed which is also due to the 3-*d* state of *Hf* atoms. In

comparison with DOS results it can be seen that in the valence region, the bands below – 1 eV consist mainly of the *p*-state electrons of *Si* and *Sb*.

Thermoelectric properties

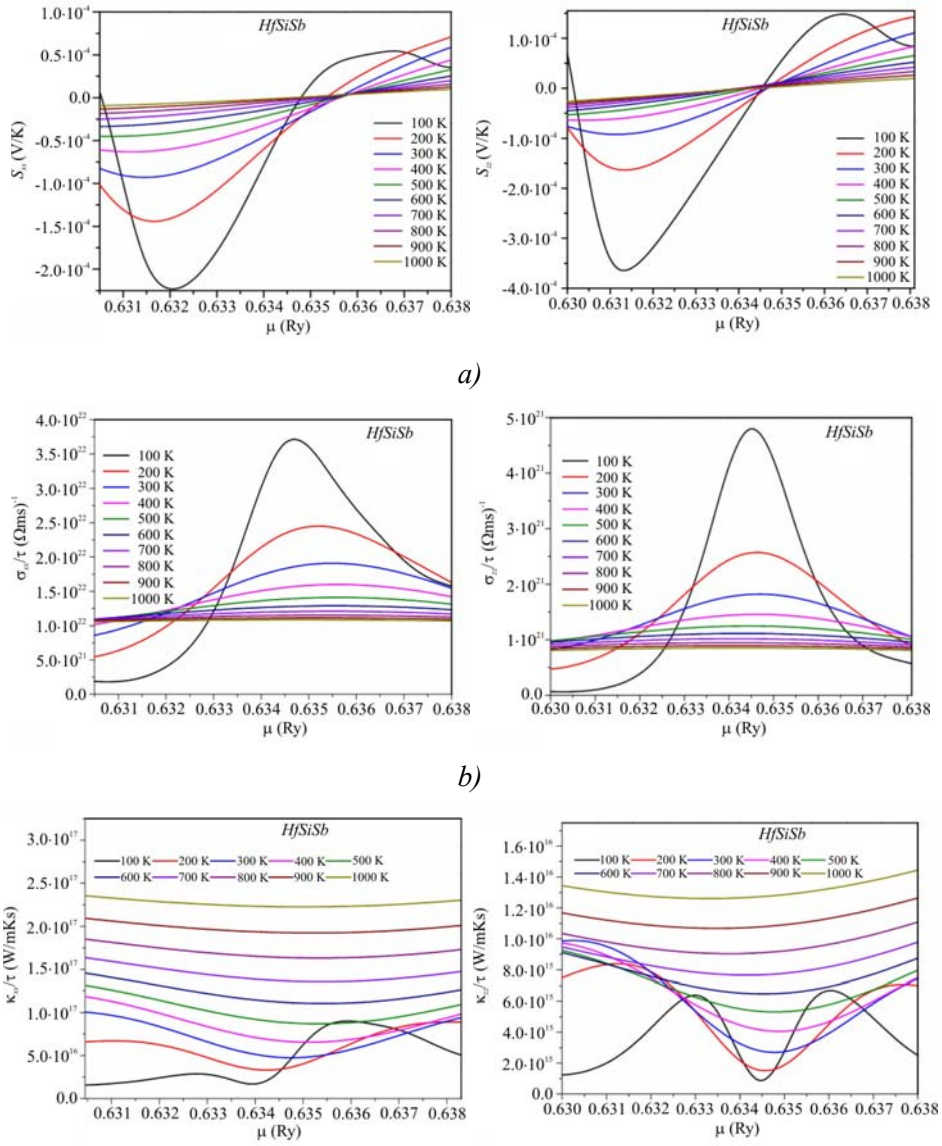
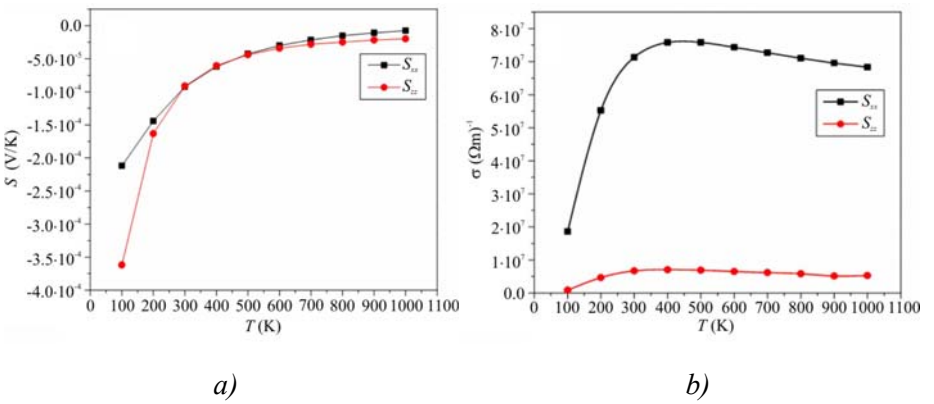
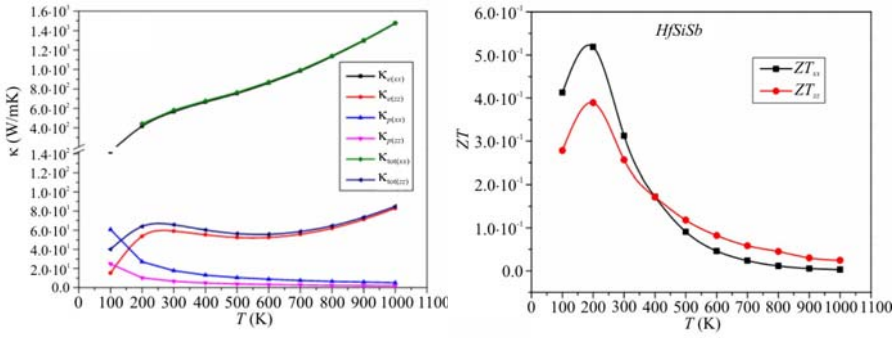


Fig. 4. Thermoelectric parameters as a function of chemical potential (μ) along X and Z directions at different temperatures (a) Seebeck Coefficient (b) Electrical conductivity and (c) Electronic thermal conductivity.





c) *d)*

Fig. 5. Thermoelectric parameters as a function of temperature (a) Seebeck coefficient (b) electrical conductivity (c) partial and total thermal conductivity (d) thermoelectric figure of merit (ZT).

Conclusion

The *Ge* based ternary antimonide was found to be a good thermoelectric material, whereas we see a different case for the *Si* based ternary antimonide. The highest *ZT* value calculated was 0.52 and 0.39 respectively for the *XX* and *ZZ* direction at 200K. However, the value is not too low to consider *HfSiSb* as a bad thermoelectric material, but is half of the benchmark value 1. These *ZT* values are only due to the dense bands in and around the Fermi level in the band structure of *HfSiSb*. The low values of the Seebeck coefficient and high values of thermal conductivity are due to the absence of narrow band gap in the band structure. If we can, however, dope with elements which modify the DOS near Fermi energy, then *HfSiSb* may show semiconductor behavior leading to a high value of *ZT*. Making nano-structural or external pressure may modify the *ZT* value.

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НОВИЙ ТЕТРАГОНАЛЬНИЙ ТЕРМОЕЛЕКТРИЧНИЙ МАТЕРІАЛ *HfSiSb* ТИПУ d^2/d^0, НАПІВГЕЙСЛЕРОВА СПОЛУКА: МЕТОД ПОВНОГО ПОТЕНЦІАЛУ ЛІНЕАРИЗОВАНИХ ПРИЄДНАНИХ ПЛОСКИХ ХВИЛЬ

Нами досліджені з перших принципів електронні й термоелектричні властивості HfSiSb в рамках функціональної теорії густини за допомогою методу повного потенціалу лінеаризованих приєднаних плоских хвиль. Електронна структура є ключем до визначення термоелектричних властивостей. Найпоширеніша апроксимація узагальненого градієнта береться до уваги для обміну електронами. Розраховані термоелектричні характеристики, такі як коефіцієнт Зеєбека, електронна теплопровідність і електрична провідність. Крім того, для одержання загальної теплопровідності ми включили теплопровідність гратки ($\kappa_{гр}$). Наявність загальної теплопровідності дає нам точне розуміння термодинаміки матеріалу і його ефективності (ZT). HfSiSb має тетрагональну структуру, термоелектричні параметри розраховані в перпендикулярному й паралельному напрямках. Низьке значення граткової теплопровідності (нижче 10 Вт/К·м) і різка зміна ZT у діапазоні (300 – 400) К прогнозує, що ця система є потенціальним термоелектричним матеріалом при кімнатній температурі.
Ключові слова: апроксимація узагальненого градієнта, зонна структура, коефіцієнт Зеєбека, теплопровідність.

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НОВЫЙ ТЕТРАГОНАЛЬНЫЙ ТЕРМОЭЛЕКТРИЧЕСКИЙ МАТЕРИАЛ *HfSiSb* ТИПА d^2/d^0, ПОЛУГЕЙСЛЕРОВО

СОЕДИНЕНИЕ: МЕТОД ПОЛНОГО ПОТЕНЦИАЛА ЛИНЕАРИЗОВАННЫХ ПРИСОЕДИНЕННЫХ ПЛОСКИХ ВОЛН

Нами исследованы из первых принципов электронные и термоэлектрические свойства HfSiSb в рамках функциональной теории плотности с помощью метода полного потенциала линеаризованных присоединенных плоских волн. Электронная структура является ключом к определению термоэлектрических свойств. Наиболее распространенная аппроксимация обобщенного градиента принимается во внимание для обмена электронами. Рассчитаны термоэлектрические характеристики, такие как коэффициент Зеебека, электронная теплопроводность и электрическая проводимость. Кроме того, для получения общей теплопроводности мы включили теплопроводность решетки (κ_p). Наличие общей теплопроводности дает нам точное понимание термодинамики материала и его эффективности (ZT). HfSiSb имеет тетрагональную структуру, термоэлектрические параметры рассчитаны в перпендикулярном и параллельном направлении. Низкое значение решеточной теплопроводности (ниже 10 Вт/Км) и резкое изменение ZT в диапазоне (300 – 400) К предсказывает, что эта система является потенциальным термоэлектрическим материалом при комнатной температуре.

Ключевые слова: аппроксимация обобщенного градиента, зонная структура, коэффициент Зеебека, теплопроводность.

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LOCALIZATION EFFECTS IN THIN FILMS OF $Bi_2Te_{2.7}Se_{0.3}$ THERMOELECTRIC COMPOUND

Thin films of $Bi_2Te_{2.7}Se_{0.3}$ thermoelectric compound were prepared using "hot wall" method by thermal evaporation in vacuum. High quality of the resulting thin films is proved by the data of X-ray diffraction and Raman scattering. Electron transport was investigated in a wide range of temperatures 1.4 – 300 K and magnetic fields up to 8 T. In the temperature dependence of electric conductivity at temperatures below 10 K there is localization of electrons caused by electron-electron interaction in a two-dimensional limit. It is supposed that the observed weak anti-localization in the field dependence of magnetoresistance is caused by the dominant contribution of surface states of a topological insulator. The length of phase failure was estimated. Bibl. 9, Fig. 2.

Key words: thin films, conductivity, magnetoresistance, localization, weak localization, weak anti-localization, topological insulator.

Introduction

Thin films of thermoelectric materials based on compounds of group $A_2^{V}B_3^{VI}$ are of interest on the one hand because according to modern theoretical concepts [1] considerable increase of thermoelectric figure of merit can be achieved in low-dimensional systems based on thermoelectric materials, and on the other hand compounds of group $A_2^{V}B_3^{VI}$ have been positioned of late as topological insulators [2].

Moreover, according to [3], thermoelectric devices based on Bi_2Te_3 and Bi_2Se_3 thin films allow achieving essential cooling to 32 K and heat flux pumping to 700 W/cm^2. Local cooling or heating occurs approximately $2\cdot10^4$ times faster than in devices based on the bulk materials. The use of thin films is also more preferable for reasons of miniaturization of devices based on these compounds.

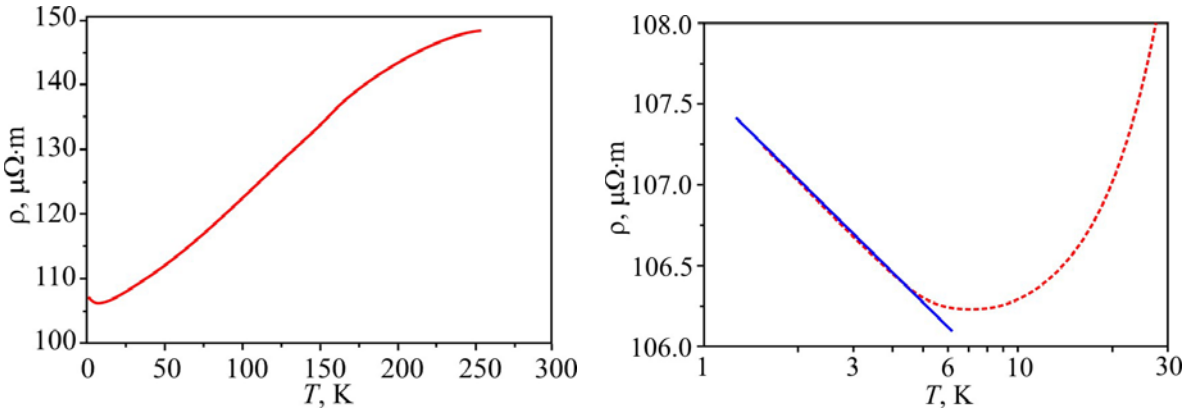
The purpose of this work was to determine the mechanism of low-temperature transport of electrons in thin films of $Bi_2Te_{2.7}Se_{0.3}$ solid solution. The choice of exactly this composition for investigation was due to the fact that the data reported in the literature [4] indicate that $Bi_2Te_{2.7}Se_{0.3}$ possesses the highest thermoelectric figure of merit in the system of $Bi_2(Te_{1-x}Se_x)_3$ solid solutions.

Experiment and discussion of the results

Thin films were prepared using "hot wall" method by thermal evaporation of synthesized substance in vacuum 10^{-5} mm mercury on the substrates of oxide silicate glass. Substrate temperature was maintained at 300°C. Thermal annealing of prepared films was made in vacuum at 200°C for 1 hour. The thickness of prepared films varied within 500 – 600 nm.

To characterize the resulting thin films, X-ray diffraction was studied on X-ray diffractometer Bruker D8 Advance, Raman scattering was studied on a 3D confocal Raman microspectrometer Nanofinder 30 (Tokyo Instr.) and film surface morphology was investigated on atomic-force microscope AIST-NT (Tokyo Instr.). The results of these investigations testify to considerable crystallization of films due to annealing in vacuum at 200°C for 1 hour and increased size of crystallites.

Another evidence of thin films crystallization after thermal annealing in vacuum is provided by the results of investigation of temperature dependence of resistivity given in Fig. 1.



a) *b)*

Fig. 1. Temperature dependence of resistivity in annealed $Bi_2(Te_{0.9}Se_{0.1})_3$ thin films (a) at temperatures $T < 300$ K and at low temperatures $T < 30$ K (b).

The temperature dependences of resistance were studied in a wide temperature region 1.4 – 300 K and in magnetic field up to 8*T*. The measurements were performed by standard four-probe scheme on alternating current of frequency 20.5 Hz using phase detection method. Point contacts were applied with the aid of silver paste. The nonannealed film shows a "dielectric" behaviour of the temperature dependence of resistivity caused by structural disorder. In this case we observe thermoactivation hopping conductivity over localized states which we reported earlier in [5]. In the thin film $Bi_2(Te_{0.9}Se_{0.1})_3$ annealed at 200°C the temperature dependence of resistivity shows a "metallic" behaviour, like in the bulk single crystals [6].

It is interesting that at low temperatures (below 8 K) with decreasing temperature the value of resistivity in the annealed film somewhat increases (Fig. 1*b*). Similar temperature behaviour of resistivity is typical with the dominance at low temperatures of quantum interference corrections to the conductivity caused by weak localization or electron-electron interaction [7]. As long as in the case of weak localization, on application of a transverse magnetic field, a negative magnetoresistance should be observed (instead, as will be shown below, there is a positive magnetoresistance), we believe that the observed localization of charge carriers is caused by electron-electron interaction. Analysis of the temperature dependence of resistivity at temperatures $T < 8$ K has shown (Fig. 1*b*)

that there is a logarithmic temperature dependence of resistance $\rho(T) \sim \ln T$ which is typical of a two-dimensional case [7].

Fig. 2 shows the results of investigation of the field dependence of magnetoresistance. In weak magnetic fields (up to 1 *T*) there is a drastic growth of resistance with increasing magnetic field (Fig. 1*a*), and in magnetic fields greater than 1 *T* there is a standard Lorentz square-law dependence typical of the field dependence of magnetoresistance in the bulk single crystals. Such drastic growth of resistance with increasing magnetic field in weak magnetic fields is characteristic of weak anti-localization effect [7]. Observation of weak anti-localization effect is not unexpected, as long as $A_2^{V}B_3^{VI}$ compounds are characterized by a strong spin-orbital interaction. However, it should be noted that weak anti-localization is not observed in the bulk single crystals and it is typical only of the thin films of $A_2^{V}B_3^{VI}$ compounds. Therefore, it is natural to assume that weak anti-localization observed in the thin films is a manifestation of interference effects in electronic subsurface states of topological insulator.

