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Address of editorial office:
Ukraine, 58002, Chernivtsi, General Post Office, P.O. Box 86.
Phone: +(380-372) 90 31 65.
Fax: +(380-3722) 4 19 17.
E-mail: jt@inst.cv.ua
http://www.jt.inst.cv.ua

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L.I.Anatychuk, *acad. National Academy of Sciences of Ukraine*,
O.J.Luste, *Doctor Phys.-math. Sciences,*
R.R.Kobylianskyi, *Candidate Phys.-math. Sciences*

Institute of Thermoelectricity of the NAS and MES of Ukraine,
1, Nauky str, Chernivtsi, 58029, Ukraine; *e-mail: anatych@gmail.com*
Yurii Fedkovych Chenivtsi National University, 2, Kotsiubynskyi str.,
Chernivtsi, 58012, Ukraine*; e-mail: anatych@gmail.com*

INFORMATION-ENERGY THEORY OF MEDICAL PURPOSE THERMOELECTRIC TEMPERATURE AND HEAT FLUX SENSORS

In this paper, temperature and heat flux sensors are analyzed as the source of measurement information. The concept of informativeness of sensors and measuring devices is used. The informativeness of microcalorimeters, temperature and heat flux sensors is determined. Bibl. 14, Fig. 3.

Key words: information-energy theory, informativeness, entropy error value, energy sensitivity threshold of measuring instruments, thermoelectric temperature and heat flux sensor.

Introduction

In [1 – 5], general means for the description of measuring instruments as information sources were formulated and quality parameter of measuring instrument, i.e. informativeness $\Omega(t) = dI(t)/dt$, was introduced which shows how much measuring information $I(t)$ can be obtained from the instrument per unit time. For an arbitrary measuring instrument with entropy error distribution $\Delta(W)$ on the scale of measuring instrument averaged during measurement time τ, the expression for calculation of informativeness is given by [5]:

$$\Omega = \tau^{-1}\left\{\log\int\frac{dx}{2\Delta(x)}\right\}. \qquad (1)$$

Among microcalorimeter sensors, medical purpose temperature and heat flux sensors, the increasing attention of researchers and developers is attracted by high-voltage thermopiles with integration density of elements 10^4 sm^{-2} [1, 2]. They found application as miniature sources of electricity with increased voltage output of milliwatt and microwatt power range, as well as miniature coolers with reduced supply currents $10^{-2} – 10^{-1}$ A. Unlike standard thermoelectric modules that are practically not used in measuring equipment because of their low volt-watt sensitivity and unsatisfactory matching with the resistance of standard electrical measuring equipment, multi-element thermopiles have considerable application possibilities in microcalorimeters, heat meters and medical thermometers.

These possibilities need to be studied from the standpoint of modern information-energy theory of measuring instruments [3].

In [5], this approach was used to determine the informativeness of eddy thermoelements and measuring instruments on their basis, and multi-element thermopiles were considered in [6 – 14].

The purpose of this work is further development of physical foundations of informativeness theory of miniature multi-element sensors on the basis of information-energy theory of measuring instruments, namely selection of physical model, calculation of informativeness dependence on the number of thermopile elements and thermopile optimization for the number of elements.

The basics of informativeness theory of measuring instruments.

An exhaustive characteristic of measurement process can be only provided by full description of the law of probability distribution of measurement error as a random variable. A more concise description is the value of boundary error according to given value of confidence probability. Claude Shannon in his information theory proposed an integral characteristic of the error distribution law. It is a cumulative function of all points of the curve of the distribution law, that is, its entropy. The entropy of the error distribution law, the so-called conditional entropy $H(X/X_n)$, that can be calculated by the law of error probability distribution around instrument reading X_n, will be a concise characteristic of misinformation or the measure of uncertainty which will remain after getting of X_n. For this distribution of the probability of different values of errors occurring in these measurements, the value of unconditional entropy $H(X)$ can characterize the a priori-initial uncertainty of the measured variable, which we have prior to measurement, and which is determined by the law of distribution of the probability of different values of this variable. The above two statements imply that the amount of information $q = H(X) - H(X/X_n)$.

Thus, the exceptional advantage of entropy as a single numerical average-weighted characteristic of distribution law is its simple and unambiguous relation to the amount of information or misinformation which is present in the study of physical variable or introduced by noises.

Theory of probability employs numerical characteristics of various error distribution laws. When there is a statistical description of a random variable, then operations with such variables are mathematically cumbersome, so the numerical coefficients are often used to characterize the distribution, which are called moments. This is related to the fact that among the numerical characteristics of random variables we are interested in the location of this variable on the numerical axis, that is, systematic component of the variable (average value), since it determines the location of the area on the axis, in which the values of random variable are grouped. Such value is called its first moment or mathematical expectation. It is designated as $M[X]$. A moment is designated as a sum of products of all possible values of our discrete random variable on the probability of these values: $M[x] = \sum_{i=1}^{n} x_i P_i$, P_i is probability of x_i value. For continuous values this mathematical expectation: $M[x] = \int_{-\infty}^{+\infty} x \cdot p(x) dx$, $p(x)$ is the density of probability distribution of x. Having calculated mathematical expectation, one can find random deviations for each deviation result: $\Delta i = x_i - M[x]$.

Proceeding from this, it is possible to remove the systematic component from the data array, therefore distinguishing the initial moments (without excluding the systematic component) and the central moments (excluding but taking into account the systematic component).

For information theory, Shannon proposed another system of criteria describing distribution laws. To characterize component systems, in this case, as before, use is made of the first initial moment, that is, the value of mathematical expectation. To characterize the centered random

component, instead of all higher order moments, use is made of the moment which is written as:

$$H(x) = \int_{-\infty}^{+\infty} p(x) \ln p(x) dx \text{ – entropy} \qquad (2)$$

Thus, entropy is a functional of the law of distribution of random variables and takes into account the peculiarities of this law.

Shannon showed that the misinformation effect of random error caused by noise or interference when transmitting a signal is determined by the entropy of noise as a random variable. He proved that if the noise in probabilistic values does not depend on the signal transmitted, then regardless of the noise signal statistics, a certain H value can be attributed to the noise, which characterizes its misinformation effect.

This provision is proved by the theorem in which it is stated that the amount of transmitted information $q = H$ per noise entropy value is equal to:

$$q = H(x) - H(\Delta). \qquad (3)$$

Hence, the amount of information is less than the entropy of transmitted signal by the noise entropy value. If, in addition to the above information transmission channel, there is another parallel channel, then in order to eliminate the errors caused by the noise with the value $H(\Delta)$, this additional channel should be used to transmit additional amount of information the value of which Δq must be not less than $H(\Delta)$. This additional information can be encoded and used to correct all the errors due to noise, with the exception of a small part of them.

The use of fundamental provisions of information theory for characterization of measurement process.

The accuracy of measurements is characterized by the numerical value of the measured or possible errors, and to describe them, the concepts of the absolute and reduced errors are used. If a measuring instrument has measurement range from x_1 to x_2, then the measured variable has values that are within this range. The measurement error of this instrument is $\pm\Delta$. In so doing, it is assumed that this error does not depend on current value x of our measured variable. If we get the value x_n (in the range from x_1 to x_2), it can be written so that this reading is the value of our variable $\pm\Delta$, and the reduced error: $\nu = \pm\Delta/(x_2 - x_1)$.

These actions from the point of view of information theory have a different meaning. In this case, the probability of getting readings less than x_1 and more than x_2 is equal to zero, and the probability of getting readings in the range from x_1 to x_2 is equal to unity. If it is assumed that the density of probability distribution of different values of the measured variable along the entire instrument scale is the same, then our knowledge on the measured variable can be presented as a plot.

As long as full probability to obtain reading in the range from x_1 to x_2 is equals to 1, under our curve there must be an area that is conditionally equal to unity (normalization requirement) With an equally probable probability density distribution, this results in the fact that $P(x) = 1/(x_2 - x_1)$.

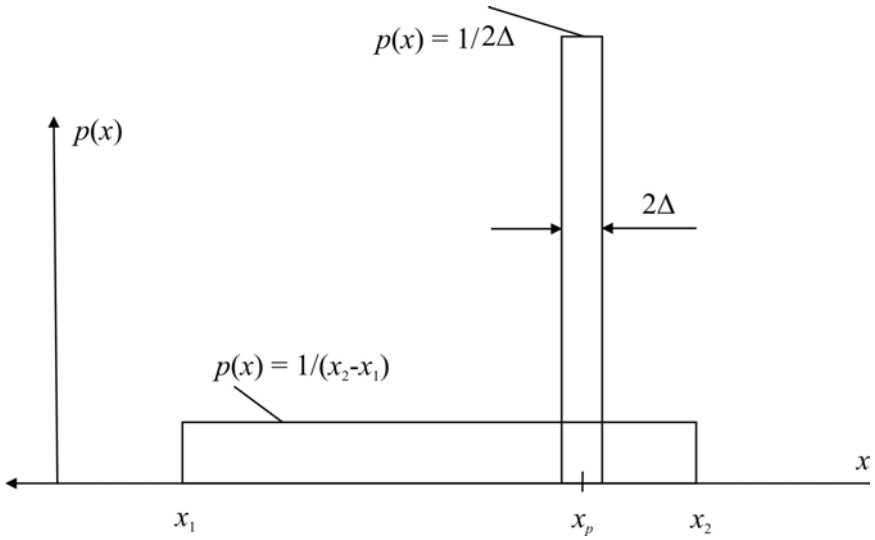

Fig.1. Narrowing of error interval in the process of measurement

After the measurements we get x_n. However, due to the error of any instrument we can write the result only in the form of x_n readings ±Δ. Then our value of the variable under study lies in the range of $x_n + \Delta$, $x_n - \Delta$, that is, in the band of width 2Δ.

Conclusion: from the point of view of information theory, the result of our measurements lies only in the fact that before the measurements the range of uncertainty should extend from x_2 to x_1 and be characterized by probability density $P(x) = 1/(x_2 - x_1)$, and after the measurements the uncertainty should reduce to the value 2Δ along the x axis and be characterized by much higher probability density equal to 1/2Δ. Therefore, to obtain information on the variable of interest for us, we must reduce the uncertainty of its value. In that case the amount of information will be:

$$q = H(x) - H(x/x_n). \tag{4}$$

As long as in the above example we deal with the uniform distribution of probability density, the value of the initial H can be written as:

$$H(x) = -\int_{-\infty}^{+\infty} p(x)\log p(x)dx = \int_{x_1}^{x_2} \frac{1}{x_2 - x_1}\log\frac{1}{x_2 - x_1}dx = \log(x_2 - x_1).$$

The part of H that will be written after readout:

$$H(x/x_n) = -\int_{x_n-\Delta}^{x_n+\Delta} \frac{1}{2\Delta}\log\frac{1}{2\Delta} = \log 2\Delta.$$

Then,

$$q = H(x) - H(x/x_n) = \log(x_2 - x_1) - \log 2\Delta = \log\frac{x_2 - x_1}{2\Delta} = -\log\frac{2\Delta}{x_2 - x_1}. \tag{5}$$

Replacement of division operation by the operation of calculating the initial variable and that which remained after measuring the uncertainties in the form of certain H values is the basic approach in the information theory of measurements.

Measurement as narrowing of the uncertainty interval.

When measuring physical variable by the natural scales, as shown earlier, the entire range of possible values of reference points was divided into a number of intervals. In so doing, the uncertainty of our variable with respect to the measured variable is determined by the fact that we do not know in which of the intervals our value is.

As a result of measurement, we established the interval between the reference points where our variable is located, that is, we reduced the uncertainty from the number of intervals to the width of one interval. Therefore, unlike metrology, from the standpoint of the information theory the result of measurement lies in the selection of given interval from the number of possible interval values. Thus, if the probability is falling of the measured variable into any of the intervals equal to each other, the uncertainty of our initial situation is equal to $H(x) = \log n$, n is the number of intervals. And a result of measurements, the amount of information that eliminates this uncertainty is $q = \log n$.

Hence it follows that measurement is a comparison of the measured variable to one way or another constructed scale of possible values of the measured variable, and the result of measurement lies in the selection of one interval from the totality of intervals of the entire scale.

The concept of the entropy value of the error.

The laws of probability distribution in different measuring instruments are largely different. This variety creates the basic difficulties in the determination of the effective value of the error that ambiguously characterized the absolute value of uncertainty interval. That is, the uncertainty that was left after instrument readout. Let us consider this problem on the basis of the distribution of the error laws for the uniform and nonuniform distributions.

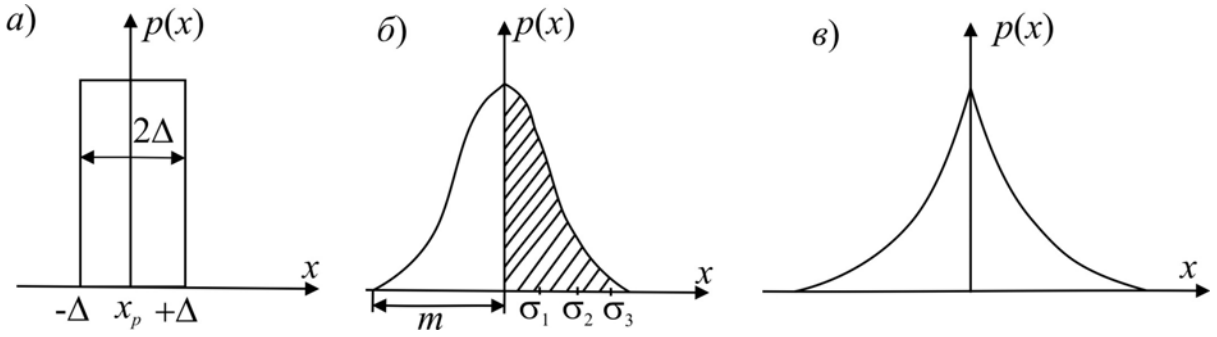

Fig.2. Entropy error for different distribution laws

In the case of error probability distribution close to uniform for multiple repetitions of x_p measurements, errors greater than +Δ and smaller than –Δ practically do not occur, and in the middle of this interval (2Δ) all error values are equally probable. In this case, the absolute value of uncertainty interval which is left after measurement process is found without information theory. The uncertainty interval is 2Δ, and indication of the error ±Δ characterizes the error of the instrument. In most instruments, the law of probability distribution is expressed by curves (b, c); for (b) it is practically impossible to specify intervals of uncertainty with increasing the error. A similar flat distribution can be characterized by the average value of the error, but the value of maximum error cannot be specified, because in (b) there may be arbitrarily large errors.

If the root-mean-square error δ for the normal distribution δ = 0.5 %, then an error of 0.5 % will fall on the average for every three measurements. However, every 22 tests we will encounter an error of the value 2δ, i.e. 1 %, and once per 370 and 15000 test we will encounter an error equal to 3 and 4δ

(1.5 % and 2 %). In this case, to determine the interval of uncertainty, we must attribute some Δ to the width of the error. This conditional value may be equal to the average probable error Δ = 0.6745σ, or 2/3 σ. In this case, if the law of the error distribution is indeed normal, then half of the errors that will occur to us will be less than this value, and the other half will make the errors that are larger than 2/3 σ. In that event it is indicated that the defining error is selected with a confidence probability 0.5, which testifies that any error that has occurred must be less that selected under the normal distribution law. If the band width is changed and chosen equal to σ, 2σ or 3σ, then under the normal distribution law it will correspond to confidence probability 0.67, 0.95 or 0.997. Without the information theory it is impossible to choose a well-grounded width of reliably identified measurement band.

Mathematical definition of the concept of entropy value of the error.