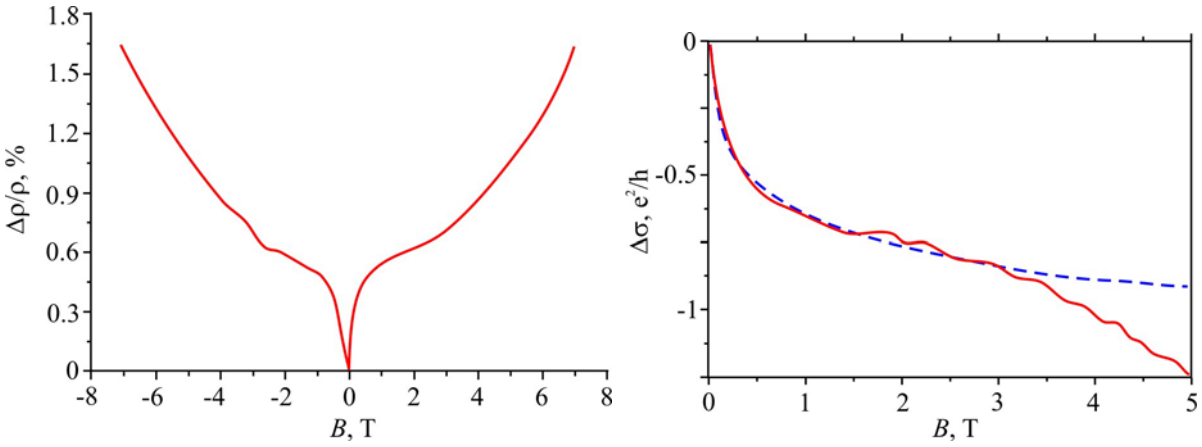


Fig. 2. Field dependence of magnetoresistance (a) and conductivity (b, dashed line is theoretical calculation) in annealed $Bi_2(Te_{0.9}Se_{0.1})_3$ thin films at temperature T = 5 K.

Theoretically, the magnetic field dependence of magnetic conductivity in the case of strong spin-orbital interaction $(\tau_\varphi >> \tau_{so}, \tau_e)$ in two-dimensional approximation for weak fields is described by the Hikami-Larkin-Nagaoka formula [8]:

$$\Delta\sigma(B) = \frac{1}{2}\frac{e^2}{2\pi^2\hbar}\left[\psi\left(\frac{1}{2}+\frac{B_\varphi}{B}\right) - \ln\left(\frac{B_\varphi}{B}\right)\right] \qquad (1)$$

Here, τ_{so}, τ_e, τ_φ, are the times of spin-orbital interaction, elastic scattering and phase failure, respectively, e is electron charge, $\hbar$ is reduced Planck constant, characteristic field $B_\varphi = \hbar / 4el_\varphi$, l_φ is phase failure length.

We have adjusted experimental data to formula (1) using two adjustable parameters: coefficient A in front of the entire formula and field B_φ. The results of adjustment are given in Fig. 2*b*. As is seen from the figure, the theoretical curve (dashed line) calculated from (1) agrees well with the experimental data with the values of parameters $A = 1.1$ and characteristic field $B_\varphi = 0.004$ T. The estimated length of phase failure is $l_\varphi = 200$ nm. Despite the fact that this value is comparable to film thickness $L \sim 500$ nm, one should take into account that localization depth of surface states of topological insulator $a < 10$ nm. Therefore, condition $l_\varphi >> a$ is satisfied strictly enough.

Conclusions

Thus, in the present paper it was shown that thermal annealing in vacuum at 200ºC leads to considerable crystallization of $Bi_2(Te_{0.9}Se_{0.1})_3$ thin films, which is confirmed by the data of X-ray diffraction and Raman scattering of light. The annealed $Bi_2(Te_{0.9}Se_{0.1})_3$ thin films show the same "metallic" behaviour of the temperature dependence of resistivity, as in the bulk single crystals, with essential distinctions in the low-temperature region.

The logarithmic resistance increase with decreasing temperature at low temperatures (below 8 K) is due to the dominant contribution of electron-electron scattering to processes of low-temperature electron transport.

The observed drastic growth of magnetoresistance with increasing value of magnetic field in weak fields (up to 1 T) at low temperatures ($T = 5$ K) is due to weak anti-localization effect characteristic of systems with a strong spin-orbital interaction. Observation of weak anti-localization points to domination of topological surface states in electron transport in magnetic fields at low temperatures.

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ЛОКАЛІЗАЦІЙНІ ЕФЕКТИ В ТОНКИХ ПЛІВКАХ ТЕРМОЕЛЕКТРИЧНОЇ СПОЛУКИ $Bi_2Te_{2.7}Se_{0.3}$

Термічним випаровуванням у вакуумі методом «гарячої стінки» отримані тонкі плівки термоелектричної сполуки $Bi_2Te_{2.7}Se_{0.3}$. Висока якість отриманих тонких плівок підтверджується даними рентгенівської дифракції й рамановського розсіювання. Досліджений транспорт електронів у широкій області температур 1.4 – 300 К і магнітних полів аж до 8 Тл. У температурній залежності електропровідності при температурах нижче 10 К спостерігається локалізація електронів, обумовлена електрон-електронною взаємодією у двовимірній границі. Передбачається, що спостережувана слабка антилокалізація в польовій залежності магнітоопору обумовлена домінуючим внеском поверхневих станів топологічного ізолятора. Оцінена довжина збою фази. Бібл. 9, Рис. 2

Ключові слова: тонкі плівки, провідність, магнітоопір, локалізація, слабка локалізація, слабка антилокалізація, топологічний ізолятор.

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ЛОКАЛИЗАЦИОННЫЕ ЭФФЕКТЫ В ТОНКИХ ПЛЁНКАХ ТЕРМОЭЛЕКТРИЧЕСКОГО СОЕДИНЕНИЯ $Bi_2Te_{2.7}Se_{0.3}$

Термическим испарением в вакууме методом «горячей стенки» получены тонкие плёнки термоэлектрического соединения $Bi_2Te_{2.7}Se_{0.3}$. Высокое качество полученных тонких плёнок подтверждается данными рентгеновской дифракции и рамановского рассеяния. Исследован транспорт электронов в широкой области температур 1.4 – 300 К и магнитных полей вплоть до 8 Тл. В температурной зависимости электропроводности при температурах ниже 10 К наблюдается локализация электронов, обусловленная электрон-электронным взаимодействием в двумерном пределе. Предполагается, что наблюдаемая слабая

антилокализация в полевой зависимости магнитосопротивления обусловлена доминирующим вкладом поверхностных состояний топологического изолятора. Оценена длина сбоя фазы. Библ. 9, Рис. 2

Ключевые слова: тонкие плёнки, проводимость, магнитосопротивление, локализация, слабая локализация, слабая антилокализация, топологический изолятор.

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RESEARCH ON THERMOELEMENTS BASED ON *n-PbTe* AND *p*-TAGS MATERIALS FOR THERMOELECTRIC GENERATOR CASCADE MODULE

The results of experimental research on creation of thermoelements based on n-PbTe and p-TAGS materials for the high-temperature stage of thermoelectric generator two-stage module optimized for the hot temperature level 500 °C are presented. The features of manufacturing technology of thermoelement samples are described, their design is presented and the results of measuring the temperature dependences of the parameters of legs obtained by the method of combined hot pressing are given. Bibl. 11, Fig. 5.

Key words: cascade modules, thermoelement, combined hot pressing, interconnects.

Introduction

The main factor restricting wide practical application of thermoelectric generators (TEG) is a low efficiency of thermal into electric energy conversion caused by the use in TEG design of single-stage modules with a low value of dimensionless figure of merit of thermoelectric materials, ZT = 1.0 – 1.6 [1]. One of the methods for increasing the efficiency of thermoelectric conversion lies in the expansion of the operating temperature range of module by cascading its design [2]. To create generator modules optimized for the operating temperature level 30 – 500 °C, it is rational to use a two-stage scheme with thermoelements based on n- and p-type *Bi-Te-Se-Sb* in the low-temperature stage and, accordingly, thermoelements based on *n*-type *PbTe* and *p*-type *GeTe-AgSbTe* (TAGS) in the high-temperature stage [3].

Manufacturing technology of the low-temperature stage of a two-stage module is similar to production processes of a single-stage module of bismuth telluride that are perfectly well proven by now, so do not require special attention. In this case, thermoelement legs are generally obtained from a single-crystal sample grown by the Czochralski method, the Bridgman technique and variations of zone melting methods [4]. On the cold side, connection of thermoelement legs to interconnect plates is done by soldering, on the hot side – using the interconnect layer of electroplated nickel [5].

In contrast to thermoelements of the low-temperature stage, the use of the above technological operations to obtain the legs of the high-temperature stage from materials based on *n-PbTe* and *p-GeTe-AgSbTe* is ineffective. According to experimental studies, brittle lead telluride single crystals under thermomechanical loading usually break down and are practically unsuitable for creation of thermoelement legs. At temperatures above 600 ºC, *n-PbTe* intensively sublimes and under the action of compression force is plastically deformed. So, connection by soldering, which is performed on preformed legs, consists of many operations and stages, requires thorough selection of fluxes, solders, as well as a complete removal of flux after soldering [4]. Moreover, during high-temperature soldering of interconnects there is a drastic thermal effect on thermoelectric material (TEM), since solders have high thermal and electric resistances. Under these conditions, a diffusion of

impurities from the solder to semiconductor takes place, decreasing significantly the operating temperature of thermoelement and reducing its efficiency [6].

In this connection, the search for and application of fundamentally new technological methods for the creation of thermoelements based on *n-PbTe* and *p*-TAGS materials are of relevance, allowing to ensure structural uniformity of the legs, their resistance to thermal stresses and, at the same time, a reliable contact between TEM and interconnect plates with minimal losses of thermoelement efficiency.

Analysis of the literature shows that this task can be solved by methods of powder metallurgy, in particular, by combined vacuum hot pressing of TEM powders and interconnects [7]. This technology offers the following advantages [8]:

– uniformity and fine-grain structure of TEM which imparts strength and thermal resistance thereto;

– increase of the actual area of contact between TEM and contact plate due to mutual penetration of powder grains at the interface with the interconnect plate;

– increased strength of interconnect transition as compared to other connection methods;

– higher *ZT* criterion values as compared to single crystals due to reduction of lattice component of thermal conductivity, which is caused by phonon scattering at the grain boundaries of pressed TEM.

Therefore, the purpose of this work is to study the temperature dependences of thermoelectric parameters of thermoelement legs from materials based on *n-PbTe* and *p-GeTe-AgSbTe*, made by the method of combined hot pressing in vacuum, for creation of the high-temperature stage of a two-stage generator module.

Technological aspects

Synthesis of materials based on *PbTe* and TAGS was performed at 1000 – 1100 ºC, based on TAGS – at 900 – 1000 ºC in graphitized and evacuated quartz ampoules in oscillating furnace during one hour. Iodine in the form of CdI_2 compound was used as a donor impurity for *PbTe*. To reduce the intrinsic acceptor defects (*Pb* vacancies), excess of lead was introduced into *PbTe* simultaneously with CdI_2. For TAGS, where carrier concentration is not controlled by doping impurities, the necessary parameters of thermoelectric material were achieved by changing the ratio *Sb*/*Ag*, which yielded an optimal alloy composition $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$.

The powders of initial materials were prepared by crushing the synthesized ingot in inert gas with a consecutive separation of TEM samples – screening and fractionation. Powders with a grain size of less than 100 μm were used for pressing of samples.

The samples of legs from *PbTe* and TAGS materials were pressed in the mode optimal for compaction of thermoelectric material. For lead telluride and TAGS the best results were obtained by vacuum hot pressing at a pressure of 1700 kg/cm^2. The warmup time is determined by the section of the sample for pressing and at the diameter of pressing 6 – 10 mm it should be at least 15 minutes. To avoid strong grain intergrowth due to secondary recrystallization (repressing), increase in pressing time would be objectionable.

To reduce the mechanical loads on the multi-layer compacted *PbTe* and TAGS material and minimize the appearance of microcracks, the bilateral pressing is used in a knock-down tool set which is schematically depicted in Fig. 1. The tool set has a die 1, into which the powder of thermoelectric material 2 is filled. On both sides the TEM charge is pressed by punches 3. The die with the TEM and punches is placed into heater 4, following which it is closed by bell jar 5 and evacuated. Pressing of

the sample is effected by the action of a mechanical load on the TEM powder through the rod (not shown in the figure) of bellows 6. Molybdenum is used as material for parts of the hot vacuum pressing mold. In the contact of the thermoelectric material with molybdenum, a thin film of chalcogenide is formed on the surface, which prevents further interaction and provides inertia of molybdenum.

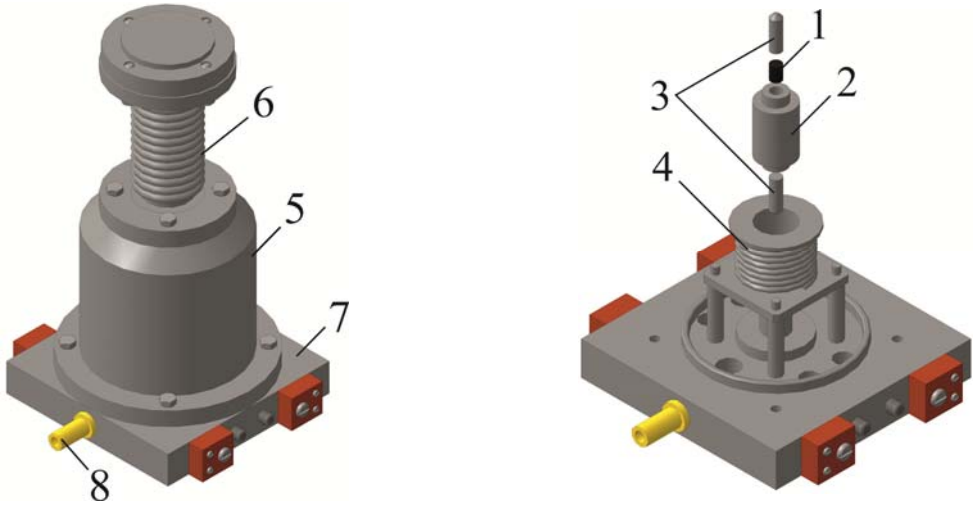

Fig.1. Schematic of a device for pressing of TEM samples: 1 – die; 2 – TEM powder; 3 – punches; 4 – heater; 5 – bell jar; 6 – bellows;7 – base; 8 –air outlet.

The resulting molybdenum chalcogenides have the properties of solid oils which reduce friction during pressing. Owing to these molybdenum properties, it is easy to disassemble the die and remove the sample after pressing. Depending on the geometry, the mold withstands the pressure up to 30÷50 MPa at temperatures close to melting temperature of lead telluride.

The structure of samples of *n*- and *p*-type legs obtained by combined hot pressing is given in Fig. 2.

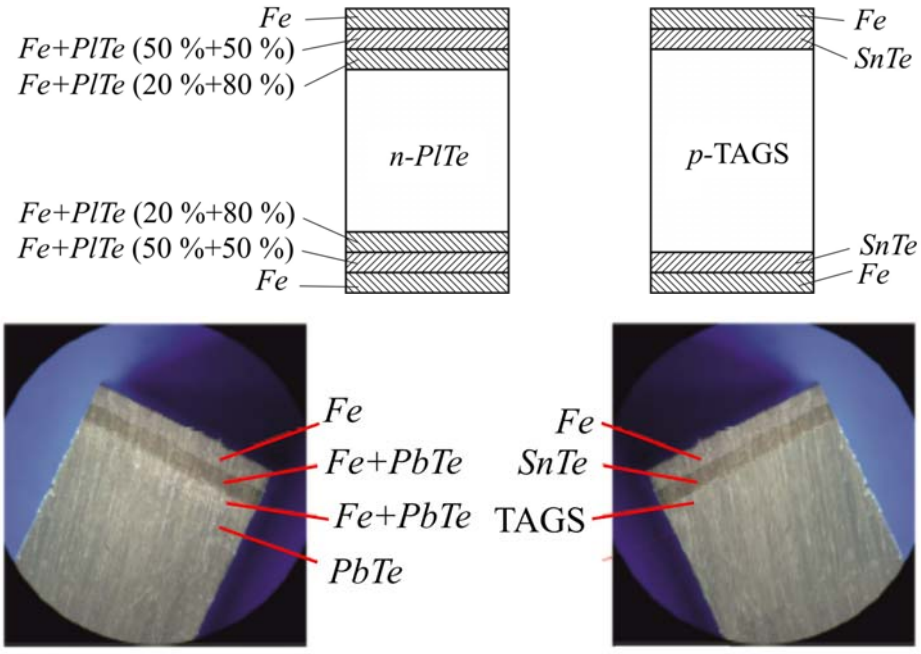

Fig.2. Thermoelement legs on the basis of PbTe and TAGS with prepressed transient and interconnect layers

The n-type *PbTe* leg consists of 7 layers which comprise the following materials: *PbTe*, mixture of *PbTe* with iron powder and pure iron. Pressed *Fe* powder is used as anti-diffusion layer and contact plate. Intermediate layers of the *Fe* and *PbTe* mixture serve to compensate the difference in linear expansion coefficients between TEM and the contact plate of pressed iron.

The first layer which is adjacent to a thermoelectric material comprises 20 % *Fe* and 80 % *PbTe*, the second – 50 % *Fe* and 50 % *PbTe*. With such layer structure of a mixture of *Fe* and *PbTe*, a smooth transition is achieved from a thermoelectric material that has high linear expansion coefficient to iron that has lower coefficient of linear expansion.

Thus, an *n*-type leg consists of two contact iron plates, two transient layers of a mixture of *Fe* and *PbTe* and a thermoelectric material. The general height of the leg is 7.1 – 7.2 mm, the diameter is 6 mm.

A *p*-type leg comprises 5 layers of pressed powder materials TAGS, *SnTe*, *Fe*. In this leg, *SnTe* is used as a compensating and anti-diffusion layer, iron is used as a contact plate.

Samples of *n-PbTe* based material obtained by pressing had unstable thermoelectric properties and essential internal stresses. In order to improve the structure, the *PbTe* samples were subject to additional annealing at a temperature of 500 °C in pyrex ampoules in the inert argon atmosphere.

Subsequently, the pressed cylindrical samples of *PbTe* and TAGS were fixed in a tool set (Fig. 3) that was fixed in a grinding machine. Grinding of samples was performed to the size of 7.0 mm to achieve flat-parallel workpiece ends.

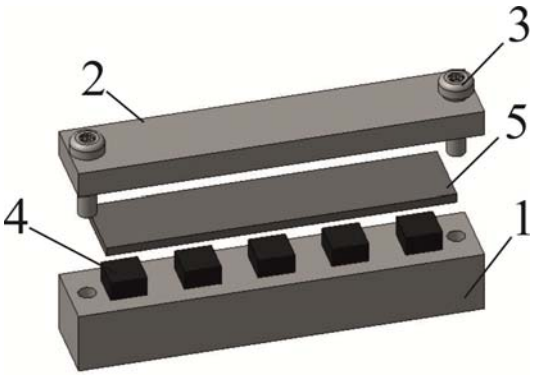

Fig.3. Tool set for grinding of thermoelements: 1 – cartridge; 2 – pressure plate; 3 – height adjuster;4 – thermoelement legs; 5 – elastic gasket.

After that, the ground samples were removed from the cartridge, washed and installed on a wire cutting machine [9], where the samples of *PbTe* and TAGS were cut into legs of size 4x4x7 mm.

The process of electrochemical deposition of intermediate layers on *PbTe* and TAGS included preparation of the surface of the samples and direct application of galvanic coating on these surfaces. The p- and n-type legs, predegreased with a solution of surface-active substance, were placed into a special tool set which is schematically shown in Fig. 4.

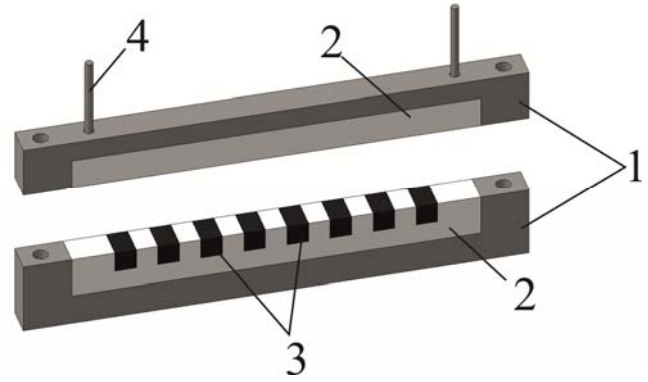

Fig.4. Tool set for metallization of thermoelement legs: 1 – base; 2 – silicone insert; 3 – thermoelement legs; 4 – electric contact.

The tool set with the pressed TEM samples was placed into an electrolytic bath for copper coating. In the process, the thermoelement legs were additionally coated with nickel layer, since it is impossible to directly apply copper on the surface of contact iron layer due to separation of the mechanically unstable copper layer from the electrolyte solution.

Measurement results

Experimental temperature dependences of thermoelectric parameters of materials based on *n-PbTe* and *p*-TAGS (Fig. 5) were obtained on the automated equipment Altec-10001, developed at the Institute of Thermoelectricity [10].

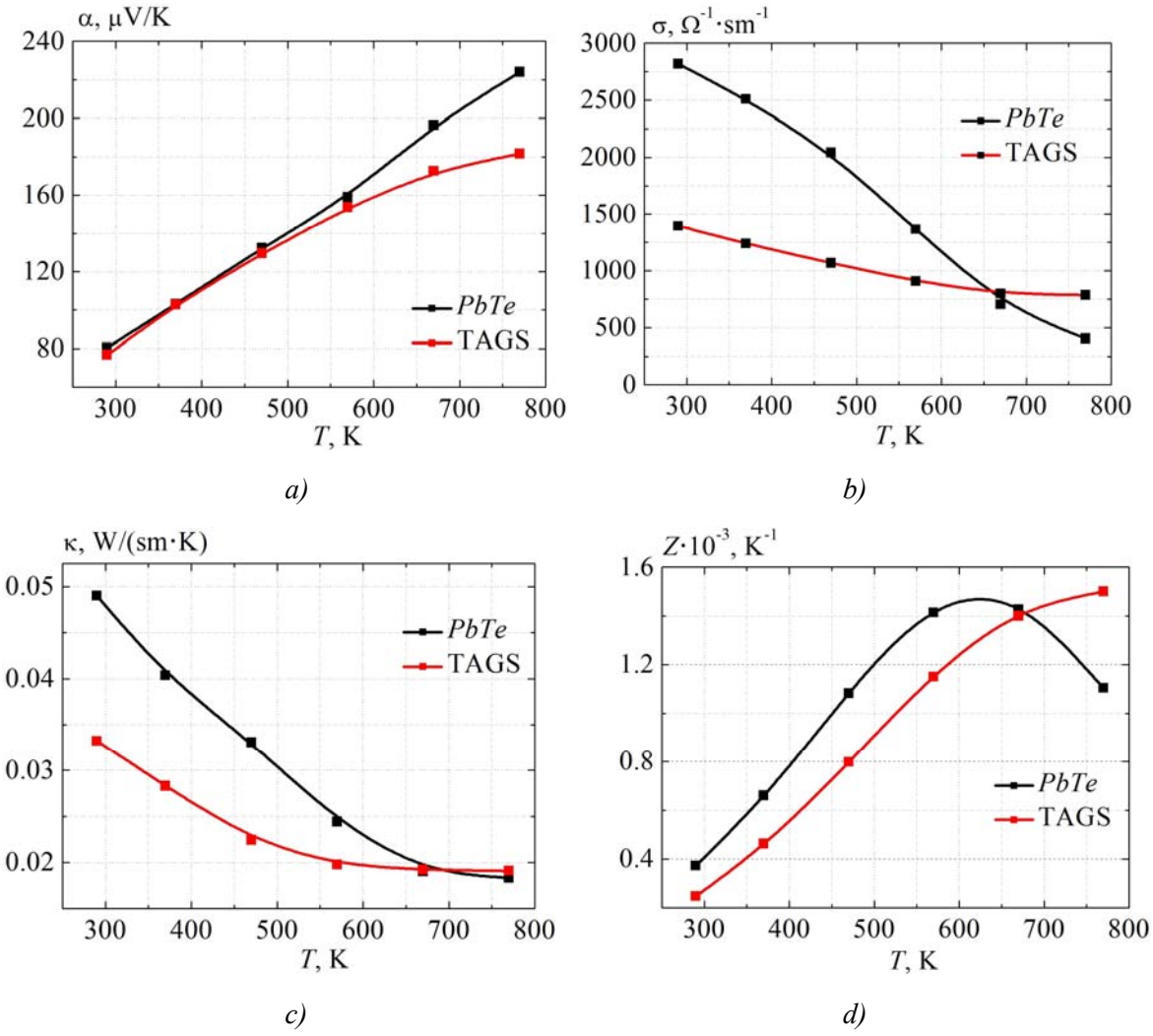

Fig. 5. Temperature dependences of thermoelectric materials based on n- PbTe and p-TAGS: a) Seebeck coefficient; b) electric conductivity; c) thermal conductivity; d) figure of merit.

From Fig. 5 it is seen that the maximum value of the Seebeck coefficient α for *n-PbTe* in the operating temperature range 500 – 770 ºK is 225 μV/K, the electric conductivity σ is 1360 – 450 $\Omega^{-1}\cdot sm^{-1}$, the thermal conductivity κ – 0.02 – 0.024 W/sm·K. The maximum value of the figure of merit Z of optimized *n-PbTe* material is $1.45x10^{-3}$ K^{-1}, which exceeds the figure of merit of known materials by a factor of 1.2 – 1.1[4, 11].

With the operating hot side temperature 770 ºK for *p*-TAGS the maximum value of α is 180 μV/K; σ = 800 $\Omega^{-1}\cdot sm^{-1}$; κ = 0.017 W/cm·K. The thermoelectric figure of merit reaches the value of $1.5x10^{-3}$ K^{-1}, which is sufficient for practical application of such material. The Z of material can be

further increased to $1.7 – 1.8x10^{-3}$ K^{-1} by increasing the ratio *Sb/Ag* or decreasing (*GeTe*)/(*AgSbTe*$_2$), however, in this case the mechanical strength of legs being pressed is reduced.

Conclusion

1. A process flow chart for thermoelement legs of materials based on *n-PbTe* and *p*-TAGS is developed, which includes synthesis of thermoelectric material, crushing and separation of synthesized TEM, combined vacuum hot pressing of TEM powders, anti-diffusion and interconnect layers with a consecutive electroplating of legs.
2. It is shown that the maximum value of the thermoelectric figure of merit of thermoelement legs obtained by hot pressing method in the operating temperature range 500 – 770 ºK is $1.45x10^{-3}$ K^{-1} for *n-PbTe* materials and, accordingly, $1.5x10^{-3}$ K^{-1} for materials based on *p*-TAGS at the hot side operating temperature 770 ºK.
3. The rationality of using powder metallurgy methods for creating the high-temperature stage of thermoelements based on *n-PbTe* and *p*-TAGS materials of thermoelectric generator two-stage module optimized for the level of hot temperatures 500 °C is experimentally confirmed.

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ДОСЛІДЖЕННЯ ТЕРМОЕЛЕМЕНТІВ З МАТЕРІАЛІВ НА ОСНОВІ *n-PbTe* І *p*-TAGS ТЕРМОЕЛЕКТРИЧНОГО ГЕНЕРАТОРНОГО КАСКАДНОГО МОДУЛЯ

Наведено результати експериментальних досліджень зі створення термоелементів на основі n-PbTe і p-TAGS матеріалів для високотемпературного каскаду термоелектричного генераторного двокаскадного модуля, оптимізованого на рівень гарячих температур 500 °C. Описано методику отримання та особливості технології виготовлення зразків термоелементів, представлено їх конструкцію, подано результати вимірювань температурних залежностей параметрів віток, одержаних методом сумісного гарячого пресування. Бібл. 11, Рис. 5.

Ключові слова: каскадні модулі, термоелемент, сумісне гаряче пресування, комутація.

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ИССЛЕДОВАНИЕ ТЕРМОЭЛЕМЕНТОВ ИЗ МАТЕРИАЛОВ НА ОСНОВЕ *n-PbTe* И *p*-TAGS ТЕРМОЭЛЕКТРИЧЕСКОГО

ГЕНЕРАТОРНОГО КАСКАДНОГО МОДУЛЯ

Приведены результаты экспериментальных исследований по созданию термоэлементов на основе n-PbTe и p-TAGS материалов для высокотемпературного каскада термоэлектрического генераторного двухкаскадного модуля, оптимизированного на уровень горячих температур 500 °C. Описана методика получения и особенности технологии изготовления образцов термоэлементов, представлена их конструкция и результаты измерений температурных зависимостей параметров ветвей, полученных методом совместного горячего прессования. Библ. 11, Рис. 5.

Ключевые слова: каскадные модули, термоэлемент, совместное горячее прессование, коммутация.

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EXPERIMENTAL STUDY OF THERMOELECTRIC LIQUID-LIQUID HEAT PUMP

Based on the elaborated design of thermoelectric liquid-liquid heat pump, its experimental prototype was manufactured and a series of tests was performed. The characteristics of thermoelectric heat pump under study were compared to its analogs and the results of computer design. Bibl. 7, Fig. 3, Table 1.
Key words: thermoelectric heat pump, experimental study, water recovery system..

Introduction

General characterization of the problem. The use of thermoelectric heat pumps (THP) in the air and liquid conditioning systems, special-purpose evaporators is related to their unique advantages [1 – 5].

An example of efficient use of thermoelectric heat pumps is systems of water recovery from liquid biowaste on board of manned spacecrafts (urine, atmospheric condensate, sanitary and hygienic water) [4, 5].

The results of computer design of thermoelectric liquid-liquid heat pump are presented in [6, 7]. By means of multi-parametric computer optimization, the design parameters of thermoelectric heat pump which provide the highest performance factors were determined. The next stage of this work is experimental study of the design of a thermoelectric heat pump.

The purpose of the work is experimental confirmation of the basic results of computer design of a thermoelectric heat pump under conditions close to its actual use as a high-efficient heater for water recovery systems of space application.

Design and operating conditions of THP

Proceeding from the requirements to THP for water recovery system of space application (Table 1), its computer design was performed and the construction of thermal pump was determined (Fig. 1).

Table

Requirements to THP

№	Parameter	Value
1.	Electric supply power of thermoelectric modules, W	300
2.	Heat carrier temperature at the inlet to hot heat-exchange circuit, ºC	36

Continuation of the Table

3.	Heat carrier temperature at the inlet to cold heat-exchange circuit, ºC	31.5
4.	Hydraulic resistance of each heat-exchange circuit, atm	0.07
5.	Heat carrier flow rate in each circuit, ml/s	22
6.	Material for heat exchangers which is in contact with liquid	titan, stainless steel AISI 304

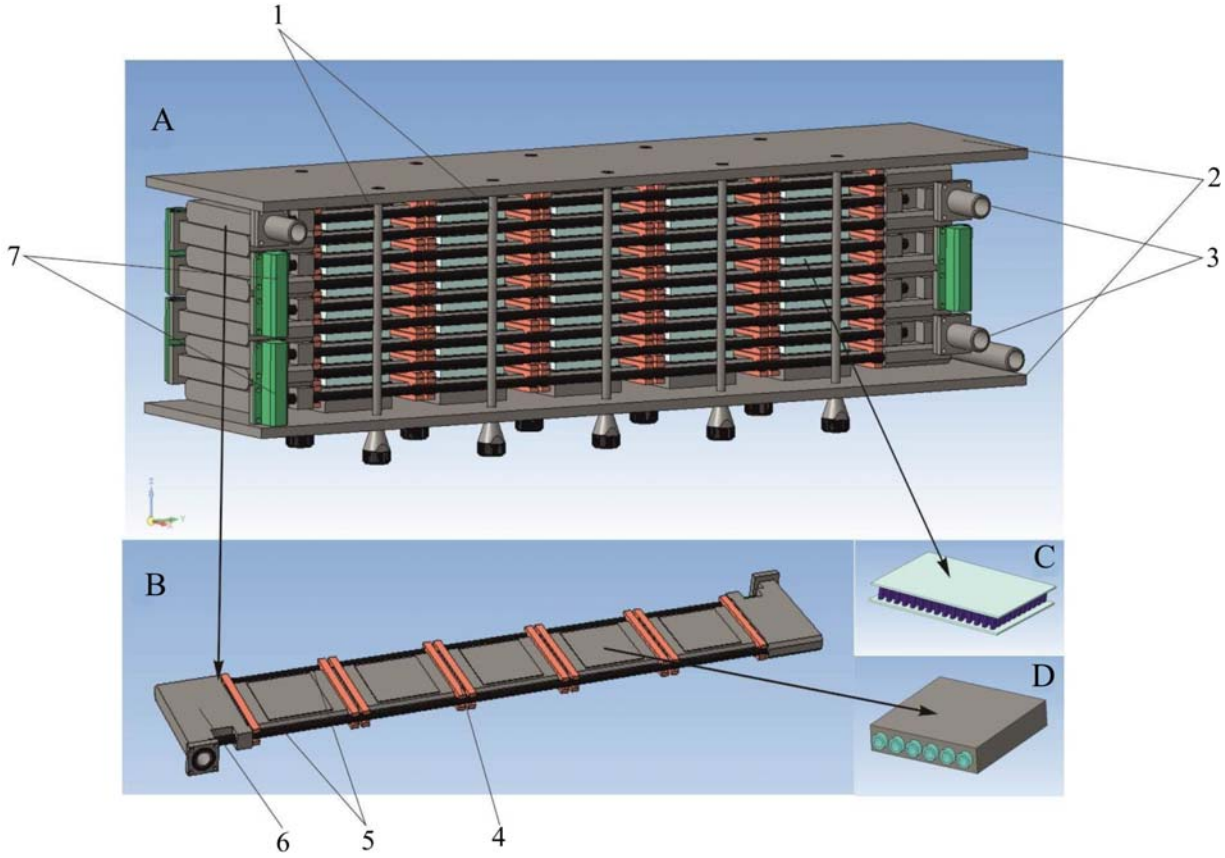


Fig. 1. Design of thermoelectric liquid-liquid heat pump: A – appearance, B – interconnect schematic of one row of heat exchangers, C – thermoelectric module, D – liquid heat-exchanger; 1 – vertical couplings, 2 – case parts, 3 – unions, 4 – clamps with gaskets, 5 – horizontal couplings, 6 – collectors, 7 – adapters

Thus, THP is composed of two identical units that comprise 40 thermoelectric modules each and differ only in the way of their electric power supply. The hydraulic connection of THP units is done in series. Each unit consists of liquid heat exchangers (D), which together with collectors (6), horizontal couplings (5) and clamps (4) form the rows of the heat pump (B). Between the rows of the heat pump there are thermoelectric modules (C). Connection of the rows is done with the help of vertical couplings (1) and adapters (7). At the inlets and outlets of the hot and cold circuits there are unions (3).

The appearance of THP units is given in Fig. 2.

Fig. 2. Appearance of thermoelectric heat pump units

Experimental study of THP

Measurement of characteristics was carried out on a specially created bench. The schematic of the measuring bench is represented in Fig. 3. In the schematic, 1 and 2 are the hot and cold thermostats that ensure motion of heat carrier of corresponding temperature along the heat pump channels (4, 5). Heat carrier temperatures at the inlet and outlet of THP are recorded by thermocouples 3. Power supply to modules of the first and second THP units is done by separate supply units 6.

Hydraulic pressure in the channels of thermoelectric heat pump was measured separately to ensure the operating conditions of THP.