Solution of this problem was proposed by Shannon: the misinformation effect of noise or error depends on its distribution law and due to this it can be clearly indicated by calculating conditions $H(x/x_n)$ of this distribution law. However, studying the misinformation effect of noises with different laws of probability distribution of their amplitudes, he noticed that there is no unique correspondence between the noise power and its misinformation (the value of its entropy), as long as at the same noise power its misinformation is different and depends on the distribution law. With a certain root-mean-square value (equivalent to full noise power) the greatest misinformation effect (H) is produced by noises with the normal law of probability distribution. Under any other law of probability distribution the noise entropy with the same root-mean-square value is always smaller. Thus, under arbitrary law of probability distribution the misinformation effect of noise is determined not by the whole power thereof, but only by its certain part which Shannon called the entropy power of noise. When studying the informative ability of different instruments, one tries to make some simplifications, because to operate all the time with complete information on the laws of distribution is very difficult. In some cases, it is more convenient to operate not with the entropy power of the error, but with the entropy value of the error itself, since this value also determines the misinformation effect. To understand the concept of the entropy value of the error, we will consider the entropy for the example of the uniform and normal laws of probability distribution of these errors.

$$H\left(\frac{x}{x_n}\right) = -\int_{-\infty}^{\infty} p(x)\ln p(x)\,dx \qquad (6).$$

The probability density $p(x)$ for the uniform law can be written as:

$$p(x) = 0 \text{ for } x < -\Delta,\ x > +\Delta,$$

$$p(x) = \frac{1}{2\Delta} \text{ for } x > -\Delta,\ x < +\Delta,\ (|x| < \Delta),$$

$$H\left(\frac{x}{x_n}\right) = -\int_{-\Delta}^{+\Delta} \frac{1}{2\Delta} ln \frac{1}{2\Delta} dx = ln 2\Delta$$

For the uniform distribution law it is seen that the entropy of the error is equal to logarithmic uncertainty interval, or one can say that uncertainty interval is the value which is under the logarithm sign in the expression for H.

According to theory of random errors, the value of uncertainty interval can be expressed through the value of root-mean-square error. For the uniform distribution law, dispersion, that is, $\sigma^2 = \int_{-\infty}^{\infty} x^2 p(x)dx$, and within the uniform distribution:

$$\int_{-\Delta}^{+\Delta} x^2 \frac{1}{2\Delta} dx = \frac{\Delta^2}{3}.$$

For the uniform distribution law $\sigma = \frac{\Delta}{\sqrt{3}}$, and $\Delta = \sqrt{3} \cdot \sigma$, then the entropy

$$\mathrm{H}\left(\frac{x}{x_n}\right) = ln2\sqrt{3}\sigma.$$

If the error of measuring instrument is distributed around x_n by the normal law for which

$$p(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{x^2}{2\sigma^2}}.$$

In this case, for the normal distribution law the values of conditional entropy:

$$\mathrm{H}\left(\frac{x}{x_n}\right) = \int_{-\infty}^{\infty} p(x)\left(ln\sqrt{2\pi}\sigma + \frac{x^2}{2\sigma^2}\right)dx = ln\sqrt{2\pi}\sigma \int_{-\infty}^{\infty} p(x)dx + \frac{1}{2\sigma^2}\int_{-\infty}^{\infty} x^2 p(x)dx.$$

As long as the integral of $p(x)dx = 1$, and, by the definition of the concept of dispersion, the second plus is equal to σ^2, then we can write $\mathrm{H}\left(\frac{x}{x_n}\right) = ln\sqrt{2\pi}\sigma + ln\sqrt{e} = ln\left(\sqrt{2\pi e}\sigma\right)$.

This expression differs from that obtained earlier which is sharply bounded by the width 2Δ only by the expression under logarithm. Whence it follows that in terms of unbounded distribution in the form of a smooth curve (b) it yields exactly the same amount of information as the sharply bounded uniform distribution (a). In this case, $2\Delta = 2\pi e\sigma$, or in other words, the effective uncertainty interval caused by the smooth distribution curve is fully equivalent in the amount of introduced misinformation uncertainty caused by the uniform error band with the width $2\Delta = 2\pi e\sigma$. If the instrument with a uniform distribution (a) from the information standpoint is comprehensively characterized by the error $\pm\Delta$, equal to $\Delta = d/2$, then the instrument with error distribution by the normal law is exactly as much characterized by the effective value of the error:

$$\Delta = \sqrt{\frac{\pi e}{2}}\sigma \qquad (7).$$

The above approach to the determination of the effective value of the error (in the entropy sense) can be used with any integral laws of error distribution, just as the concept of the effective value of electric current is used in any form of the curve of this current.

The shape of the signal is characterized by the form coefficient K_f which is equal to the ratio of the effective value to the average rectification of the value of the alternating current (form factor).

Therefore, the entropy value of the error is the value of error with the uniform distribution law which has such a misinformation effect as the error with the given distribution law.

This definition reduces to the following.

If the error with the normal distribution law has conditional entropy, the effective uncertainty interval, irrespective of the distribution law, will be:

$$2\Delta = \exp\left(H\left(\frac{x}{x_n} \right) \right). \tag{8}$$

and the entropy value of the error which is defined as half the uncertainty interval, will be

$$\Delta = \pm \frac{1}{2} \exp H\left(\frac{x}{x_n} \right) \tag{9}$$

Thus, as a result of the introduction of the concept of entropy value of the error, we gained an opportunity to always replace any error with an arbitrary distribution law by the error with a uniform distribution and sharply bounded edges and the same entropy value. This will allow replacing the real error band of some distribution with smooth drops by the sharply bounded band with a uniform probability distribution, equivalent to it in the informative sense.

Brillouin's negentropy principle of information.

Since 1951 – 1956 Brillouin has published a number of works relating information theory to thermodynamics. For information storage we have to use ordered physical systems (strokes, electric pulses, magnetized spots, etc). These information media have one common property: they gradually lose the information stored in them due to interdiffusion of materials, demagnetization, etc. Therefore, the information entered into the system always decreases at a certain rate, in the extreme case it remains constant, but never increases.

When ordering is introduced into the system, it consumes energy, so the ordered system has a certain store of energy and can do the work. Moreover, due to insufficient isolation of the system from the environment this store of energy will be inevitably spent. In terms of thermodynamics, the possibility of implementation of work by the system is characterized by its negative entropy (negentropy). According to the 2nd principle of thermodynamics, the increase in entropy can be positive, it can only grow and never decreases. Accordingly, negentropy can only decrease, it decreases as the work progresses.

The properties of information, as understood in the theory of information, and the properties of thermodynamic entropy are identical. The formulae which describe these two concepts are also identical.

The Boltzmann-Planck formula:

$$S = k \cdot ln \cdot P .$$

The formula of information theory:

$$q = K \cdot ln\mathrm{N} ,$$

S is entropy; *P* is the number of elementary states of the system; *k* is the Boltzmann constant; *q* is information; *N* is the number of possible system states; *K* is coefficient that depends on the selection of system of units. If *K* = *k*, the information will be formally determined by the Boltzmann-Planck unit.

Entropy is related to probability, and it is possible to artificially create a closed isolated system with a very improbable structure. If this system is left as such, it will evolve to a more probable structure. On this basis, we conclude that probability has a natural tendency to increase, just like entropy.

Entropy can be interpreted in two ways: like a measure of disorder in the physical system or like a measure of lack of information on the structure of the system. The main conclusion made by Brillouin is that information can only be obtained as a result of energy expenditure, so any experiment yielding us information on the physical system or any physical measurements of the system parameters can be performed as a result of an increase in the entropy of the system or its environment. In so doing, the average entropy increase according to the 2nd law of thermodynamics is always greater than the information obtained.

Initial boundary certainty of measured variable.

In our attempt to more precisely determine the value of the measured variable we at some stage will encounter the impossibility of further refining it.This is most clearly observed when measuring discrete variables. For the majority of physical variables this limitation is not very obvious, since most physical variables are perceived not as discrete, but as continuous (analog). However, the continuity of measured physical properties is some kind of abstraction or approximation to real natural phenomena.Therefore, physically possible degree of certainty is finite and determined either by its own discreteness or fluctuations caused by principal discreteness of energy and substance. This limit of certainty in the microworld is known as the Heisenberg uncertainty principle.The energy of thermodynamic fluctuations, of both molecular phenomena and electric current phenomena in a closed circuit, is determined by the Nyquist equation. According to this equation, the average power of thermodynamic fluctuation $\overline{\mathrm{P}}_s = 4 \cdot k \cdot \theta \cdot \Delta f$, where k is the Boltzmann constant; θ is temperature; Δf is frequency band where these fluctuations are considered. If n readings are taken during the time of measurement of some variable, then the power of thermodynamic fluctuations of the averaged result will be reduced in inverse proportion to the number of averaged results, that is, $\overline{\mathrm{P}}_s = \dfrac{4 \cdot k \cdot \theta \cdot \Delta f}{n}$.

However, such a reduction of the average power of fluctuations will take place till the readings that are averaged will be independent of each other. According to sampling theorem, the number of independent readings of the function that has boundary value Δf during *t: n* = 2 · Δ*f* · *t*.