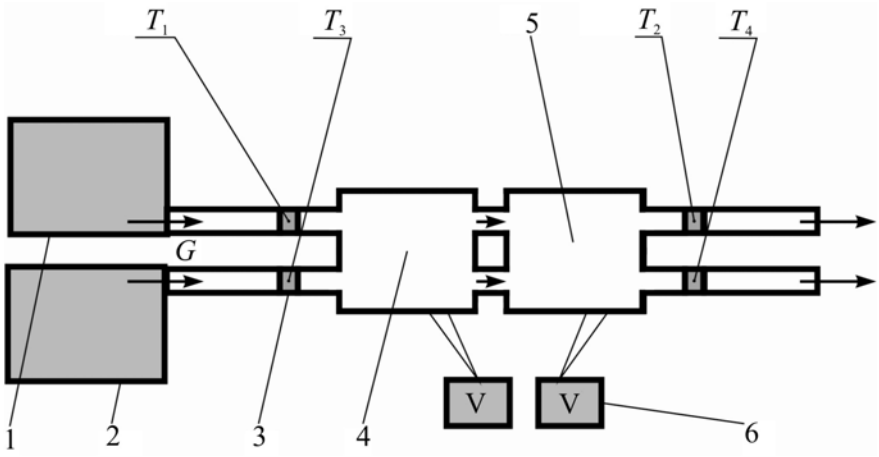


Fig. 3. Schematic of measuring bench to study THP:
1 – hot thermostat, 2 – cold thermostat, 3 – set of differential thermocouples with a recording device,
4 – 1 THP unit, 5 – 2 THP unit, 6 – power supply units of 1 and 2 THP units,
T_1 – heat carrier temperature at the inlet to hot circuit of THP, T_2 – heat carrier temperature at the outlet of the hot circuit of THP, T_3 – heat carrier temperature at the inlet to cold circuit of THP,
T_4 – heat carrier temperature at the outlet of cold circuit of THP.

Heat flow which is transferred by thermoelectric modules to the hot circuit of THP was determined by formula (1):

$$Q_H = C \cdot G \cdot \Delta T_1, \tag{1}$$

where Q_H is calorific power, C is heat carrier heat capacity, G is heat carrier flow rate, $\Delta T_1 = T_2 - T_1$ is the difference in temperature between the inlet and outlet of the hot circuit.

Heating coefficient in this case is found by formula (2):

$$\mu = Q_H / W , \tag{2}$$

where W is electric supply power of THP.

To control the heat balance in THP, measurements of cooling capacity and coefficient of performance of THP were also carried out in its cold circuit by the similar method:

$$Q_C = C \cdot G \cdot \Delta T_2 , \tag{3}$$

where Q_C is cooling capacity, C is heat carrier heat capacity, G is heat carrier flow rate, $\Delta T_2 = T_3 - T_4$ is the difference in temperature between the outlet and inlet to the cold circuit.

Coefficient of performance in this case is found by formula (4):

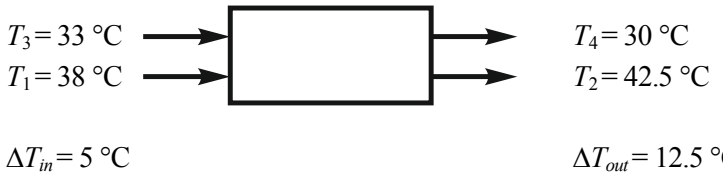
$$\varepsilon = Q_C / W , \tag{4}$$

where W is electric supply power of THP.

Results of measurement of THP characteristics

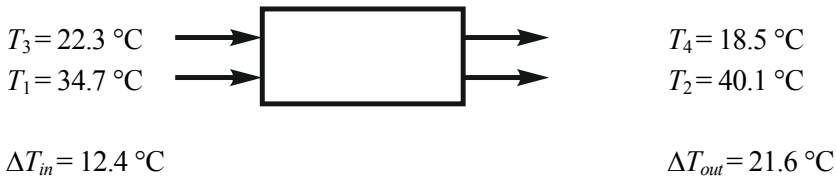
Investigations of THP characteristics were performed for each unit separately, as well as for the case of two units that are hydraulically connected in series, but with individual power supply.

Results of measurement of unit 1:



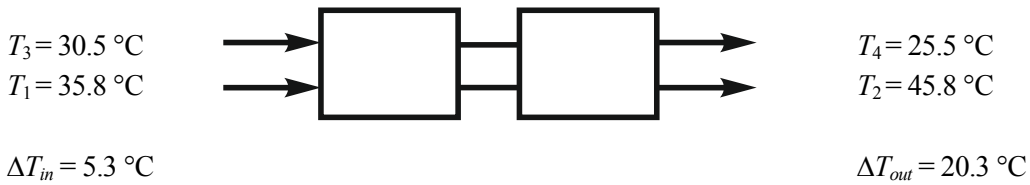
Under the conditions of power supply to thermoelectric modules U = 28 V, I = 4.6 A, W=129 W, at heat carrier flow rate G = 22.7 ml/s and the hydraulic resistance Δp = 0.025 atm, the calorific power of THP unit 1 is Q_h = 429 W, and heating coefficient μ = 3.3.

Results of measurement of unit 2:



Under the conditions of power supply to thermoelectric modules U = 27.9 V, I = 6.7 A, W =186.9 W, at heat carrier flow rate G = 22.2 ml/s and the hydraulic resistance Δp = 0.025 atm, the calorific power of THP unit 2 is Q_h = 503.5 W, and heating coefficient μ = 2.7.

Results of measurement of two THP units:



Under the conditions of power supply to thermoelectric modules $U = 27.9$ V, $I = 11.1$ A, $W = 309$ W, at heat carrier flow rate $G = 21$ ml/s and the hydraulic resistance $\Delta p = 0.05$ atm, the calorific power of THP is $Q_h = 882$ W, and heating coefficient $\mu = 2.85$.

From the measurement results it is seen that the first unit works at a lower inlet temperature difference ($\Delta T_{in} = 5$ °C), which results in a higher value of heating coefficient $\mu = 3.3$. The second unit works at the inlet temperature difference ($\Delta T_{in} = 12.4$ °C), which results in heating coefficient value $\mu = 2.7$. Optimization of THP units was done precisely for these specific temperature ranges, which yielded final heating coefficient $\mu = 2.85$. Comparison of the obtained results to the characteristics of previously developed THP [4, 5] shows the advantages of the elaborated THP design by 10 – 15 %.

Moreover, an estimation of the discrepancy between the results of computer simulation carried out in [6, 7] and the results of experimental study performed in this paper was performed. It was established that in terms of heating coefficient the results of experimental study are lower by ~ 7 %.

Conclusion

1. Experimental study of THP characteristics was performed and its calorific power $Q_h = 882$ W and heating coefficient $\mu = 2.85$ were determined under conditions close to its actual use as a high-performance heater for water recovery systems of space application
2. An estimation was performed of the discrepancy between the results of computer simulation carried out in [6, 7] and the results of experimental study, which makes ~ 7 %.
3. Comparison of the results obtained to the characteristics of previously developed THP [4, 5] shows the advantages of the elaborated THP design in terms of heating coefficient by10 – 15 %.

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ЕКСПЕРИМЕНТАЛЬНЕ ДОСЛІДЖЕННЯ ТЕРМОЕЛЕКТРИЧНОГО ТЕПЛОВОГО НАСОСА РІДИНА-РІДИНА

На основі спроектованої конструкції термоелектричного теплового насоса рідина-рідина виготовлено його експериментальний зразок та проведено серію випробувань. Здійснено порівняння характеристик досліджуваного термоелектричного теплового насоса із його аналогами та з результатами комп'ютерного проектування.

Ключові слова: термоелектричний тепловий насос, експериментальне дослідження, система регенерації води.

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ЭКСПЕРИМЕНТАЛЬНОЕ ИССЛЕДОВАНИЕ ТЕРМОЭЛЕКТРИЧЕСКОГО ТЕПЛОВОГО НАСОСА ЖИДКОСТЬ-ЖИДКОСТЬ

На основе спроектированной конструкции термоэлектрического теплового насоса жидкость-жидкость изготовлен его экспериментальный образец и проведена серия

испытаний. Осуществлено сравнения характеристик исследуемого термоэлектрического теплового насоса с его аналогами и с результатами компьютерного проектирования.
Ключевые слова: термоэлектрический тепловой насос, экспериментальное исследование, система регенерации воды.

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THERMOELECTRIC DEVICE FOR THE DIAGNOSIS OF INFLAMMATORY PROCESSES AND NEUROLOGICAL MANIFESTATIONS OF VERTEBRAL OSTEOCHONDROSIS

The paper presents the results of development of a thermoelectric device intended for simultaneous measurement of temperature and heat flow density on the surface of the human body by contact method. A specialized computer program "TermoMonitor" was developed for processing measurement results, their accumulation and reproduction in given form on a personal computer which makes it possible to monitor the temperature and thermal state of a person in real time. Structural features of the device, its technical characteristics and the results of preliminary clinical trials are presented. Bibl. 28, Fig. 3, Table 2.
Key words: thermoelectric sensor, heat flow density, temperature, inflammatory processes of the human body, vertebral osteochondrosis.

Introduction

General characterization of the problem. Vertebral osteochondrosis and its neurological manifestations are one of the topical problems of modern medicine. This is due to the widespread prevalence of pathology in the active working age, the frequent inclination of the disease to a stable and prolonged course, the continuous progress of the number of such patients with age. Of noteworthy place in this list are neurological manifestations of osteochondrosis of the lumbar spine, which make up 60 – 70 % of all diseases of the peripheral nervous system and cause more than 70 % of cases of temporary disability. The prevalence of this pathology in Ukraine today is 10 thousand persons per 100 thousand of population. It should be noted that many aspects of this pathology have not yet been studied; modern methods of diagnosis and treatment of this disease require further improvement [1 – 5].

In recent years, especially at the State Institution "Institute of Traumatology and Orthopedics of the National Academy of Medical Sciences of Ukraine" the method of epidural adhesiolysis began to be widely applied [6 – 9]. The purpose of this type of treatment is to remove inflammation and minimize mechanical effect on nerve structures. This technique is realized with the help of a catheter,

a thin tube inserted unto the middle of spinal canal. The procedure is carried out under fluoroscopic control. First, through a cleft in the sacral bone, a puncture with a thicker needle is done near the attachment point of the coccyx. All this is done under local anesthesia. Inside the needle there is a thin tube (catheter) with a metal wire which is visible on the X-ray. The doctor controls the position of the tube using an X-ray machine. Once the end of the catheter is properly installed, the metal wire is pulled out and inside the spine there remains only a soft plastic tube at the end of which there are holes. Through this tube, once or several times, medicines, usually prolonged corticosteroids and a hypertonic solution, are introduced which accelerates resorption of hernia and relieves pain.

This method is used as an alternative to surgical intervention. It does not replace traditional surgery, but a significant proportion of patients can alleviate pain and do without further surgical interventions. Also, this method is recommended for alleviation of pain in patients who refuse from surgery or cannot be operated because of their health status. To evaluate treatment efficacy, improved methods started to be applied for assessing changes in heat release and temperature reactions of human organism in response to the procedure [10 – 13].

It is known that semiconductor thermoelectric sensors of heat flow [14 – 24], which combine miniature size, high sensitivity and stability of parameters in a wide range of operating temperatures and are consistent with modern recording equipment [25 – 28], are promising for the investigation of local human heat release. The use of such sensors makes it possible to achieve high locality and accuracy of heat flow measurements. This, in turn, makes it possible to obtain information on the characteristics of objects under study and analyze them in detail in order to detect, at an early stage, the inflammatory processes of the human body.

It is also important to control heat release in the areas of the human body where there was a surgical intervention. With normal healing of the wounds, the heat release, though increased, is within the appropriate limits. However, if healing is accompanied by significant inflammatory processes (for instance, caused by sterility disorder), then such processes can first of all be informed of by thermoelectric sensor that will record the local thermal anomalies. Thus, monitoring of the human body heat release is extremely important, since it can provide information on both the course of the disease exacerbation and, on the contrary, on the rehabilitation processes.

Therefore, *the purpose of the work* is to develop a thermoelectric device for the diagnosis of inflammatory processes and pain syndrome in degenerative-dystrophic diseases of the lumbar-sacral spine.

Design and technical characteristics of the device

A two-channel thermoelectric device for measuring temperature and heat flows was developed at the Institute of Thermoelectricity of the NAS and MES of Ukraine (Fig. 1). Technical characteristics of the device are given in Table 1.

The device is designed to measure temperature and heat flow density on the surface of the human body by contact method, which makes it possible to reveal at the early stages the inflammatory processes of human organism, various diseases and perform instant diagnosis during mass examination of patients. In this paper, the device is used for the diagnosis of inflammatory processes and pain syndrome in degenerative-dystrophic diseases of the lumbar-sacral spine.

The device comprises control unit 1 and thermoelectric sensors of temperature and heat flow 2. Measurement of temperature and heat flow density occurs simultaneously using two thermoelectric sensors and recording measurement results on MicroSD memory card and computer display on PC (with operating system Windows 7 – 10). Data recording is done in "Comma-separated values" (csv)

format, which allows one to open measurement results record files without any additional conversion in the majority of programs for work with spreadsheets, such as "Microsoft Excel", "Open office", etc., as well as in the specialized program of the device "TermoMonitor" for the construction of measurement plots.

The operating principle of the device lies in conversion of heat flow and temperature of the human body by means of two thermoelectric sensors of heat flow density and temperature into equivalent in magnitude electric signals that are shown on the digital display of control unit in the units of heat flow density (mW/sm^2) and temperature (°C).

Fig. 1. Thermoelectric device for measuring temperature and heat flows:
1 – control unit, 2 – thermoelectric sensor of temperature and heat flows

Table 1

Technical characteristics of the device

№	Technical characteristics of the device	Parameter values
1.	Operating temperature range of thermoelectric sensor	(0 ÷ +50) °C
2.	Accuracy of temperature measurement	± 0.1 °C
3.	The range of measuring the density of heat flow	(1 ÷ 100) mW/sm^2
4.	Maximum error in measuring the density of heat flow	5 %
5.	Number of thermoelectric sensors	2
6.	Overall dimensions of thermoelectric sensor	(14×14×3) mm
7.	Overall dimensions of control unit	(90×55×25) mm
8.	Weight of thermoelectric sensor	20 g
9.	Weight of the device	150 g
10.	Time of continuous operation of the device	48 h

The upper wall of the device accommodates two connectors for thermoelectric sensors of temperature and heat flow and a power button. The right side wall has a connector for microSD memory card and a miniUSB-connector for connecting the device to personal computer. Also, through the miniUSB-connector the battery of the device is powered.

A liquid-crystal display is mounted on the front wall of the device, in which the values of heat flow density of the corresponding parts of the human body and the temperature values are displayed in the form of plots. Thus, the measured results can be analyzed directly from the plots shown on the display. The presence in the device of two thermoelectric sensors simultaneously makes it possible to compare the results of measurements of the affected and healthy area of the human body surface.

Besides, on the front wall of the device there are 6 buttons for control of the device operation − "LEFT", "RIGHT", "UP", "DOWN", "OK", "MENU". The “MENU” buttons have the following designation:

– "START RECORDING” / "STOP RECORDING" – the device starts recording of measurement results into a new file, stops the corresponding record and saves information on the memory card;

– "MODE SELECTION" – causes sub-menu to select one of 9 modes of information display in the form of on-line plots;

– "RECORDING PERIOD" – is intended to select a period of time through which the measurement results will be recorded in a file on a memory card and shown on the device display;

– "TIME/DATE" – transition to time and date setting mode;

– "BATTERY" – shows voltage on device battery;

– "INFORMATION" – shows information on the device.

Structural scheme of the device (Fig. 2) is composed of the following functional units: a thermoelectric sensor of heat flow with embedded temperature sensor, an analog-to-digital converter (ADC) for conversion of analog signals of the sensor to digital, a multiplexor for switching digital signals from ADC and their alternate transmission to a microcontroller, which is used to ensure processing of digital signals, their saving on a memory card, graphical visualization of information on the display and personal computer.

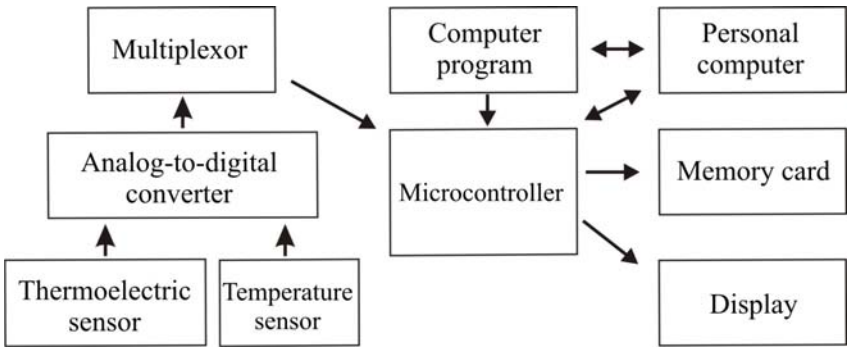

Fig.2. Structural scheme of thermoelectric device for measuring temperature and heat flows

The main functional part of the control unit is a microcontroller operating at a frequency up to 20 MHz that ensures high processing speed of the thermoelectric sensor temperature and heat flow signals. With the help of a personal computer, the microcontroller is programmed, which, in turn, manages the operation of other functional parts of the device.

The device has its own power source in order to enable its use in offline mode with the patient. This, in turn, extends the functionality of the device. The device is powered from a lithium-ion battery of capacity 1200 mA/h, which ensures 48 hours of continuous operation of the device.

Description of computer program of the device

Computer program of the device (Fig. 3) is written in programming language Delphi. The program allows exchanging data with control unit through USB-interface. Data exchange is carried out using the Human Device Interface (HID) protocol, which enables one to connect the device to a personal computer without the need to install additional drivers.