Hence, the boundary reduction of thermodynamic fluctuations due to increase in the number of readings can be achieved:

$$\overline{\mathrm{P}}_s = \frac{2 \cdot k \cdot \theta}{t} \qquad (10).$$

For electrical measuring instrument with the input resistance r, if external voltage is applied, the effective value of the noise voltage can be determined as:

$$\sqrt{\overline{U_s^2}} = \sqrt{\overline{\mathrm{P}}_s r} = \sqrt{\frac{2 \cdot k \cdot \theta \cdot r}{t}} \qquad (11).$$

The root-mean-square error: $\delta_s \dfrac{\sqrt{\overline{U_s^2}}}{\mathrm{E}} = \sqrt{\dfrac{2 \cdot k \cdot \theta}{\mathrm{P} \cdot t}}$, where P is power; t is time.

Probability distribution of thermal noise is subject to the Gaussian law (normal distribution law), so the entropy value of the error introduced by these values will be determined by K for the normal distribution law (K=2.07). That is, the entropy value of the error due to fluctuations

$$\gamma_s = 2{,}07\ \delta_s = \sqrt{\frac{\pi \cdot e}{2} \cdot \frac{2k\theta}{Pt}} \qquad (12).$$

Thus, even when measurement is performed at the absolute temperature θ, if measuring instrument does not introduce losses, then measurement error of continuous value cannot be less than γ_s which is defined by the noise energy ratio W_s depending on the temperature and energy ($P \cdot t$) consumed by the device from the object of measurement. Relation (12) for minimum possible error γ_s was obtained only due to the fact that the noise is subject to the normal distribution law and based on the law of thermodynamics. Thus, this relation is valid for any measuring devices. The meaning of this relation is that the input certainty (negentropy) of any physical variable for a certain $T \neq 0$ K is finite and limited by the found error value γ_s.

The energy threshold of sensitivity and logarithmic indicator of relative quality of measuring devices.

The threshold of sensitivity of measuring device is defined as such a value of measured variable $x = \Delta$ whereby measurement error $\gamma = 1$, or 100 %, so even an ideal device in which due to design improvement the loss of information is reduced to zero, and the loss of accuracy $æ = \gamma/\gamma_s = 1$, will have the threshold of sensitivity determined by the error caused by noise.

Since at normal temperature (T) $W_s = 3.5 \cdot 10^{-20}$J, then with the energy exchange between measuring device and measured object equal to this value or less than it, no measurement is possible. Thus, this energy value is the quantum of the energy of exchange between the device and the object which determines the price for obtaining the result of measurement. This concept belongs to Brillouin. Based on this understanding of energy expenditure, he introduced the concept of entropy price of measurement, defining it as the least possible amount of negentropy necessary in observation to answer the first binary question with the probability of correct and incorrect answers 50 %. However, such definition of this concept is somewhat simplified, since it is based on the acceptance for a priori probability distribution of the discrete law error. However, this assumption leads Brillouin to the value of entropy price of measurement $0.95 \cdot 10^{-23}$J/degree, which at a temperature of 293K corresponds to the energy threshold value $W_s = 0.28 \cdot 10^{-20}$J. Taking into account that thermodynamic noise obeys the normal distribution law, it is natural to assume that error distribution laws also obey this law, so in conformity with the value of entropy coefficient for the normal law $K = \sqrt{\frac{\pi e}{2}}$ and with regard to the fact that according to sampling theorem the average fluctuation power during time t:

$$\overline{P}_s = \frac{2k\theta}{t}.$$

This expression includes $2k\theta$, rather than $4k\theta$ taken by Brillouin, so the resulting value of the exchange energy $3.5 \cdot 10^{-20}$J is $\frac{\pi e}{l\mathrm{n}\ 2}$ times larger than the energy price value obtained by Brillouin.

Due to the logarithmic coincidence between information and energy, the entropy and energy price of each subsequent unit of information increases. So, if one single unit of energy is required to

receive one decimal unit, then the exchange of one hundred units of energy is required to obtain two units of information and 10.000 units of energy – to obtain three units of information.

Conclusion: instead of such concepts as information and energy of the measurement value, it is necessary to use the term the energy threshold of sensitivity of given measuring instrument, which more accurately reflects the essence of this concept. Then, for an ideal instrument in which all errors are eliminated, except for the error of measured value fluctuation, the energy threshold of sensitivity will be equal to $W_{ш}=3.5\cdot10^{-20}$J, and for actual measuring instruments the real sensitivity threshold will be greater than the ideal in conformity with:

$$C = \frac{W_s}{\eta_{en}}.$$

Energy threshold of sensitivity.

Energy threshold of sensitivity is a generalized indicator of measuring devices with the help of which one can unambiguously determine such characteristics as energy efficiency: $\eta_{en} = \frac{W_s}{C}$, loss of accuracy: $æ = \sqrt{\frac{C}{W_s}}$, loss of information: $\Delta q = \frac{1}{2}\lg\frac{C}{W_s}$. On the other hand, the energy threshold of sensitivity is a cumulative characteristic of accuracy, sensitivity, consumption and response speed of measuring instruments, since it can be expressed through individual indicators of measuring instruments as follows: taking into account that the error $\gamma_s = \sqrt{\frac{W_s}{Pt}}$, the loss of accuracy $æ = \frac{\gamma}{\gamma_s}$, and the energy efficiency $\eta_{en} = \frac{1}{æ^2}$, we can get the following general expression:

$$\eta_{en} = \frac{1}{æ^2} = \frac{\gamma_s^2}{\gamma^2} = \frac{W_s}{\gamma^2 Pt} = \frac{W_s}{C},\ C = \gamma^2 Pt \qquad (13).$$

This expression is generalized and is a record of the law that the energy threshold of sensitivity of the measuring instrument is the product of the quadratic error on the power consumption and the time of establishment of the measurement error. In the event that the instrument is characterized only by the zero error, the energy threshold of sensitivity (*C*) will be just the energy which is consumed from the object during the measurement when the measured variable is equal to the sensitivity threshold of the device.

The concept of the energy threshold of sensitivity can be easily extended to galvanometer or other non-equilibrium indicators and expressed through *C* in *I*, or *U*:

$$\left.\begin{aligned} C &= \Delta_i^2 rt \\ C &= \frac{\Delta_U^2 t}{r} \end{aligned}\right\} \qquad (14).$$

Here, r is resistance of the zero-indicator circuit. The most valuable property of this characteristic is the fundamental limitation of its numerical values, which cannot be less than the noise

power of 3.5 10 – 20 J, i.e. no improvement can help to reduce C. It is also specific that all information characteristics of measuring instruments, such as energy efficiency, loss of accuracy and loss of information, are just functions of the correlation between the actual values of the energy threshold and its boundary value C, which is equal to W_s. In this connection, it was expedient to introduce a visual relative characteristic that must be expressed in relative units or percentages and show us the degree of approach of real measuring instruments to the limit of their absolute perfection. Such a characteristic is η_{en}. However, since real instruments have the energy sensitivity threshold in the best case $10^{-12} – 10^{-14}$J, and the power $W_s = 3.5\ \ 10^{-20}$ J, then $\eta = \dfrac{W_s}{C} \approx 10^{-4} - 10^{-8}$ and its expression in percentages is not illustrative, since its value is very small. Therefore, in order to characterize the relative perfection of measuring instruments, a more convenient indicator is introduced, namely the energy quality factor, which is its logarithmic designation: $pC = \dfrac{\lg C}{\lg W_s}$.

The value of the logarithmic indicator will vary from zero to 100 % for real instruments, and it can be used to evaluate the perfection of these instruments.

Physical model of a thermopile.

The paper uses a particular case of the general model of thermoelectric measuring instrument proposed in [5], specified for multi-element sensors. In this model, heat flux W that comes to the sensor is converted into its output voltage U and then – to signal S at the output of the recorder. The specificity of multi-element thermopiles is taken into consideration, namely contact noise between the elements and thermal conductivity along the multi-element thermal insulation. Conversion coefficients ($W \rightarrow U \rightarrow S$), noise and response time of not only the sensor, but also the recorder are taken into account. For this purpose the sensor and the recorder are considered as aperiodic links of the dynamic system.