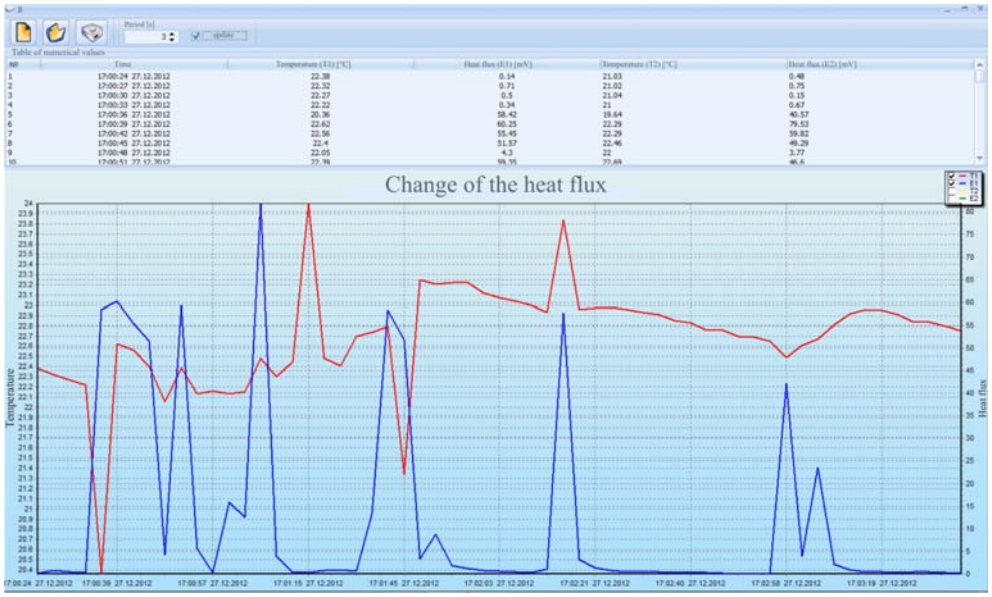

Fig.3. Interface of computer program "TermoMonitor" for processing measurement results, their accumulation and reproduction in given form on a personal computer (the change in temperature and heat flow of the 1st thermoelectric sensor)

When selecting “UPDATE DATA” in the computer program, a loop that sends requests for data transmission from the control unit is started. In response to such requests, the control unit sends a package of data on the temperature and thermal flow of thermoelectric sensors with a given time interval. The received data package is processed, following which information is displayed on a personal computer in the form of tables and plots.

When you click the “SAVE” button, all data from the table is converted to “string” values (plain text), separated by a dot and a comma, and written to a file with the extension "csv", which can be opened by any spreadsheet program (Microsoft Excel, etc.). When you open a file, such a program decodes the "csv" format into a floating-point data package, which allows one to display information in a table and associated plots on a personal computer.

Results of preliminary clinical trials

The purpose of preliminary clinical trials was to evaluate with the help of a thermoelectric device a change in the temperature and heat release of the human body in order to determine the efficacy of using epidural adhesiolysis in the treatment of pain syndrome in degenerative-dystrophic diseases of the lumbar sacral spine. Clinical trials were performed in the laboratory of neuroorthopedics and pain problems at the Institute of Traumatology and Orthopedics of the National Academy of Medical Sciences of Ukraine.

The main group under examination included 11 patients aged 39 to 69 years with signs of vertebral canal stenosis at the lumbar-sacral level that had a long-term pain syndrome, which forced the attending physician to conduct an epidural adhesiolysis. The number of men treated was 4, and

women – 7. The distribution according to age groups was uneven: 1 man in the young age, 2 men and 1 woman of the middle age, 1 man and 6 women of the elderly age.

In the room where the examination was conducted the temperature was maintained within 20 – 22 °C and relative air humidity – 50 – 60 %. On the eve of the examination, all physiotherapy and warm-up procedures, as well as anti-inflammatory, antipyretic, vasodilator or vasoconstrictive drugs were canceled. 3 – 4 hours before the examination the patients were to stop smoking. 2 – 3 hours before the examination, various ointment applications were removed and the surface of the skin was degreased with a mixture of 40 % ethyl alcohol and ether (4: 1 ratio). Immediately before the examination, the patients underwent a temperature adaptation for 15 – 20 minutes. At that time they were in a state of rest, without the static and dynamic tension of the muscles. Measurement of thermometric parameters from the patient's skin surface was performed in real time for 3 minutes with a thermoelectric device for measuring temperature and heat flows. During the measurement, the time of thermal adaptation (in sec) – t (the time from the beginning of examination to the attainment of "saturation" of the main device indicators) was fixed, as well as the temperature and heat flow density under "saturation". Thermoelectric sensors were applied in the region of the spine symmetrically on both sides paravertebrally at the level of the spinous processes of the L4-L5 vertebrae.

Control group included 20 persons aged 23 to 62 years. Male persons were 8, and female – 12. In the young age, 7 men and 5 women were examined, in the middle age – 1 man and 6 women, in the elderly age – 1 woman.

As the trials have shown, in control group, the fluctuation of the basic thermometric parameters in the paravertebral areas was symmetrical and practically did not differ according to the "left / right" test. Heat and thermal adaptation of skin cover in contact with the surface of thermoelectric sensors took place simultaneously and had the form of a flat curve with clearly visible saturation. In so doing, all control group kept the total volume of movements in the lumbar sacral region of the spine, there were no painful sensations of spinous processes and paravertebral areas in the lumbar sacral zone, there were no signs of sensory impairment, reflexes in the affected areas. It should be noted that there was a tendency to change the basic figures, depending on the age, which is given in Table 2.

According to preliminary trials, in control group persons, the temperature of the skin in paravertebral areas in the lumbar-sacral division of the spine increases with age and the time of attainment of "saturation" decreases and the value of heat flow density in these zones drops.

Table 2

Thermometric indicators of control group persons

Age categories	Men			Women		
	t, (c)	t, °C	q, (mW/sm^2)	t, (s)	T, °C	q, (mW/sm^2)
Young age n = 12 (m = 7, w = 5)	45.3 ± 0.3	34.6 ± 0.5	17.1 ± 0.1	41.0 ± 0.2	34.3 ± 0.6	19.1±0.4
Middle age n = 7 (m = 1, w = 6)	28.1 ± 0.3	35.1 ± 0.2	14.8 ± 0.5	36.2 ± 1.2	35.1 ± 0.9	14.7±0.8
Elderly age n = 1 (m = 0, w = 1)	–	–	–	31 ± 0.6	36.2 ± 0.4	11.6±0.3

The following trend has been noted in persons who have been diagnosed with vertebral canal stenosis in the lumbar sacral region of the spine on the background of degenerative-degenerative diseases. For the young man, the time of attainment of "saturation" has sharply decreased to 14 s (normally - 45.3 ± 0.3 s); the temperature of the skin has decreased to 30.9 °C (normally – 34.6 ± 5 °C); the value of the heat flow density has increased to 45.2 mW/sm^2 (compared with

17.1 ± 0.1 mW/sm^2 in the control group). After the epidural adhesiolysis he showed a decrease in all the initial indicators: the time to "saturation" decreased to 20 s, the temperature of the skin surface to 29.8 °C and the density of the heat flow – up to 30.9 mW/sm^2. This suggests that long-term pain syndrome has led to oppression of the sympathetic part of the nervous system and the body needs a long time to restore its adaptive capacity.

The following study outcome has been obtained for middle-aged men. For each of the two patients, until the procedure, the time to reach the saturation reduced to 20 s and 9 s, respectively (in the control group – 28.1 s), the skin surface temperature in paravertebral areas decreased to 27.5 °C and 30.9 °C (versus 35.1 °C in control group). Against this background, one man reduced the density of the heat flow to 6.8 mW/sm^2 (in control this figure was 14.8 mW/sm^2). Such a phenomenon can be explained by the expressed signs of stagnation in venous plexus of the epidural space. After the epidural adhesiolysis in these patients the temperature indicators increased by 6.6 °C and 5.1 °C, the values of the heat flow density increased by 5 mW/sm^2 and 28 mW/sm^2. For one patient, the time to "saturation" increased by 4.4 s, while for the other – decreased by 2 s, which can be explained by the degree of thermoreceptor storage within the epidural space due to the long-term pain syndrome. A middle-aged woman maintained a similar tendency with regard to the time of attainment of "saturation" (14 against versus 36.2 ± 1.2 s in control), a decrease in temperature (29.0 °C versus 35.1 ± 0.9 °C in control). A similar reduction was shown by heat flow density: 10.5 mW/sm^2 versus 14.7 mW/sm^2. Five days after the manipulation, a woman showed a slight tendency to increase in the temperature of the skin in the paravertebral area by 0.4 °C and a significant increase in the density of the heat flow by 19.7 mW/sm^2. The time to attainment of “saturation” increased to 38 s after the procedure. Such changes can be explained by the peculiarities of neuroendocrine changes in females at this age.

In the elderly age, males who had been treated with epidural adhesiolysis were not observed. In this age group, 6 women were observed. The following results were obtained. All women drastically reduced the time from the beginning of examination to the attainment of "saturation" (15.0 ± 0.3 s versus 31 s from the control group). The temperature indicators in this area decreased (31.9 ± 0.2 °C in the main group versus 36.2 ° C in the control group), the density of the heat flow increased to 23.4 ± 2.4 mW/sm^2 versus 11, 6 mW/sm^2 for the woman in the control group. The obtained data could show that elderly-aged women with prolonged pain syndrome on the background of spinal stenosis in degenerative-dystrophic diseases of the lumbar-sacral spine showed increased activity of the sympathetic department of the autonomic nervous system on the background of inhibition of the activity of the parasympathetic region as a result of prolonged venous congestion in this spine region. After the manipulation (epidural adhesiolysis), the time to attain the "saturation" of thermal indicators did not change significantly. There was a tendency to normalize the temperature indicators in this age group (the temperature increased by 2.54 ± 0.9 °C compared to the first day of the examination), as well as a sharp increase in the density of the heat flow after the procedure (the density of the heat flow was 54.2 ± 2.4 mW/sm^2). This could indicate that in the elderly-aged persons, as a result of prolonged illness, there is a sharp suppression of the parasympathetic part of the autonomic nervous system and a longer time is required for its recovery compared to persons of younger groups.

Thus, preliminary clinical trials provide an opportunity to diagnose inflammatory processes, in particular, in neurological manifestations of spinal osteochondrosis, and to monitor the efficacy of conservative treatment in degenerative-dystrophic diseases of the lumbar-sacral spine.

It should be noted that the authors of this work are pioneers in the neuro-orthopedics of this method of examination of patients, and to confirm the reliability of the results of preliminary clinical

trials, it is necessary to recruit more numerous main and control groups and conduct similar studies for more patients, which will be the goal of further research in this direction.

Conclusion

1. A two-channel thermoelectric device for measuring temperature and density of heat flows has been developed which has the ability to store, process and visualize the measurement results on the display of the device and the personal computer in real-time mode.
2. Based on the preliminary clinical trials, it was established that the thermoelectric device makes it possible to diagnose inflammatory processes, in particular, in neurological manifestations of vertebral osteochondrosis, and to determine the efficacy of using epidural adhesiolysis in the treatment of pain syndrome in degenerative-dystrophic diseases of the lumbar-sacral spine.
3. The proposed device is promising for monitoring temperature and thermal human state in real time, which makes it possible to reveal at the early stages the inflammatory processes, various diseases and perform instant diagnosis during mass examination of patients.

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ТЕРМОЕЛЕКТРИЧНИЙ ПРИЛАД ДЛЯ ДІАГНОСТИКИ ЗАПАЛЬНИХ ПРОЦЕСІВ ТА НЕВРОЛОГІЧНИХ ПРОЯВІВ ОСТЕОХОНДРОЗУ ХРЕБТА ЛЮДИНИ

У роботі наведено результати розробки термоелектричного приладу, що призначений для одночасного вимірювання температури і густини теплових потоків поверхні тіла людини контактним способом. Розроблено спеціалізовану комп'ютерну програму "TermoMonitor" для обробки результатів вимірювань, їх накопичення і відтворення у заданому вигляді на персональному комп'ютері, що дає можливість здійснювати моніторинг температурного та теплового стану людини у реальному часі. Наведено особливості конструкції приладу, його технічні характеристики та результати попередніх клінічних випробувань. Бібл. 28, рис. 3, табл. 2.

Ключові слова: термоелектричний сенсор, густина теплового потоку, температура, запальні процеси організму людини, остеохондроз хребта.

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ТЕРМОЭЛЕКТРИЧЕСКИЙ ПРИБОР ДЛЯ ДИАГНОСТИКИ ВОСПАЛИТЕЛЬНЫХ ПРОЦЕССОВ И НЕВРОЛОГИЧЕСКИХ ПРОЯВЛЕНИЙ ОСТЕОХОНДРОЗА ПОЗВОНОЧНИКА ЧЕЛОВЕКА

В работе приведены результаты разработки термоэлектрического прибора, который предназначен для одновременного измерения температуры и плотности тепловых потоков поверхности тела человека контактным способом. Разработано специализированную компьютерную программу "Termomonitor" для обработки результатов измерений, их накопления и воспроизведения в заданном виде на персональном компьютере, которая дает возможность осуществлять мониторинг температурного и теплового состояния человека в реальном времени. Приведены особенности конструкции прибора, его технические характеристики и результаты предварительных клинических испытаний. Библ. 28, рис. 3, табл. 2.

Ключевые слова: термоэлектрический сенсор, плотность теплового потока, температура, воспалительные процессы организма человека, остеохондроз позвоночника.

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COMPUTER SIMULATION AND OPTIMIZATION OF THE DYNAMIC OPERATING MODES OF THERMOELECTRIC REFLEXOTHERAPY DEVICE

The paper presents the results of computer simulation of optimal dynamic operating modes of thermoelectric reflexotherapy device. Optimal time function of control of power supply current to thermoelectric micromodules in the multichannel reflexotherapy device was determined which ensures given cyclic temperature influence on the bioactive points of the human body. Bibl. 13, Fig. 6.

Key words: computer simulation, optimal dynamic mode, temperature influence, thermoelectric probe, reflexotherapy device.

Introduction

General characterization of the problem. Reflexotherapy is a complex of therapeutic and diagnostic methods of influence on the bioactive acupuncture points of the human body surface. For influence on such bioactive points, irritants of different strength, character and duration are employed. They are applied by special needles (acupuncture), burning or cooling (thermo-reflexotherapy or cryo-reflexotherapy), electric current using special appliances (electro-reflexotherapy), dilute air (vacuum reflexotherapy), permanent magnetic field (magneto-puncture), laser pulsed radiation (laser reflexotherapy), ultrasonic radiation (ultrasonic reflexotherapy) and others. [1 – 4].

The above reflexotherapy methods are based on stimulation of the reflex zones of the nervous system, resulting in pulses transmitted to the corresponding centers of the nervous system. The nervous system, in turn, directs pulses to the affected biological tissues that activate the self-healing process. Reflexotherapy helps to treat diseases of the spine (osteochondrosis, radiculitis, etc.); hernias of intervertebral discs and protrusions; headaches and dizziness occurring on the background of a cervical osteochondrosis; intercostal neuralgia, as a consequence of osteochondrosis in the thoracic spine, and also fights with the following problems: insomnia, recovery from trauma, depression, overweight, weakening of immunity, weakness, problem skin, stress, neurosis, etc. [3, 4].

Thermoreflexotherapy – the effect of heat on the biological points of the human body, as well as cryoreflexotherapy (exposure to cold) have come in widespread acceptance [5 – 7]. Cold causes a rapid constriction of the blood vessels, and then their expansion. This gives a powerful impetus to the blood circulation system, and, as consequence, the activation of metabolic processes. As a result, pain

in the affected area is reduced, venous and lymphatic blood flow, as well as the condition of connective and cartilaginous tissues is improved.

In [8 – 11] it was shown that the traditional method of thermal influence on the biologically active points of the human body has a number of disadvantages; their elimination is possible due to the use of thermoelectric devices whose operation is based on the use of the Peltier effect. The use of such devices makes it possible to obtain the assigned, precisely controlled temperature, while excluding the mechanical impact on the corresponding areas of the human body. However, thermoelectric devices developed by this time have no possibility of computer control of power supply current to thermoelectric modules to reproduce the necessary pre-set dynamic temperature modes.

So, *the purpose of this work* is development of computer methods for simulation and optimization of the dynamic operating modes of thermoelectric reflexotherapy device.

Design and technical description of thermoelectric reflexotherapy device

An experimental sample of thermoelectric reflexotherapy device "ALTEC-7009" (Fig. 1) intended for treatment of various human diseases by means of reflexotherapy method – thermopuncture – was developed at the Institute of Thermoelectricity of the NAS and MES of Ukraine. The operating principle of this device is based on a cyclic thermal effect on the acupuncture bioactive points of the human body (heating or cooling of several bioactive points simultaneously). Technical characteristics of the device are given in [11].

Fig. 1. Thermoelectric reflexotherapy device "ALTEC–7009":
1 – device power supply and control unit, 2 – thermoelectric probe,
3 –personal computer (PC)

The device makes it possible to reproduce given optimal functions of changing the temperature of thermoelectric probe in the range (–10 ÷ +50)°C and the time of exposure to given temperature. The transition from one temperature value to another occurs automatically after the expiration of the specified time of exposure. The device schematic provides for the opportunity of smooth setting the time of exposure to selected temperature value in the range of 10 ÷ 250 s. Thus, a doctor has an opportunity to select the necessary temperature mode and the time of its influence on the bioactive points of the human body.

Said device is composed of two main parts – power supply and control unit and 20 thermoelectric probes.

The power supply and control unit of the thermoelectric device "ALTEC-7009" consists of the following functional units: a programmable microcontroller (temperature and cycle duration setting unit), a thermostat (temperature setting unit), a timer (time setting unit), a temperature and time

display unit, a connecting board for functional units and power supply. The thermostat and timer, in turn, contain an input amplifier, a current generator, a time pulse generator, two comparators, and units for protecting thermoelectric micromodules from overcooling and overheating (in case of emergency). It should be noted that the use of programmable microcontroller allows you to set from the keyboard of PC virtually any temperature and time modes of the device. With the well-proven clinical methods of thermoelectric probe influence on the bioactive points of the human body, in the memory of the device one can write a set of typical dynamic operating modes, which accelerates considerably the process of device preparation for carrying out therapeutic procedures. The block-diagram of the device is given in [11].

The thermoelectric probe contains a thermoelectric micromodule, which is mounted on the radiator housing.

The thermoelectric probe is located in a housing with a meshed cover. There is also a thermoelectric micromodule with a built-in temperature sensor and a fan for cooling the hot side of the micromodule. The design and overall dimensions of the thermoelectric probe are given in Fig. 2 [8 – 11].

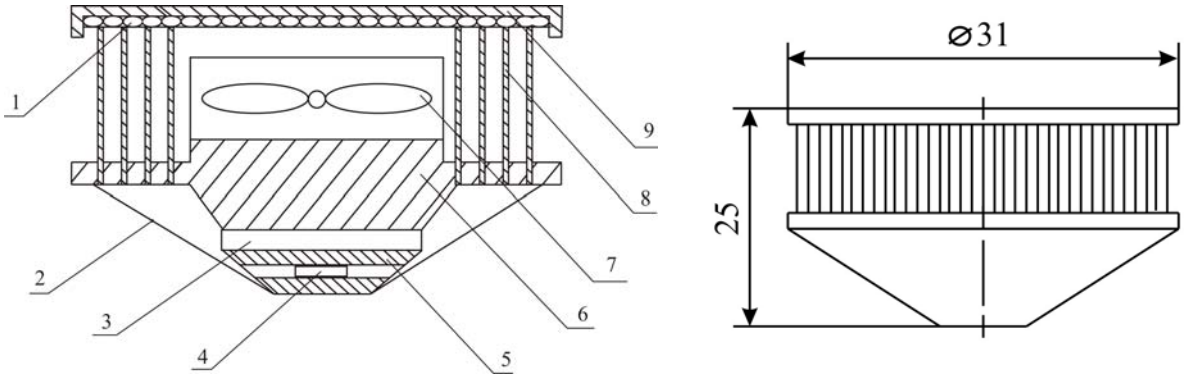


Fig.2. Design and overall dimensions of thermoelectric probe:
1 – protective net, 2 – outer case of stainless food steel, 3 –thermoelectric micromodule,
4 – temperature sensor, 5 – concentrator, 6 –radiator housing (base),
7 –fan, 8 –radiator, 9 – cover

The device design employs thermoelectric micromodules "ALTEC-98A", the technical characteristics of which for the mode of maximum cooling capacity have the following values: $I_{max} = 1.8$ A; $U_{max} = 3.9$ V; $Q_{max} = 3.6$ W at a temperature of $T = 300$ K. The ceramic plates of the micromodule are covered with nickel and gold, which allows the air radiator to be soldered to the hot surface of the micromodule, and to the cold surface – a concentrator made of high-temperature material and designed for temperature influence on the bioactive point or area of the human body.

Thermoelectric probes are mounted with regard to optimal thermal mode of their operation and protection against the influence of external thermal and mechanical factors. As temperature sensors, silicon pulse diodes are used, the voltage drop on which has a practically linear temperature dependence in the operating temperature range. A special mount is provided for the fixation of thermoelectric probe which has different dimensions depending on the location of the probe on the human body. The thermoelectric probe protective case is made of stainless food steel, since it is in contact with human skin.

On the basis of the existing methods during therapeutic sessions of thermal effect on the bioactive points in the traditional way [1 – 4] and the results obtained during previous clinical trials, the optimal temperature and time interval of cryothermic influence on the bioactive points of the

human body was established [8 –11]. Full cycle schedule of the device operation in the mode of maximum value of the time of exposure to set temperature in the range of -10 °C÷+50 °C is shown in Fig. 3.

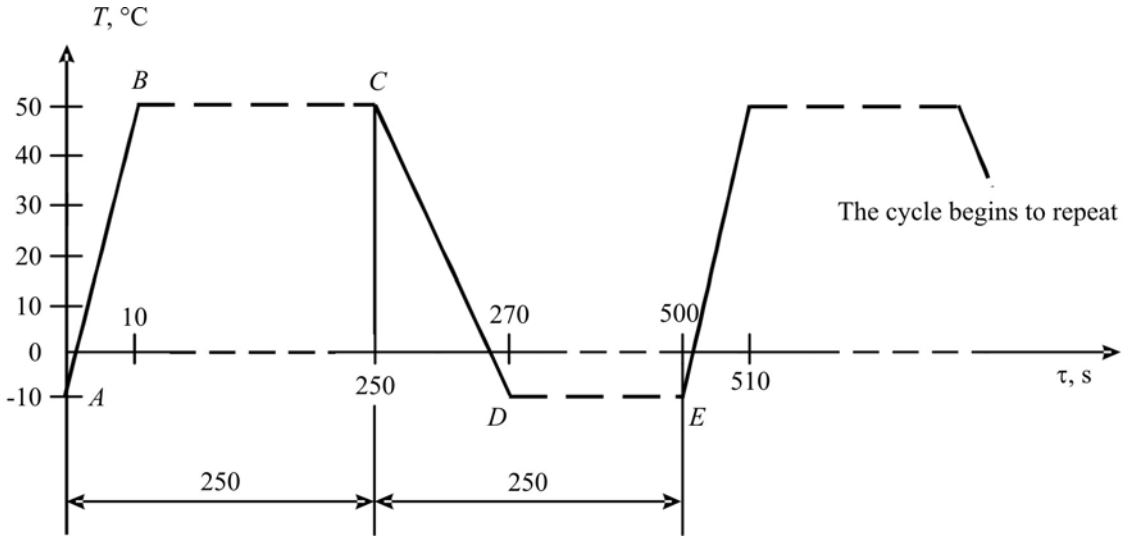


Fig. 3. Full cycle schedule of thermoelectric reflexotherapy device:
AB –heating mode – 10 s; BC –steady-state mode – 240 s; ABC = AB + BC = 250 s;
CD –cooling mode – 20 s; DE – steady-state mode – 230 s; CDE = CD + DE = 250 s.

As is seen from Fig. 3, transition from the established temperature value -10 ºC to +50 ºC takes place in 10 sec, transition from +50 ºC to –10 ºC – in 20 sec, and, hence, maximum exposure to steady-state in case of heating is 240 s, and in case of cooling – 230 s. The rate of temperature change in heating mode is 6 ºC per second, and in cooling mode – 3 ºC per second.

Consequently, due to the establishment of the correct cyclic thermal effect on the acupuncture points of the human body, various diseases can be treated and prevented from occurring.

In order to determine optimal time functions of control of power supply current to thermoelectric modules ensuring given dependences of cooling temperature change with time, computer simulation methods should be used. The results of computer simulation are given below.

Computer simulation of optimal dynamic mode of thermoelectric reflexotherapy device

The problem of computer simulation of the unsteady-state operating mode of the reflexotherapy device is to determine the time function of control of power supply current to thermoelements $I(t)$ which ensures given time dependence of the device working surface temperature $T_c(t)$.

The problem was solved with the use of the following approximations in the device model. It is assumed that all thermoelements of the module which is used in the device are identical and are under the same conditions. Thermoelement legs of height l and cross-section s are made of materials of n- and p-type conduction. Characteristics of leg materials, namely the Seebeck coefficient $\alpha_{n,p}(T)$ and resistivity $\rho_{n,p}(T)$ are temperature-dependent, and coefficients of thermal conductivity $\kappa_{n,p}$ and heat capacity $c_{n,p}$ are assumed to be constants due to their inessential temperature dependence in thermoelectric materials for coolers. It is assumed that heat-releasing surface of thermoelements is maintained at a fixed temperature T_h, the lateral surfaces of legs are adiabatically insulated. On the hot junctions of thermoelements we take into account the absorption or release (depending on the direction of current) of the Peltier heat and the release of the Joule heat on the contacts of junction with contact

resistance r_c. Account is taken of the total volumetric heat capacity g of interconnect and insulating plates of the module and copper cone-shaped device probe per one thermoelement. Thermal load of power q_0 which is created in working mode on thermoelement cold junction due to heat release from the human body is taken into consideration.

For such a model the temperature distribution in thermoelement legs is given by a system of one-dimensional equations of the unsteady-state heat conduction in the form

$$\begin{cases} c_n \dfrac{\partial T_n}{\partial t} = \kappa_n \dfrac{\partial^2 T_n}{\partial x^2} + \rho_n(T)\dfrac{I^2(t)}{s^2} - T_n \dfrac{\partial \alpha_n(T)}{\partial T_n}\dfrac{I(t)}{s}\dfrac{\partial T_n}{\partial x} \\ c_p \dfrac{\partial T_p}{\partial t} = \kappa_p \dfrac{\partial^2 T_p}{\partial x^2} + \rho_p(T)\dfrac{I^2(t)}{s^2} - T_p \dfrac{\partial \alpha_p(T)}{\partial T_p}\dfrac{I(t)}{s}\dfrac{\partial T_p}{\partial x} \end{cases}, \tag{1}$$

where $x \in [0, l]$, $t \in [0, t_{\max}]$. $I(t)$ is current in thermoelement legs which is a function of time. Equations (1) take into account the influence of the Thomson effect that arises in the bulk of thermoelement legs due to temperature dependence of the Seebeck coefficients $\alpha_{n,p}(T)$.

The boundary conditions for these equations are given by

$$\left[\kappa_n s \frac{\partial T_n}{\partial x} + \kappa_p s \frac{\partial T_p}{\partial x}\right]_{x=0} - \left[\alpha_p(T(t)) + \left|\alpha_n(T(t))\right|\right] I(t) T_c(t) - g\frac{\partial T_c(t)}{\partial t} + 2\frac{r_c}{s} I^2(t) + q_0 = 0,$$
$$T_n(l,t) = T_p(l,t) \equiv T_h, \tag{2}$$

where $T_c(t)$, the temperature of thermoelement working surface, is the assigned function of time.

The initial temperature distribution in the legs corresponds to the steady-state distribution at initial current value I_0 and is assigned as a function

$$T_{n,p}(x,0) = C_0 I_0^2 x^2 + C_1 x + C_2. \tag{3}$$

where C_0, C_1 and C_2 are constants determined by solutions of steady-state thermal conductivity problem in thermoelement legs at direct current I_0.

As mentioned before, the problem is to find current control function $I(t)$ such that ensures given time dependence of cold temperature $T_c(t)$.

The method of solving this problem is described in [12]. For the formulated problem the solution is obtained in the form of the following integral equation:

$$I(t) = \frac{1}{\alpha T_c(t)}\left[\frac{r_c}{s} I^2(t) + \frac{\kappa}{c}\frac{\rho}{sl}\int_0^{at} K(t-\tau) I^2(\tau) d\tau + \Phi(t, T_c(t))\right], \tag{4}$$

where

$$\Phi(t, T_c(t)) = -g\frac{dT_c(t)}{dt} - \frac{r_c}{s} I_0^2 + A - \frac{\kappa s}{l}\int_0^{at} \vartheta_1(t-\tau)\frac{dT_c(\tau)}{d\tau} d\tau - \frac{\kappa}{c}\frac{\rho}{sl} I_0^2 \int_0^{at} K(\tau) d\tau,$$

$$A = \alpha I_0 \frac{\dfrac{\kappa s}{l} T_h + q_0 + \left(0.5 + \dfrac{r_c}{\rho l}\right)\dfrac{\rho l}{s} I_0^2}{\alpha I_0 + \dfrac{\kappa s}{l}},$$

$$a=\frac{\kappa}{cl^2},\quad K(t)=\vartheta_1(t)-\vartheta_0(t),\quad \vartheta_1(t)=1+2\sum_{k=1}^{\infty}\exp(-\pi^2k^2at),\quad \vartheta_0(t)=1+2\sum_{k=1}^{\infty}(-1)^k\exp(-\pi^2k^2at),$$

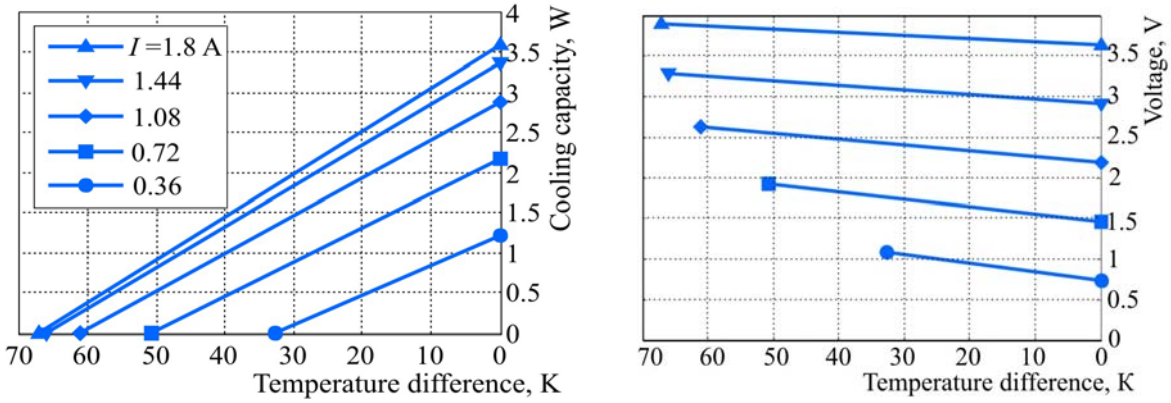
$$\alpha=(\overline{\alpha_p}+\left|\overline{\alpha_n}\right|)/2;\quad \rho=(\overline{\rho_p}+\overline{\rho_n})/2,\quad \kappa=(\kappa_p+\kappa_n)/2,\quad c=(c_p+c_n)/2,$$

$$\overline{\alpha_{n,p}}=(\alpha_{n,p}(T_h)+\alpha_{n,p}(T_c(t)))/2,\qquad \overline{\rho_{n,p}}=\frac{1}{(T_h-T_c(t))}\int_{T_c(t)}^{T_h}\rho_{n,p}dT.$$

Equation (4) is nonlinear and solved by numerical successive approximation method. The algorithm for solving such an equation is implemented using computer simulation software developed in the MathLab environment.

Computer simulation results

Simulation of current control function which would ensure given time dependence of operating temperature (Fig. 3) was performed for thermoelectric module "ALTEC-98A" used in the reflexotherapy device, which comprises 62 legs of height $l = 0.093$ sm, cross-section area $s = 0.058\times0.058$ sm^2, and contact resistance value $r_c = 5\cdot10^{-6}$ Ω·sm^2. The legs are made of *Bi-Te* based materials of *n*- and *p*-type conductivity with standard thermoelectric characteristics $\alpha_{n,p}$, $\rho_{n,p}$, $\kappa_{n,p}$, $c_{n,p}$ [13]. Module characteristics, namely dependences of cooling capacity and voltage on temperature differences for different supply currents are shown in Fig. 4.



a) *b*)

Fig. 4. Characteristics of thermoelectric micromodule "ALTEC-98A": a)dependences of cooling capacity on temperature difference on the module for different supply currents, b) dependences of voltage on temperature difference.

The total volumetric heat capacity of interconnect and insulating plates of the module and copper probe per one leg was $g = 0.0064$ J/K. The heat release of the human body was assumed to be equal to 5 mW/sm^2, which creates thermal load on the device thermoelectric leg $q_0 = 0.017$ mW.

In conformity with medical requirements, in the working mode the reflexotherapy device should provide a periodic time dependence of temperature on the skin surface $T_c(t)$ shown in Fig. 5.

The operating mode starts from cooling temperature -10 °C. The initial steady-state temperature distribution in thermoelements, whereby on the device cooling surface under no thermal load the temperature -10 °C is set, is ensured by supplying the module with direct current I_0. The value I_0 is determined on the basis of characteristics of module "ALTEC-98A" (Fig. 4a) and makes $I_0 = 0.45$ A. In the operating mode (Fig. 5) within 10 s the device probe should warm up from -10 °C to +50 °C and maintain this temperature for 240 s with subsequent cooling to -10 °C within 20 s.

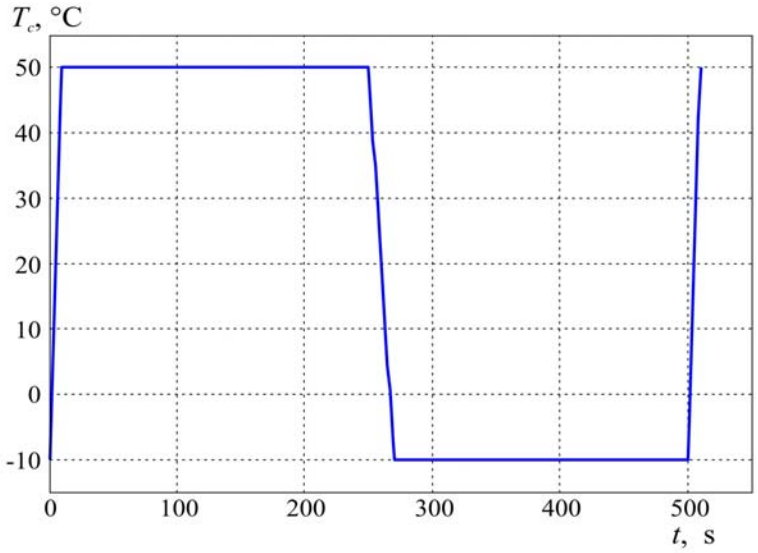


Fig. 5. Given time dependence of operating temperature $T_c(t)$ of thermoelectric reflexotherapy device.

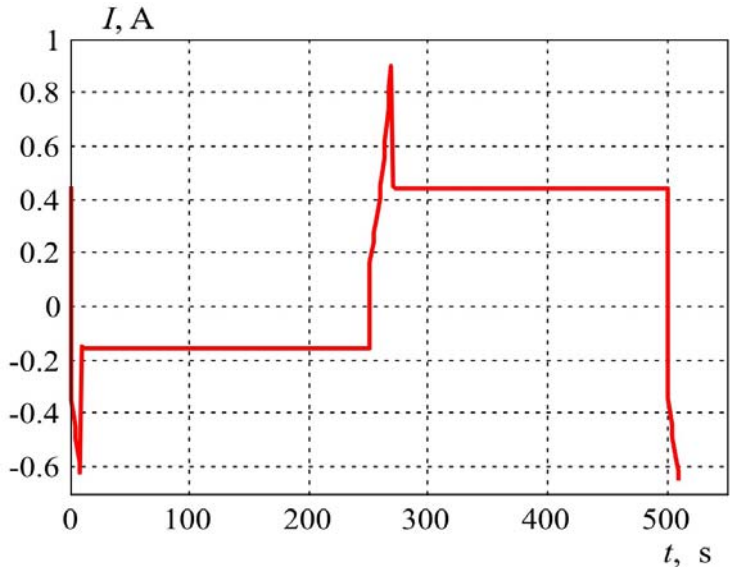


Fig. 6.Calculated function of control of power supply current to thermoelectric module I(t).