Investigation procedure. The methods of the theory of dynamic systems are used according to which the transfer function of measuring device $F(p)$, the functions of sensor F_t and recorder F_r are of the form $F(p) = F_t(p)F_t(p)$, where $F_t(p) = \dfrac{A_t}{\tau_t p + 1}$, $F_r(p) = \dfrac{K_r}{\tau_r p + 1}$, (15)

A_t is volt-watt sensitivity of thermopile, K_r is recorder amplification coefficient, τ_t, τ_r are time constants of the sensor and recorder, p is the Laplace transformation argument.

Results of investigations. For the above model of multi-element thermopiles with a series connection of n elements with regard to (10) from the general expression for informativeness (9) we get its dependence on the number of elements n:

$$\Omega(n) = \frac{\tau_r + \tau_p}{\tau_r \tau_r} \log \frac{D}{\sqrt{2\pi e}\left(A_t \left(\dfrac{1}{n} + \dfrac{r_0}{R_r} \right) u_0 + k_c n \right)}, \qquad (16)$$

where D is a dynamic measurement range, r_0 is electric resistance of thermopile element, R_r is recorder resistance, u_0 is absolute error of measuring the electric voltage by recorder, k_c is total noise

power of one thermopile element reduced to thermal input. The specific feature of this dependence (Fig.1) is the presence of asymmetric maximum at $n = \sqrt{\frac{k_c}{A_t u_0}}$. (17)

The presence of this maximum is due to two competing factors. The first one is that with a small number of thermopile elements the main contribution to entropy error $\Delta(W)$ is from the recording device, as long as in this case the output voltage of sensor U is close to the absolute error of the recorder u_0. Therefore, increasing the number of thermopile elements increases the output voltage U and leads to informativeness increase. However, at $n \sim 10^2 - 10^3$, another factor of maximum becomes apparent, namely the essential thermal and contact noise of thermopile elements the power of which is proportional to the number of elements.

The asymmetry of the revealed informativeness maximum is of practical importance. It indicates a significantly greater loss of informativeness with a deviation from the optimum towards smaller number of elements than with the use of thermopiles with a number of elements larger than the optimal.

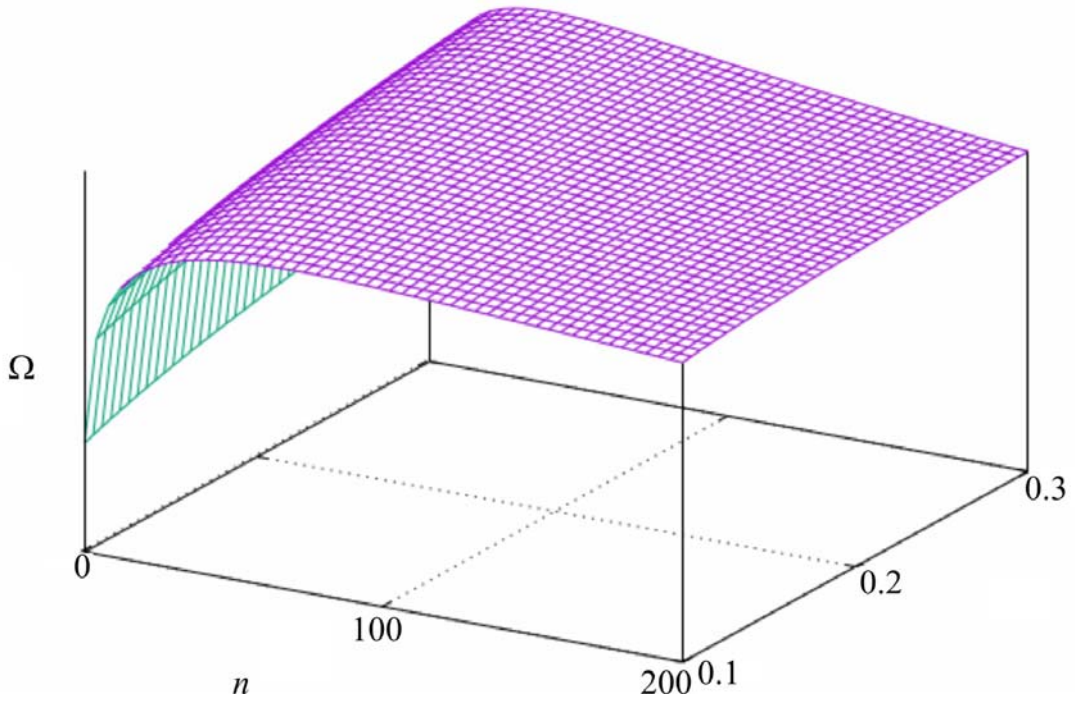

Fig.3. Dependences of informativeness of multi-element thermopiles on the number of elements:
A_t = 1 V/W, k_c = 0.1 nW – 0.3 nW.

Conclusion

1. Physical foundations of information–energy description of multi-element thermopiles as temperature and heat flux sensors have been developed, namely the physical model of a thermopile in the form of aperiodic linear dynamic system, the method of informativeness calculation as a function of thermopile elements, thermopile optimization for the number of elements.
2. An asymmetric maximum of informativeness as a function of the number of elements has been determined. The optimal number of thermopile elements has been determined depending on the

volt-watt sensitivity of thermopile element and the element noise power for the given resolving power of recording device.

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Анатичук Л.І., *ак. НАН України,*
Лусте О.Я., *докт. фіз.-мат. наук.*,
Кобилянський Р.Р., *канд. фіз.-мат. наук*

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна, *e-mail: anatych@gmail.com*;
Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatych@gmail.com

ІНФОРМАЦІЙНО-ЕНЕРГЕТИЧНА ТЕОРІЯ ТЕРМОЕЛЕКТРИЧНИХ СЕНСОРІВ ТЕМПЕРАТУРИ І ТЕПЛОВОГО ПОТОКУ МЕДИЧНОГО ПРИЗНАЧЕННЯ

У роботі проаналізовано сенсори температури і теплового потоку як джерела вимірювальної інформації. Використано поняття інформативності сенсорів і вимірювальних пристроїв. Визначено інформативність мікрокалориметрів, давачів температури і теплового потоку.. Бібл. 14, Рис. 3.

Ключові слова: інформаційно-енергетична теорія, інформативність, ентропійне значення похибки, енергетичний поріг чутливості вимірювальних приладів, термоелектричний сенсор температури і теплового потоку.

Анатычук Л.И., *ак. НАН Украины,*
Лусте О.Я., *докт. фіз.-мат. наук,*
Кобылянский Р.Р., *канд. физ.-мат. наук*

Институт термоэлектричества НАН и МОН Украины, ул. Науки, 1,
Черновцы, 58029, Украина, *e-mail: anatych@gmail.com*;
Черновицкий национальный университет имени Юрия Федьковича,
ул. Коцюбинского 2, Черновцы, 58012, Украина
e-mail: anatych@gmail.com

ИНФОРМАЦИОННО-ЭНЕРГЕТИЧЕСКАЯ ТЕОРИЯ ТЕРМОЭЛЕКТРИЧЕСКИХ СЕНСОРОВ ТЕМПЕРАТУРЫ И ТЕПЛОВОГО ПОТОКА МЕДИЦИНСКОГО НАЗНАЧЕНИЯ

В работе проанализированы сенсоры температуры и теплового потока как источники измерительной информации. Использованы понятия информативности сенсоров и измерительных устройств. Определена информативность микрокалориметров, датчиков температуры и теплового потока. Библ. 14, Рис. 3.

Ключевые слова: информационно-энергетическая теория, информативность, энтропийное значение погрешности, энергетический порог чувствительности измерительных приборов, термоэлектрический сенсор температуры и теплового потока.

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P. V. Gorskiy

P.V.Gorskyi, *Doctor Phys.-math. science*

Institute of Thermoelectricity of the NAS and MES of Ukraine,
1, Nauky str, Chernivtsi, 58029, Ukraine; *e-mail: anatych@gmail.com*

OPTIMIZATION OF MATERIALS BASED ON ZINC ANTIMONIDE FOR THERMOCOUPLE THERMOELEMENTS

This paper offers a theoretical approach to the optimization of thermoelectric materials, based not only on the experimental data "in pure form", but also on certain model approximations of physical mechanisms for the formation of the kinetic coefficients of material. From amongst the characteristics required to determine the thermoelectric figure of merit of material, only the thermoEMF, the electrical conductivity, and part of the thermal conductivity due to free charge carriers are analyzed. The lattice component of material thermal conductivity is considered to be known and inversely proportional to temperature. In the process, several model approaches to the description of free charge carrier scattering in material are considered and analyzed. The efficiency of the developed approach is illustrated by the example of optimization of thermoelectric material for thermocouple thermoelements based on zinc antimonide. It is shown that with the provision of a proper concentration of free charge carriers in this material, its thermoelectric figure of merit can be brought to 0.39 instead of 0.2 – 0.35 at 300K and to 1.21 instead of 0.95 at 600K. Bibl. 11, Fig. 3.