Obviously, this function is periodic. Current direction which ensures working surface heating is considered to be negative, and cooling – positive. Within 10 s, current value should be changed from 0.45 A to -0.6 A, varying current direction, and its value should be reduced to -0.18 A, in order to maintain heating at the level of 50 °C within 240 s. Afterwards, for cooling, current direction is changed for the opposite, within 20 s its value is increased to 0.9 A and reduced to 0.45 A, in order to maintain the temperature of device working surface at the level of -10 °C for the next 230 s. This cycle is periodically repeated.

Thus, the results of computer simulation give an opportunity to increase the accuracy of prediction of cyclic temperature influence on the bioactive points of human body and obtain a positive curative effect in the course of therapeutic procedures.

Conclusion

1. Computer simulation was used to determine optimal time function of control of power supply current to thermoelectric micromodules in a multichannel reflexotherapy device which ensures given cyclic temperature influence on the bioactive points of the human body
2. Functions of this type are used for the design and auto-calibration of special electronic controller which provides the work of automatic temperature control system for thermoelectric reflexotherapy device.

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КОМП'ЮТЕРНЕ МОДЕЛЮВАННЯ ТА ОПТИМІЗАЦІЯ ДИНАМІЧНИХ РЕЖИМІВ РОБОТИ ТЕРМОЕЛЕКТРИЧНОГО ПРИЛАДУДЛЯ РЕФЛЕКСОТЕРАПІЇ

У роботі наведено результати комп'ютерного моделювання оптимальних динамічних режимів роботи термоелектричного приладу для рефлексотерапії. Визначено оптимальну часову функцію керування струмом живлення термоелектричних мікромодулів у багатоканальному приладі для рефлексотерапії, якою забезпечується заданий циклічний температурний вплив на біоактивні точки тіла людини. Бібл. 13, рис. 6.

Ключові слова: комп'ютерне моделювання, оптимальний динамічний режим, температурний вплив, термоелектричний зонд, прилад для рефлексотерапії.

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КОМПЬЮТЕРНОЕ МОДЕЛИРОВАНИЕ И ОПТИМИЗАЦИЯ ДИНАМИЧЕСКИХ РЕЖИМОВ РАБОТЫ ТЕРМОЭЛЕКТРИЧЕСКОГО ПРИБОРА ДЛЯ РЕФЛЕКСОТЕРАПИИ

В работе приведены результаты компьютерного моделирования оптимальных динамических режимов работы термоэлектрического прибора для рефлексотерапии. Определено оптимальную временную функцию управления током питания термоэлектрических микромодулей в многоканальном приборе для рефлексотерапии, которой обеспечивается заданное циклическое температурное влияние на биоактивные точки тела человека. Библ. 13, рис. 6.

Ключевые слова: компьютерное моделирование, оптимальный динамический режим, температурное влияние, термоэлектрический зонд, прибор для рефлексотерапии

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FURTHER DEVELOPMENT OF KELVIN APPROACHES TO CREATING AN ABSOLUTE TEMPERATURE SCALE

Based on the analysis of Lord Kelvin's scientific achievements, in particular in the field of thermodynamics and thermoelectricity, and guided by the advances in nanotechnology, the possibility of temperature quantization and reasonably grounded basis for creating a quantum temperature standard is demonstrated. For the application of the standard, in addition to the quantum standards of electric resistance and electric voltage, it is proposed to employ the thermoelectric method, since the thermoelectric power, in the concept of the Chernivtsi School of Thermoelectricity, integrates the action of elementary eddy currents caused by the flow of individual electrons through the current-temperature converting element of the standard. As a result, due to the creation of a quantum temperature standard, it becomes possible to achieve an increase in the accuracy of the reproduction of the International Practical Temperature Scale, first proposed in its modern form by Lord Kelvin. Bibl. 21, Fig.4 .

Key words: quantum temperature standard, temperature scale, reduced quantum temperature unit, base SI units.

The story behind and current state of affairs in the implementation of temperature scales

Early temperature scales

The temperature scales changed during the development of technical thought. In a more or less modern form, that is, the scale with two fixed points (beginning and end of the scale), was proposed by the Frenchman René A. Reomyr in 1730 (now the degrees Reoumur completely out of use). Its zero was the point of freezing water, and one degree (°R) corresponded to a change in the volume of alcohol with a solid strength of 96° to 1/1000. Considering that when the temperature changes from 0°C to 100°C, the volume of alcohol changes by 8%, the boiling point of water is defined as 80°R. The commonly used degrees Celsius, which in reality are not degrees Celsius, and just degrees of "centigrade scale" did not appear immediately. In 1742 the Swedish astronomer A. Celsius proposed a "reverse" scale: in it the water boiled at zero degrees, and froze – at a hundred. Already after his death in 1744 the scale was "turned" by M. Strömer (ice melting temperature was now taken as 0°C, and water boiling temperature – as +100°C). In this form the scale is used up to now.

The so-called Leiden degrees (°L), which were used at the beginning of the 20th century by the Kamerlingh-Onnes Laboratory in Leiden, became the prototype for the "absolute" temperature scale. In this scale, the boiling point of liquid hydrogen (–253 C), which consisted of 75% orthohydrogen and 25% parahydrogen, was taken as zero. Another reference point is the boiling point of liquid oxygen

(–193°C). Eventually, two absolute temperature scales appeared that are used today – Kelvin and Rankin. The zero of both coincides with the absolute zero temperature, and one degree corresponds to a change of 1°C/K (Kelvin scale) or 1°F (Rankin scale – USA) (Fig. 1).

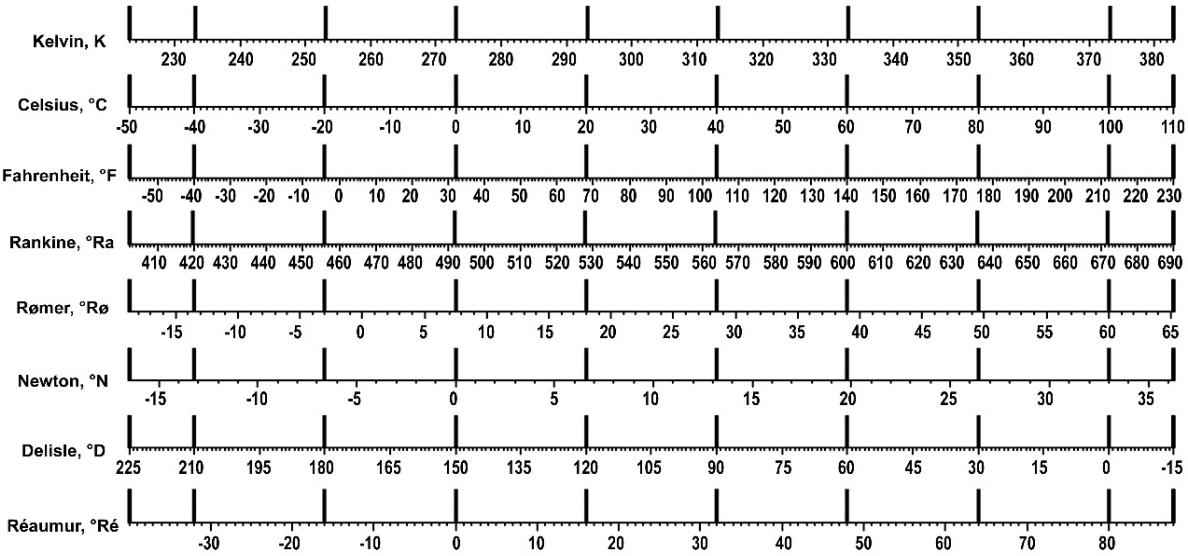

Fig. 1. Known temperature scales and the ratios of thermometer readouts when they are simultaneously used to measure equal temperatures (vertical line); to the left are the names of thermometric scales.

Kelvin (K), until 1968 – degree Kelvin (°K), SI base unit. Named after the Irishman William Thomson (1824-1907), who was born in Scotland and became a great English scientist, awarded for his scientific achievements the title of Lord Kelvin – the name of the river flowing through the University of Glasgow. 0 K corresponds to –273.15°C and, on the contrary, 0°C is equal to +273.15 K. At the moment, "kelvin" is the name of the thermodynamic temperature scale and at the same time the dimension of the unit of temperature of the same scale. The definition of this scale is based on the materials of the 10th General Conference of Weights and Measures in 1954, which assumed that the main reference point of the scale is the temperature of the triple point of water –273.16 K. In addition, kelvin is the interval of the International Temperature (Kelvin) Practical Scale.

Since Lord Kelvin substantiated the above-mentioned scale, as well as the 2nd law of thermodynamics, he is considered to be one of the three founders of thermoelectricity. For example, the primary reference thermocouple is a thermocouple that has a specific temperature dependence of the integral thermo-EMF determined in accordance with the methods of implementing the Kelvin International Practical Temperature Scale.

Temperature scale and other scientific achievements of Lord Kelvin

In addition to the talent for mathematics, Lord Kelvin (William Thomson) was able to solve applied problems. Among his main inventions and discoveries are:

- the absolute temperature scale;

Kelvin understood that it would be useful to accurately determine the extremely low temperatures. He noticed that the molecules stop their movement at an absolute zero, and in 1848 he proposed an absolute temperature scale – now called "Kelvin Scale" – where the absolute zero corresponds to a temperature of 0 Kelvin (0 K). The Kelvin definition of the absolute temperature scale is particularly important in the field of superconductivity. This phenomenon was discovered after the death of Kelvin. And nowadays, as a snake bites its own tail, the superconducting carbon

nanotube, which is considered below, is the main core in the creation of the Quantum Temperature Standard, which can become the major support of the modernized Kelvin scale. Moreover, the next feature embodied in the design of the temperature standard relates to Lord Kelvin's next achievement – thermocouple and thermo-EMF.

- the second law of thermodynamics;

The study of the nature of heat led Kelvin to formulate the second law of thermodynamics and, at the same time, to form the basis of thermoelectricity.

- telegraph cables and a mirror galvanometer;

In 1856, Kelvin became director of the Atlantic Telegraph Company, who was hired to install a telegraph cable across the Atlantic Ocean. The laying of the first Atlantic cable in 1857 failed. In 1858, the laying succeeded with the use of a measuring instrument called a mirror galvanometer (Kelvin's invention) for measuring electric current passing through a cable. The nowadays technology, in the end, could not substitute the mirror galvanometer of Kelvin.

- marine measuring equipment, including high-precision watches;

Kelvin was a keen sailor and used his skills to solve maritime problems; invented several tools that improved navigation and safety at sea**.** His inventions included: nautical compass; machine for audio signals; astronomical clock. Kelvin's talent as a physicist and an interest in navigation led him to create and patent in 1869 his own version of the astronomical clock. Below we will note the need for accurate time measurement to ensure the operation of the Quantum Temperature Standard.

- atomic research;

In the 1860s, Kelvin was interested in the structure of atoms. He watched the rings of smoke, and suggested that the atoms are mutually structured in a spiral, like whirls one around another. His hypothesis was taken with enthusiasm for 20 years and was refuted by later studies. Today, the peculiarities of the atomic motion are thoroughly studied by scientists at the National Physical Laboratory of Great Britain, which is considered to be the leading research center in the world. On May 18-19, 2015, about 50 researchers in the field of thermometry from all over the world gathered at the International Center of the Royal Society in Chicheley Hall, Buckinghamshire, to discuss the progress of the implementation of the new kelvin in 2018 before redefining as the base SI unit. At that time Michael de Podesta presented probably the most accurate measurements of temperature in human history, based on the observations of the atomic motion.

- tetrakaidekagedron (a geometric body with a minimum possible surface area limited by 14 planes);

Kelvin simulated a geometric figure (polyhedron), formed by 14 faces – a three-dimensional shape with the smallest surface area. No one was able to improve this model until 1993, when the Weaire-Phelan model with a surface area appeared to be only 0.3% less than the Kelvin model. So, we can conclude that Kelvin is involved in the creation of an energy efficient type of outer housing. It is not improbable that further study of the heat dissipation intensity from the heating zone of the Quantum Temperature Standard will allow the application of the Kelvin solution to minimize heat losses and improve the accuracy of the transfer of the temperature unit size to the reference thermocouple.

Improvement of temperature scale and transfer of temperature standard to quantum physical base

Introduction

At the end of the 20th century, as a result of intensive research in the field of nanotechnology, six *(*m, A, kg, s, mole, cd) of the seven base units of the SI system, except for the temperature unit, K, were expressed through fundamental physical constants [1]. A similar result was obtained for a number of other quantities of the SI system. The obtained standards are considered "internal", since they are determined on the basis of the mentioned constants, and not constructed using the invariability of material artifacts, such as platinum-iridium wire in the standard unit of length. Their work is based on the determination of the discrete value of a particular physical quantity or its fixed size (quantum), which makes it possible to construct a scale of this quantity.

Formation of a new generation temperature standard based on fundamental physical constants

The state for 2015-2016 is best presented in [2]. The current definition of the unit of thermodynamic temperature, kelvin, is based on the material artifact, namely on the temperature of the triple point of water. The latter depends on its isotopic composition, purity, etc., and therefore is characterized by significant uncertainty. The need for a measurable and reproducible quantum temperature standard was demonstrated by the work of scientists presented at the 13th International Symposium TEMPMEKO-2016, whose activities concerned this radical thermometry problem: CODATA found the need to redefine the concept of "Temperature" [3], as long as temperature – a physical quantity that characterizes the internal energy of bodies, is not directly measured nowadays. All measuring means convert the temperature to any other physical quantity which can be recorded experimentally. Taking into account that the temperature is connected with the energy through the Boltzmann constant, it was proposed to replace the temperature measurements with the energy ones and thus to avoid the methodological error caused by the calibration of means for measuring the temperature of the triple point of water T_{TPW} [4]. A series of leading metrology centers (USA, UK, etc.) have developed [2-3] a new definition of the unit of temperature: Kelvin, K, is the unit of thermodynamic temperature; its size is determined by fixing the numerical value of the Boltzmann constant equating to 1.380 65 ... $\cdot 10^{-23}$ and expressed in units of $s^{-2}m^2kgK^{-1}$ which are equivalent to J/K. The result of the introduction of the proposed definition is as follows: 1 K will be determined by the change in the thermodynamic temperature, which leads to a change in thermal energy per kT – 1.380 65 ... $\cdot 10^{-23}$ J. The benefits of such replacements are obvious: the size of kelvin, by the new definition, becomes independent of material; fixed reference point (the temperature of the triple point of water) with the uncertainty of its definition (~ 0.01 K) is no longer needed.

This contributes to a more precise definition and transfer of the thermodynamic temperature unit size directly by the methods of primary thermometry, in particular at very high and low temperatures (the primary thermometry assumes that a specific measuring instrument is related to a certain measurand (T), which can be determined by direct calculation of the results without use of any other unknown quantities, but only using fundamental physical constants, as the coefficients of proportionality). In this case, it is necessary to pre-determine with the highest accuracy the value of the Boltzmann constant, to which a series of perfect works based on various physical principles is devoted. Current value of k, recommended by CODATA, is determined by the results of acoustic thermometry of gases [4-5].

Unfortunately, the one-sided approach to replacing the direct determination of the temperature by the indirect (due to the use of the expression $E = kT$, the energy measurements are carried out with the well-known Boltzmann constant), forms new difficulties. Replacing temperature measurements with the energy ones is inevitably involved with a number of problems in the area of ultralow energy measurements which may be due to the sensitivity of measuring instruments, the establishment of the minimum size of energy or unit energy, the insufficient thermal insulation and heat removal,

particularly intensive in the low-temperature range [6-7]. Moreover, when the proposed method is used as the basic one, an additional error is introduced into the obtained results, since according to the principles of metrology [8] the indirect measurement is less accurate than the direct measurement: the error δT is replaced in the indirect method by the sum of two errors: $\delta E + \delta k$. So, it was proposed to involve the only fundamental physical constant, namely the Boltzmann constant. The temperature quantum, just as the energy quantum, was not singled out.

The state for 2017 has changed in connection with the achievements of the Lviv School of Thermometry [9]. For the second time after M. Planck, who has introduced the temperature T_P (temperature quantum in the Planck system of units) which can act as the defining unit of the temperature scale: 0°C = 273.15 K = $1.9279 \cdot 10^{-30}$ T_P [10], the existence of a quantum temperature measurement unit was proved [11]. Moreover, the possibility of its realization was shown [12] on the basis of the existing quantum standards: of electric resistance [13] and voltage U [14] and the draft installation for getting a controlled and pre-determined temperature jump with the use of thermoelectric device was discussed.

Investigation and determination of a temperature quantum

Macro- and nanoproperties expressed through the fundamental physical constants in the case of temperature as the major physical quantity in the SI system. Taking into account in consideration only the Boltzmann constant related to electron scattering energy in collisions with atoms may be incomplete, and, hence, not quite correct. By ignoring the processes of acquiring energy by electrons, where other fundamental physical constants may be involved, such as the Planck constant, the model under consideration can not be considered perfect. Taking into account the two aspects of the process contributes to the balanced solution of the problem of determining the temperature quantum, as a manifestation of thermal energy release (in the case of passing electric current) by conduction electrons when they interact with atoms.

There is an effective way to study the macroproperties of materials through their nanoproperties. It is clearly demonstrated by the example of the Hall quantum effect research [13]: a relation between the macrocharacteristic (the von Klitzing constant having a resistance dimension) was found, expressed in the quantized value of the measured electric resistance 25812.807 557 ± 0.0040 Ohm, with nanosized characteristics of the substance (electron charge e and the Planck constant h). There is a similar relation between the electric voltage and the above fundamental physical constants [15].