Key words: optimization, thermoelectric figure of merit, charge carrier concentration, temperature and concentration dependence of figure of merit, mean free path of charge carriers, mobility, impurities, shielding, band spectrum nonparabolicity.

Introduction

By now previous authors [1,2] have developed an approach to the optimization of thermoelectric materials for generators and refrigerators, based on the use of experimentally determined dependences of the kinetic coefficients of these materials on the concentration of charge carriers and temperature. Being mathematically approximated, these dependences are initial for computer optimization of materials in accordance with the modes and conditions of their application in specific thermoelectric devices, including for creation of the so-called functionally-graded materials in which the calculated and practically implemented inhomogeneous distribution of doping impurities along the length of thermoelectric leg allows increasing the efficiency of thermoelectric energy conversion, including through the use of the Thomson effect and the volumetric Seebeck and Peltier effects. Very fruitful in the computer design of similar materials and devices is the use of the mathematical theory of optimal control. However, the present author is of the opinion that in addition to obvious advantages, this approach is not devoid of shortcomings. The most essential of them is the form of approximation models which is not based on some physical representations, hence is fairly arbitrary. Having a rather complicated form with respect to the estimated parameters, these models, although they describe with satisfactory accuracy the experimental data, cost much time for construction and processing. In addition, the amount of experimental data should be sufficiently large, which requires additional time to collect them and then transform into the form suitable for further processing. Moreover, the obtained models, being formally-statistical, rather than physical, cannot be extended beyond the limits of the experimentally investigated region of concentrations and temperatures. Therefore, the purpose of this paper is development of an approach that lacks the

mentioned drawback and its approbation by the example of a material for thermocouple thermoelements based on zinc antimonide. Zinc antimonide was chosen because of the increased interest in it, as environmentally friendly and such that has no deficit components, and, consequently, because of the need to increase its thermoelectric figure of merit [3].

Construction of model dependences of the kinetic coefficients of thermoelectric materials and their application to material optimization for thermocouple thermoelements based on *ZnSb*.

We begin the construction of the desired model dependences from thermoEMF, since this is the simplest case. For a parabolic band spectrum, isotropic or anisotropic in the one-valley approximation, or even in the approximation of several equivalent valleys, the form of this dependence in the impurity region is well known [4]. Therefore, we make the first model assumption concerning the value of scattering coefficient r. Namely, considering that in the temperature range relevant for zinc antimonide application, the scattering of charge carriers occurs with energy-independent mean free path and with regard to band spectrum parabolicity, we assume that $r = -0.5$. Under this assumption, the general formula for thermoEMF becomes:

$$\alpha = \frac{k_B}{e}\left[\frac{2F_1(\eta)}{F_0(\eta)} - \eta\right], \tag{1}$$

where $k_B -$ the Boltzmann constant, $e -$ electron charge, $\eta -$ reduced chemical potential of charge carrier gas, $F_r(\eta) -$ the Fermi integrals determined as follows:

$$F_r(\eta) = \int_0^\infty \frac{x^r dx}{\exp(x-\eta)+1}. \tag{2}$$

The reduced chemical potential η in the impurity region is found from the equation:

$$\frac{8\pi N_v \sqrt{2m_1^* m_2^* m_3^*}\,(k_B T)^{3/2} F_{1/2}(\eta)}{h^3 n_0} - 1 = 0, \tag{3}$$

where $N_v -$ the number of equivalent ellipsoids, $m_1^*, m_2^*, m_3^* -$ effective masses in the directions of the principal ellipsoid axes, $T -$ absolute temperature, $h -$ the Planck constant, $n_0 -$ volumetric concentration of charge carriers.

Thus, relation (1) with regard to (2) and (3) completely determines the model temperature and concentration dependence of thermoEMF, provided we also consider valid the second model assumption that tensor components of the effective mass of charge carriers are temperature-independent.

We will also write a model expression for the Lorentz number, since it is necessary to determine the concentration and temperature dependences of a part of the thermal conductivity of thermoelectric material due to free charge carriers:

$$L_0(\eta) = \left(\frac{k_B}{e}\right)^2 \left[\frac{3F_2(\eta)}{F_0(\eta)} - \frac{4F_1^2(\eta)}{F_0^2(\eta)}\right]. \tag{4}$$

This expression, as well as the expression for thermoEMF (1), is a particular case of a more general expression [4], following from the above model assumption with respect to scattering coefficient.

We now turn to the construction of a model expression for the electrical conductivity σ of thermoelectric material. In so doing, as in the case of thermoEMF, we proceed from the most general formula:

$$\sigma = n_0 e b, \tag{5}$$

where b – charge carrier mobility, other designations were explained above. Under the stipulated assumption concerning scattering coefficient for charge carrier mobility, we suppose that in direction "1" the following expression holds:

$$b_1 = \frac{e l_1 \sqrt{m_1 + m_2 + m_3} F_0(\eta)}{3\sqrt{3k_B T} m_1 F_{1/2}(\eta)}. \tag{6}$$

Similar expressions are valid for mobilities in directions "2" and "3":

$$b_2 = \frac{e l_2 \sqrt{m_1 + m_2 + m_3} F_0(\eta)}{3\sqrt{3k_B T} m_2 F_{1/2}(\eta)}. \tag{7}$$

$$b_3 = \frac{e l_3 \sqrt{m_1 + m_2 + m_3} F_0(\eta)}{3\sqrt{3k_B T} m_3 F_{1/2}(\eta)}. \tag{8}$$

It is clear from these expressions that if the effective masses of charge carriers are assumed to be known and independent of temperature or charge carrier concentration, then simulation of the temperature and concentration dependences of the mobility tensor components reduces to simulation of corresponding dependences for the mean free paths l_1, l_2, l_3 of charge carriers. Now we turn to this simulation.

Since in the temperature range relevant for practical applications, as is traditionally believed, the scattering of charge carriers by acoustic phonons dominates, it is logical to assume at the initial stage of simulation that this path is determined mainly by the temperature and depends on it according to the following law:

$$l_{1,2,3}(T) = l_{1,2,3}(T_0)\frac{T_0}{T}. \tag{9}$$

It is this temperature dependence of the mean free path of charge carriers that determines the known "three - halves power law", which for zinc antimonide in the temperature range relevant for practical applications is considered to be performed fairly well. Then, using the values of the components of effective mass tensor given in [5] for zinc antimonide, namely: $m_1 = 0.363m_0, m_2 = 0.434m_0, m_3 = 0.225m_0$, as well as the value of charge carrier concentration equal to $n_0 = 10^{16}$ cm^{-3} and the value of mobility in direction "1" at 300K $b_1 = 50$ cm^2/(V·s) [6], we get that the mean free path of charge carriers $l_1(300) = 31.73$ nm. However, if we assume that the above length does not depend on charge carrier concentration and use this assumption to determine the thermoelectric figure of merit of zinc antimonide at 300K in the concentration range $n_0 = 10^{16} \div 10^{19}$ cm^{-3}, it turns out that its maximum value in this range will be $ZT = 0.67$, as will be discussed below. Such a great value is not observed in reality. Note also that in the course of

simulation we always assume that the lattice thermal conductivity of zinc antimonide in direction "1" at 300 K is W / (m·K), it is inversely proportional to temperature and does not depend on the concentration of free charge carriers [7].

Suppose now that even at high temperatures, two scattering mechanisms operate in zinc antimonide, namely by phonons and ionized impurities, and they are independent of each other. Then, at scattering with an energy-independent cross section, the mean free path due to scattering by impurities with an unshielded potential is, with an acceptable accuracy, equal to the mean distance between them, i.e. if impurities are assumed to be singly charged, and, consequently, the final dependence of the mean free path of carriers on the concentration of charge carriers and temperature is given by:

$$l_{1,2,3}(T,n_0)=\frac{l_{ph}(T_0)(T_0/T)n_0^{-1/3}}{l_{ph}(T_0)(T_0/T)+n_0^{-1/3}}, \tag{10}$$

In this formula, $l_{ph}(T_0)-$ mean free path due to "pure" scattering by phonons, say, at $T_0=300\,\mathrm{K}$. Under our conditions, it turns out that if we determine $l_{ph}(T_0)$ from the previously found carrier mean free path at 300K and $n_0=10^{16}\,\mathrm{cm}^{-3}$ and use this model to determine the thermoelectric figure of merit of material at 300K, its maximum value in the above carrier concentration range will be $ZT=0.12$. In contrast to the value obtained in the previous model, this value is, on the contrary, too small in comparison with that observed in the experiment. This situation forces us to abandon the additive model of charge carrier scattering and move to a multiplicative model that seems to be fully justified from the physical point of view, because, for example, the increase in charge carrier concentration increases the part of the deformation potential due to all-round compression. And this means that the mechanisms of scattering are not independent.

Within the framework of the multiplicative model, the mean free path can be represented as:

$$l_{1,2,3}(T,n_0)=l_{1,2,3}(T_0,n_{00})(T_0/T)(n_{00}/n_0)^{\gamma}, \tag{11}$$

where $l_{1,2,3}(T_0,n_{00})-$ mean free paths determined from the experimental data on the electric conductivity or charge carrier mobility for some fixed values of temperature and concentration of free charge carriers, say, $T_0=300\,\mathrm{K}$ and $n_{00}=10^{16}\,\mathrm{cm}^{-3}$. Analysis of the experimental data given in [6] shows that, for instance, for silver-doped zinc antimonide we can assume with a reasonable degree of accuracy $\gamma=0.08552$.

Let us justify the multiplicative model (11). For this purpose we use the following physical model. Since the concentration of doping impurities is significant, we will assume that even at high temperatures the scattering of charge carriers occurs mainly on these impurities. Moreover, considering impurities as singly charged, we will assume that the concentration of impurities is equal to the concentration of charge carriers. If the assumption is true that scattering coefficient $r=-0.5$, it means that cross-section of charge carriers on impurities does not depend on energy. However, to assume that the impact distance is equal to half the mean distance between the impurities, as is done in the derivation of the Conwell-Weisskopf formula, would be incorrect, since at a significant concentration of charge carriers the Coulomb impurity potential is shielded. Taking this into account, scattering cross-section can be approximately determined as:

$$\sigma_s=\pi r_D^2, \tag{11}$$

where r_D – the Debye shielding length.

The solution of the Poisson equation for the electrostatic potential of carrier gas in thermoelectric material leads to the following final expression for the mean free path of charge carriers in it:

$$l_{1,2,3} = \frac{e^2 F_{-1/2}(\eta)}{2\pi\varepsilon^*_{1,2.3}\varepsilon_0 kTF_{1/2}(\eta)}, \tag{12}$$

where ε_0 – vacuum permittivity, $\varepsilon^*_{1,2.3}$ – components of tensor of "effective" dielectric constant of thermoelectric material.

On a formal level, expression (12) differs from that which would be obtained from the Brooks-Herring formula at low energies by the numerical coefficient. However, this is of no fundamental importance, since we estimate the "effective" permittivity of thermoelectric material from the requirement that the mobility of charge carriers should coincide in the corresponding direction with the experimentally observed value, for example, at 300 K.

Analysis of expression (12) with regard to (3) shows that in the range of carrier concentrations from 1016 to 1019 cm^{-3}, their mean free path in the temperature range of relevance for zinc antimonide practically does not depend on the concentration of charge carriers, hence, of impurities, provided we assume that the "effective" permittivity of a thermoelectric material does not depend on this concentration. Thus, taking the semi-empirical relation (11) as the expression for the mean free path of the charge carriers means that we consider the "effective dielectric constant" to be independent of temperature, but weakly dependent on the concentration of the charge carriers in accordance with the law $\varepsilon^*_{1,2.3} \propto n_0^{0.08552}$. This dependence reflects, though purely empirically, the influence of free charge carriers, and, consequently, impurities introduced by doping, on the initial "matrix" of the thermoelectric material. Experimental data on the mobility of charge carriers in silver-doped zinc antimonide show that, for example, for direction "1", the following relation holds:

$$\varepsilon^*_1 = 7.01 \cdot \left(n_0 / 10^{16}\right)^{0.08552}. \tag{13}$$

The results of calculations of the thermoelectric figure of merit of silver-doped zinc antimonide depending on impurity concentration at temperatures 300, 400 and 600K are presented in Figs. 1 and 2a, b.

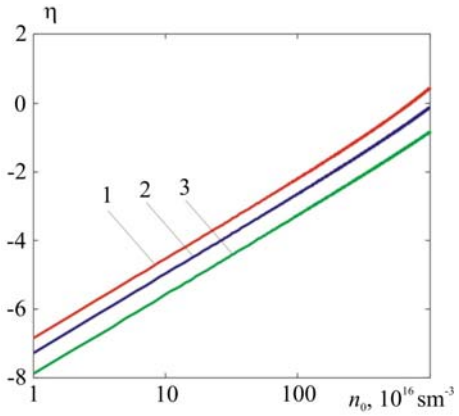
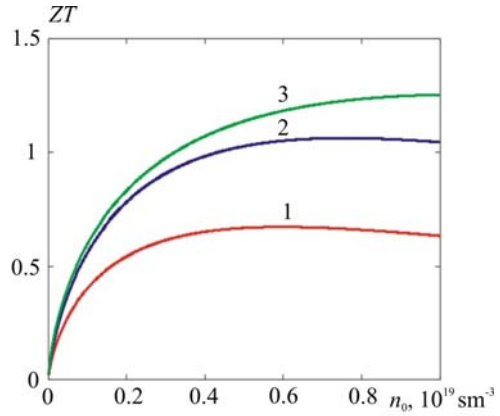
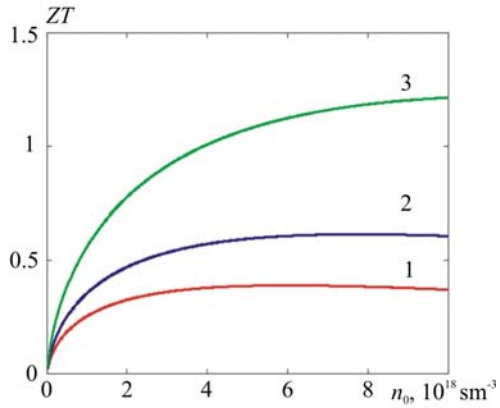


Fig.1. Dependences of chemical potential of charge carriers on the concentration of singly charged doping impurities at temperatures: 1)300K; 2)400K; 3)600K



a)



b)

Fig.2. Dependences of thermoelectric figure of merit of zinc antimonide on the concentration of singly charged doping impurities: a) without regard to the influence of this concentration on charge carrier mobility at temperatures: 1)300K; 2)400K; 3)600K; b) with regard to the influence of this concentration on charge carrier mobility at temperatures: 1)300K; 2)400K; 3)600K

From Fig. 1 it is seen that in the entire range of charge carrier concentrations and temperatures considered, charge carrier gas in silver-doped zinc antimonide is nondegenerate or weakly degenerate, since reduced chemical potential is mainly negative and linearly or almost linearly depends on the logarithm of charge carrier concentration.