Possibility of temperature quantization and the existence of a temperature quantum. We will prove the possibility of the existence of a temperature quantum as a manifestation of the properties of a macroscale substance at the electron-phonon interaction, that is, the interaction at the nanoscale. We will consider the passage of small currents through a material with the Klitzing effect. It can be a semiconductor material or one of the types of carbon materials (graphene [17] or nanotubes [18]). Specifically, the process takes place at low-medium temperatures [17] on the contacts of the superconducting carbon nanotube, on graphene or other substance, where the quantum Hall effect is fixed, with a conductor/semiconductor material (for carbon nanotubes of several nanometers in diameter the conduction electron exhibits mainly wave properties. Through such nanotubes, the electrons pass in the same way as light waves pass through light guideways. Thus, electricity in the nanoworld turns into optics, and the Joule heat is dissipated only at the boundary of the nanoworld, where a nanotube is connected to an external wire, that is, on the contacts with the lead-in wires. We derive the formula: $R_{Kl} = h/e^2$ relating a quantum of resistance to the fundamental physical constants. Suppose voltage U is applied between the specified contacts of the nanotube, and the current strength

in it is *I*. Since energy is not dissipated, its change between sections *A* and *B* is $\Delta E = eU$. This occurs during time interval Δt equal to transit time between the contacts. The Heisenberg uncertainty relation imposes restrictions on the changes, which implies that $U \geq \frac{h}{e\Delta t}$. We estimate the current in a nanotube as a one-dimensional quantum structure. In it, as in the helium atom, only two electrons with different spins can coexist. It means that current *I* between the contacts is $I = 2e/\Delta t$. Hence, it is easy to derive the formula for the desired resistance: $R_{Kl} = U/I = h/e^2$. Since nanotubes do not give off heat, they are able to pass currents of huge density – more than 10^7 A/cm^2. If the carbon nanotubes were of normal conductivity, then at these currents their temperature would increase to 20000 K, exceeding the combustion temperatures – 700 K).

Structurally, it is proposed to perform research on one of the most commonly used designs of field-effect transistors (CNTFET), namely on a transistor with a superconducting carbon nanotube embedded as a gate [18]. The source and drain are made of different materials forming together a quasi-thermocouple through the nanotube as the hot junction. A similar structure is characterized by the electric resistance 25812.807 557 ± 0.0040 Ohm caused by the resistive properties of the lead contacts only.

When studying electric energy dissipation ($I^2R = U^2 / R$) on such electric resistance in the region of temperature measurement:

$$E = U^2 \Delta t / R_{Kl} = I^2 R_{Kl} \Delta t = N \frac{3}{2} kT, \tag{1}$$

we will note that it is possible to evaluate the temperature jump ΔT due to dissipation of *N* electrons. Replacing the equation by $I = \frac{\Delta Q}{\Delta t} = \frac{Ne}{\Delta t}$ (Δt – time), we reduce it to:

$$\frac{(Ne)^2 h}{(\Delta t)^2 e^2} \Delta t = N \frac{3}{2} kT, \tag{2}$$

which describes electric current formation per unit time by *N* conduction electrons which transfer their own energy $\frac{3}{2}kT$ to atoms. Hence, the jump of temperature ΔT at current *I* through superconducting nanotube (cooling is considered to be minor) is determined as:

$$\Delta T = \frac{2hI}{3ke} = \frac{2hN}{3k\Delta t}, \tag{3}$$

Otherwise, the increase in temperature is due to the relaxation of electrons on phonons in the contact zone of the transistor gate with the source/drain. At a fixed number of electrons per second it is determined through the fundamental physical constants (*h* and *κ*) and equals $2h \cdot 1s./3k = 3.2 \cdot 10^{-11}$ K under the condition of dissipating 1 e/s. When powered by an array of the Josephson contacts, it is possible to pass a certain controlled number of electrons through an element with the quantum Hall effect. The quantity reduced to dissipation of one electron on phonons per unit time or to a single-electron current is called by us as the reduced quantum temperature unit (RQTU) and is defined by the expression:

$$\Delta T\big|_{\substack{\Delta t \to 1s \\ N \to 1}} = \frac{2h}{3k}\left[\frac{K}{s}\right] \cdot 1[s], \tag{4}$$

Its value does not depend on the factors of influence and the type of substance, but is completely determined by the ratio of 2 fundamental physical constants (*h*/*k*). The RQTU under consideration is recommended for creation of quantum temperature standard. The operation of such

standard is based on 2 quantum effects (the Klitzing and the Josephson effects). The value of RQTU, measured in realtion to the SI units, is characterized by uncertainty, which is determined by the sum of two uncertainties: the Planck constant h and the Boltzman constant k [19], forming together the total relative uncertainty $59.2 \cdot 10^{-8}$.

We draw attention to the fact that the uncertainties of the Planck constant and the Boltzmann constant are given in the NIST tables as the averaged values of the physical constants determined by several relevant physical methods. For example, to study the Planck constant, the method of power balance was applied, the methods of studying: the density of crystal by X-ray scattering, the magnetic resonance, the Faraday constant, the Josephson constant. As a result, the recommended by CODATA 2010 rms uncertainty for determining the Planck constant is $u_h = 4.4 \cdot 10^{-8}$.

The methods for determining the Boltzmann constant are as follows: from the equation of state of ideal gas; by studying the dielectric constant of gas; by studying the velocity of sound propagation therein; from the Nyquist equation when studying the electron thermal noise; by measuring the radiation intensity of the blackbody; by measuring of sound velocity in gas-like helium which is in quasi-spherical resonator (of volume 0.5 l) at a temperature close to the temperature of a triple point of water (273.16 K) [20]. Moreover, a laser method for measuring the Boltzman constant is introduced, which allows achieving the uncertainty of $2 \cdot 10^{-4}$ as a result of successive 61-hour measurements [21].

Interrelations of the major SI units and their determination through the fundamental physical constants

According to the results of the study it was established that presented in [14] interrelations of the base SI units (Fig. 2) and the principles of determining these units through the fundamental physical constants (Fig. 3) undergo a modification, and it is indicated by the corresponding arrows.

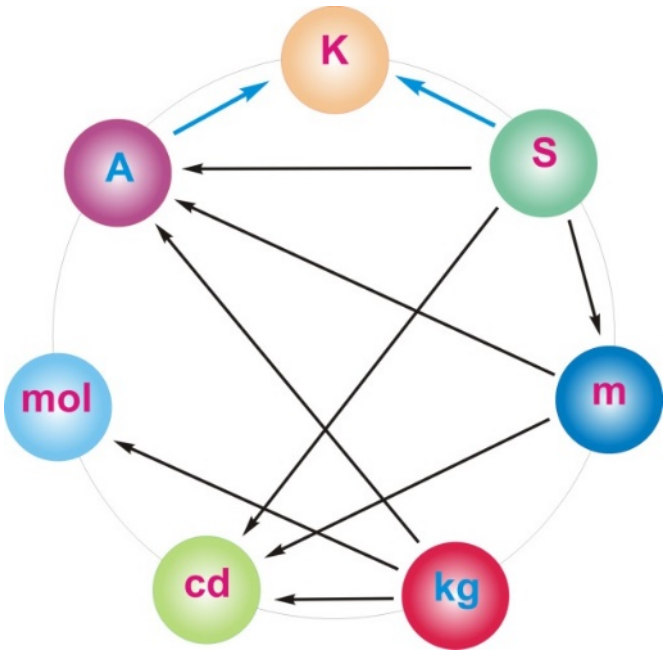

Fig. 2. Interrelations and mutual definitions of the major SI units: blue arrows show the revealed relationship between the investigated quantity T and the quantity I, A (through the quantities V and R), as well as the quantity t, s.

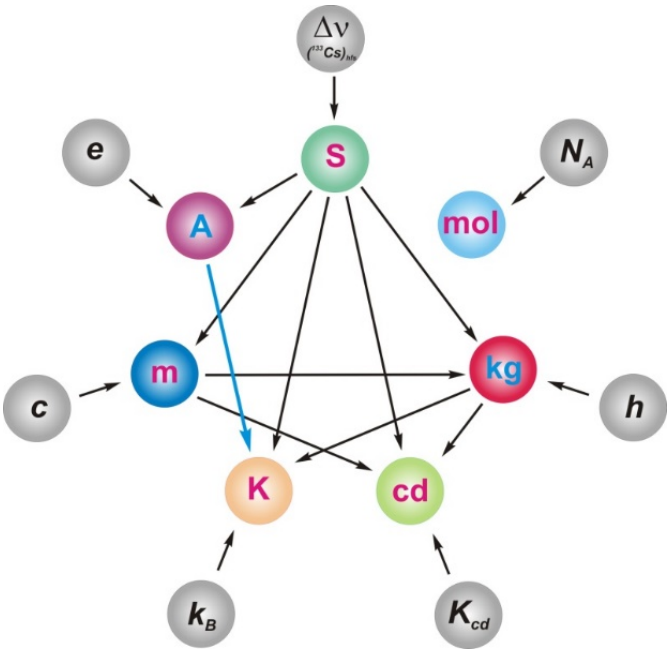

Fig. 3. Principles of studying the SI units through the fundamental physical constants: elimination of relationship between units m and T (black arrow), and the appearance (blue arrow) of the relationship between units I, A and T, K.

Metrological concept of a temperature quantum and the possibility of its implementation

The obtained RQTU is defined through known from [19] values of constants *h* and *k* and makes $3.199\ 493\ 42 \cdot 10^{-11}$ K with a relative standard uncertainty $59.2 \cdot 10^{-8}$. Note that this consideration is purely phenomenological, since the authors understand the simplicity of the above considerations regarding the dissipation of a single electron and the transfer of all of its acquired energy to phonons. In fact, for minimal, hard to observe changes in the temperature ~ 10^{-11} K due to one-electron relaxation, we are not able to fix such small jumps of temperature, and therefore have to work with considerably larger currents, to which statistical thermodynamics can already be applied.

This means that theoretically and practically one should: a) increase the current through a nanotube/semiconductor with a quantum Hall effect; b) use electronic phenomena with a pronounced integration effect to register a weak temperature signal. First of all, it is a thermoelectric effect, which is based on elementary eddy currents corresponding to the cooperative motions of groups of electrons. Since 1 A is defined as $6.2415093 \cdot 10^{18}$ electrons passing through the conductor cross section per 1 second, then, provided that the electronic pump is capable of counting 10^8 electrons per 1 second or an ammeter of measuring the electric current of $6.24 \cdot 10^{-10}$ A, we must measure the temperature jump $3.2 \cdot 10^{-11}$ K $\cdot$ 108 = $3.2 \cdot 10^{-3}$ K. This value is measurable: at a sensitivity of ~ 43 μV/K of K-type thermocouple, the measured value is ~ 0.14 μV, and with a tenfold higher sensitivity of the semiconductor thermocouple, the resulting value obtained reaches 1.4 μV. The above uncertainty of $59.2 \cdot 10^{-8}$ allows us to assert that the desired value (temperature jump $3.2 \cdot 10^{-3}$ K) is determined with an absolute uncertainty of ~ $1.9 \cdot 10^{-9}$ K.

This is the main advantage of the temperature standard created on the basis of fundamental physical constants. Proceeding from the predetermined value of the temperature jump with a certain relative and absolute uncertainty, one can propose a methodology for creating an extremely helpful temperature standard which refers to primary thermometric means and is qualified by analogy with the known quantum standards of other quantities of the SI system as an “internal standard”.

Creation of temperature standard on the basis of a temperature quantum

The study opens the opportunity in principle and indicates the way to create a temperature standard based on fundamental physical constants. For these purposes, it is proposed to involve the existing standards based on the fundamental physical constants: 1) electrical resistance standard based on the inverse of conductance quantum [13]; 2) voltage standard based on the Josephson contacts [14] which can produce voltage pulses quantized in integer values of h/2e with precision frequency-to-voltage transformations (the synthesized voltage is determined through known values of the number of pulses, clock frequency and fundamental physical constants) (Fig. 4).

The quantum temperature standard is realized as follows. In the quantum standard of electrical resistance, based on one of the common types of field transistor designs, CNTFET [18], the source and drain are made of two dissimilar conductive materials, for example, of nickel and copper. The latter form a thermocouple with a quasi-junction in the form of a superconducting carbon nanotube (3d intermediate body in the circle based on the basic laws of thermoelectricity) of ~ 0.1 μm long. Thus, provided the number of electrons passing through the nanotube contacts is determined, we can measure the temperature jump by a thermoelectric method with a minimal methodological error (or with maximum reliability in the uncertainty approach) on the structural element of the standard.

The operating mode of the installation is as follows. The same device serves as a generator of the known temperature jump at the 1st stage, and is used to measure the temperature by thermoelectric method at the 2nd stage. Since the device under study is powered by a sequence of short (~ 10^{-2} s) voltage pulses, at the 1st stage, a given current is fed to the device, and at the 2nd stage (in the absence of an electric current), with the help of the thermocouple described above, the temperature increase is measured. Thus, the same device – the "internal" temperature standard – serves as a generator of a previously known temperature jump at the 1st stage, as well as a temperature measuring instrument at the 2nd stage.

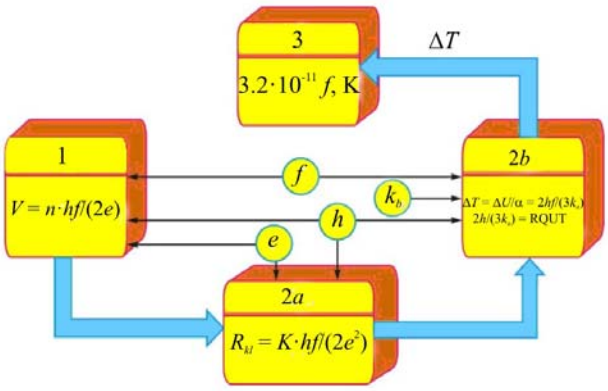

Fig. 4. Block-diagram of temperature standard based on RQTU and transfer of unit size from it to working standards: 1 – voltage standard based on the array of the Josephson junctions; 2a – carbon nanotube as the base of a field-effect nanotransistor; 2b – unit size transfer block; 3 – working temperature standard (reference thermocouple).

Further transfer of a given value of the temperature jump from the standard to the reference thermocouple is carried out in a traditional way, placing its hot junction close to the CNT-quasi-junction of the temperature standard. With a deviation of temperature increase recorded by it from the value of standard temperature jump which may be due to heat losses, a correction factor is introduced.

For more significant heat losses, it is possible to offer the use of thermal screens, even executed in the form of a 14-hedron, that is, according to Lord Kelvin.

Conclusion

For almost two centuries the inventions and discoveries of the great scientist live and work for humanity, being used in everyday life, scientific and applied research. Each time we measure the temperature, we inevitably turn to Kelvin. Carefully approaching the achievements of the present, we will try to evaluate them through the prism of heritage of the great William Thomson, the 1st Lord Kelvin.

1. Progress in the measurement of physical quantities is determined by provision the measuring instruments with standards built using quantum effects, based on the invariance of fundamental physical constants. Accordingly, the progress in temperature measurements and the improvement of the absolute temperature scale was hampered by the absence of such a standard. Considering electron-phonon dissipation on electric resistance inversely proportional to conductance quantum, the existence of temperature quantum expressed in terms of the ratio of fundamental physical constants h/k (the Boltzmann constant and the Planck constant) was first proved.
2. It is shown that at a dissipation of one electron per second, a temperature jump is obtained, defined as a reduced quantum of temperature, equal to $3.199\ 493\ 42 \cdot 10^{-11}$ K, with a relative standard uncertainty of $59.2 \cdot 10^{-8}$ determined due to the known values of fundamental physical constants. For the experimental fixation of the effect of the temperature jump through the quantum resistance, it is necessary to pass the electric current at least 0.1 nA = 10^8 e/s; then a temperature jump of $\sim 10^{-3}$ K is obtained, which is sufficient for fixing it with a built-in nanothermometer (nanothermocouple), as well as for further transferring the temperature unit size, for example, to the reference thermocouple. The thus built temperature standard can provide step-by-step transfer of temperature size (quantum), starting from the temperature sufficiently close to the absolute zero.
3. The proposed temperature standard can be recommended for use as an "internal" standard, which does not require repetitive measurements and verification to ensure and validate the declared accuracy, in contrast to the classical standards for physical quantities of the SI system. "Internal" standards are becoming increasingly important metrological instruments for the spread of accurate measurements, as an example in cyber-physical systems, whose elements are scattered in space and time.

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ПОДАЛЬШИЙ РОЗВИТОК ПІДХОДІВ КЕЛЬВІНА У СТВОРЕННІ АБСОЛЮТНОЇ ШКАЛИ ТЕМПЕРАТУР

На основі аналізу наукових здобутків Лорда Кельвіна, зокрема у галузі термодинаміки й термоелектрики, та керуючись досягненнями нанотехнологій, показано можливість квантування температури й обмірковано підстави для створення квантового еталону температури. Для прикладної реалізації еталону, окрім квантових еталонів електричного опору та електричної напруги, запропоновано використати термоелектричний метод, оскільки термоЕРС, у концепції Чернівецької школи термоелектрики, інтегрує дію елементарних вихрових струмів, зумовлених протіканням окремих електронів крізь струмо-температурний конвертувальний елемент еталону. У результаті, внаслідок створення квантового еталону температури можна досягнути підвищення точності відтворювання Міжнародної практичної температурної шкали, вперше запропонованої в її сучасному вигляді саме Лордом Кельвіном. Бібл. 21, рис. 4.

Ключові слова: квантовий еталон температури, температурна шкала, приведена квантова одиниця температури, система СІ

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ДАЛЬНЕЙШЕЕ РАЗВИТИЕ ПОДХОДОВ КЕЛЬВИНА В СОЗДАНИИ АБСОЛЮТНОЙ ШКАЛЫ ТЕМПЕРАТУР

На основе анализа научных достижений Лорда Кельвина, в частности в области термодинамики и термоэлектричества, и руководствуясь достижениями нанотехнологий, показана возможность квантования температуры и обсуждены основания для создания квантового эталона температуры. Для прикладной реализации эталона, кроме квантовых эталонов электрического сопротивления и электрического напряжения, предложено использовать термоэлектрический метод, поскольку термо-ЭДС, в концепции Черновицкой школы термоэлектричества, интегрирует действие элементарных вихревых

токов, обусловленных протеканием отдельных электронов сквозь токо-температурный конвертирующий элемент эталона. В результате, вследствие создания квантового эталона температуры, можно достичь повышения точности воспроизведения Международной практической температурной шкалы, впервые предложенной в ее современном виде именно Лордом Кельвином. Библ. 21, рис. 4.

Ключевые слова: квантовый эталон температуры, шкала температур, приведенная квантовая единица температуры, система СИ

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