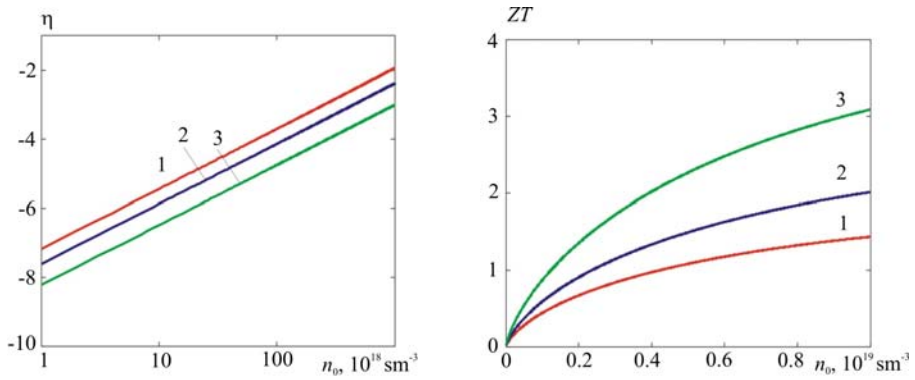
It can be seen from Fig. 2a that if the influence of the concentration of doping impurities on the mobility of charge carriers is not taken into account, then in the concentration range considered at 300 and 400 K there are maxima of thermoelectric figure of merit, though weakly expressed, and at 600 K this maximum does not exist. Therefore, the maximum thermoelectric figure of merit ZT of silver-doped zinc antimonide at 300K is 0.67 and is reached at impurity concentration equal to 5.5×1018 sm^{-3}, at 400 K this maximum is 1.06 and is reached at impurity concentration equal to 7.1×1018 sm^{-3}. At 600K at the end of the interval, i.e. at impurity concentration of 10^{19}cm^{-3}, the value of ZT equal to 1.253 is achieved. The shift in the maximum of thermoelectric figure of merit towards high impurity concentrations with a rise in temperature is attributable to the fact that with increasing concentration of impurities, hence, of charge carriers, the rate of thermoEMF increase decreases with temperature.

However, from Fig. 2b it can be seen that if we take into account the decrease in charge carrier mobility with increase in impurity concentration, as is the case in reality, and attribute this decrease to increase in dielectric permittivity of thermoelectric material in doping, the maxima of thermoelectric figure of merit decrease with each temperature. Namely, the maximum thermoelectric figure of merit *ZT* of silver-doped zinc antimonide at 300 K becomes 0.39 and is reached at impurity concentration equal to $6 \cdot 1018$ sm^{-3}, at 400 K this maximum becomes equal to 0.61 and is reached at impurity concentration equal to 7.1×1018 sm^{-3}. At 600 K at the end of the interval, i.e. at impurity concentration of 1019 sm^{-3}, a value of 1.21 is achieved.

Concerning the comparison of these results with the experimental data of [3], we note that the maximum values of *ZT* attained in it for zinc antimonide obtained in the course of investigating the possibilities of its optimization were 0.35 at 300 – 350 K, 0.47 at 400 K, and 0.95 at 600 K, which implies that the possibilities of increasing the thermoelectric figure of merit of this material are not yet exhausted.

At the same time, taking into account the nonparabolicity of zinc antimonide band spectrum, it also makes sense to consider the mechanism related to this nonparabolicity of the influence of impurity concentration on charge carrier mobility, hence, on the thermoelectric figure of merit of material. The physical reason for this influence is as follows. In the presence of nonparabolicity, the effective mass of charge carriers grows with increase of their concentration, hence of impurity concentration. And this should directly lead to a decrease in mobility in accordance with the general relations (6) – (8). Besides, the dependence of effective mass on charge carrier concentration by virtue of relation (3) should influence the concentration dependence of carrier gas chemical potential, hence, the thermoEMF.

Analysis shows that if the effective dielectric permittivity of thermoelectric material is considered to be independent of impurity concentration and equal to 7.01, then for a satisfactory explanation of experimental data on the mobility of charge carriers in silver-doped zinc antimonide, their effective mass should increase with concentration by the law $m^* \propto n_0^{0.166}$. The results of calculations of the thermoelectric figure of merit of this material in the previously specified range of concentrations and temperature on the assumption of the validity of this law are given in Fig. 3a, b.



a) *b)*

Fig. 3, a) Dependences of chemical potential of charge carriers in the presence of band spectrum nonparabolicity on the concentration of singly charged doping impurities at temperatures: 1)300K; 2)400K; 3)600K
b) Dependences of thermoelectric figure of merit of zinc antimonide on the concentration of singly charged doping impurities with regard to band spectrum nonparabolicity at temperatures: 1)300K; 2)400K; 3)600K

Fig. 3*a* shows that in the presence of nonparabolicity, the degree of degeneracy of the carrier gas decreases, since for an equal concentration of charge carriers, an increase in the effective mass should reduce their chemical potential. And it means that the mean free path of charge carriers under the assumption of constant material permittivity is independent of charge carrier concentration. Consequently, the dependence of the mobility of charge carriers on their concentration, and, consequently, on the concentration of impurities, is almost entirely due to the dependence of the effective mass on this concentration. On the other hand, the removal of the degeneracy of the carrier gas leads to a sharp increase in the thermoEMF, especially at high temperatures. It is these circumstances that determine the concentration dependence of the thermoelectric figure of merit of zinc antimonide presented in Fig. 3*b*. In this case, in the considered range of charge carrier concentrations, hence, of impurities, the thermoelectric figure of merit ZT of zinc antimonide increases all the time, reaching at the end of the range at temperatures 300, 400 and 600K, respectively, the values equal to 1.44, 2.01 and 3.09, respectively. Thus, a significant nonparabolicity of the band spectrum, be it realized in zinc antimonide in the concentration range of charge carriers, and hence impurities, from 1016 to 1019 sm^{-3}, would be a powerful factor of increasing its thermoelectric figure of merit.

In conclusion, we consider the question of which degree of band spectrum nonparabolicity is needed to achieve the above-mentioned high values of thermoelectric figure of merit of material. Since we assume that the effective mass of charge carriers depends on their concentration by the power law, it is clear that the energy of charge carriers depends on their quasi-momentum by the analogous law. Suppose that power exponent in this law is equal to *v*, i.e. $\varepsilon(k) \propto k^{\nu}$. Then, by definition, $m^* \propto k^{\nu-2}$. However, on the other hand, we always have $n_0 \propto k^3$. Therefore, $m^* \propto n_0^{(\nu-2)/3}$. Hence, for the implementation of the required dependence of effective mass on charge carrier concentration, the exponent ν should be equal to 2.498.

Fig. 4 in relative units shows the required law as compared to the parabolic law, on the one hand, and the law described by the Fivaz model, on the other. The width of allowed hole band is considered by convention to be equal to $2\Delta_0$.

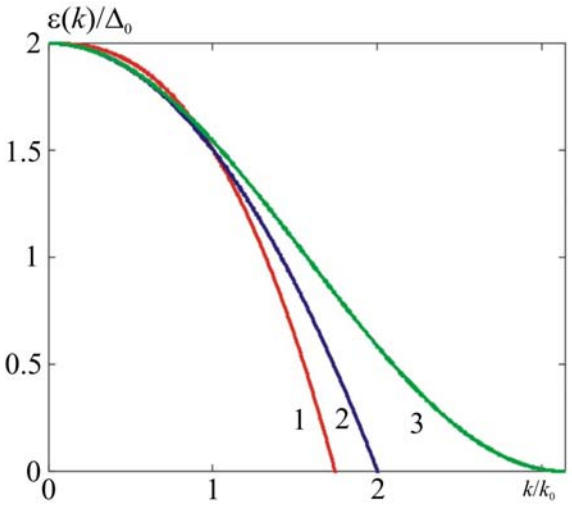


Fig. 4.Band spectra of charge carriers in the alloys of the Zn-Cd-Sb system:
1) necessary to achieve high thermoelectric figure of merit of alloys; 2) traditional parabolic;
3) described by the Fivaz model

It is seen from the figure that at low values of charge carrier concentration, i.e. low k/k_0 values, the highest thermoelectric figure of merit is ensured by the law of the form $\varepsilon(k) \propto k^{2.498}$, and at high values of charge carrier concentration – the law described by the Fivaz model. Traditional parabolic law at low charge carrier concentrations in terms of increasing the thermoelectric figure of merit is as good as the law described by the Fivaz model, but is inferior to the law $\varepsilon(k) \propto k^{2.498}$. Here, however, it is necessary to explain in more detail the meaning of the concepts of "high" and "low" charge carrier concentrations. In this case, we mean not so much the absolute number of charge carriers per unit volume as the corresponding degree of filling of the allowed band at absolute zero of temperature. Analysis shows that the law $\varepsilon(k) \propto k^{2.498}$ is efficient at such charge carrier concentrations whereby the allowed band is filled not more than by 18% of its width. Exactly such concentrations are low. Therefore, taking into account that the widths of the allowed valence bands in zinc and cadmium antimonides reach 15 eV [8], it should be assumed that in the impurity region, the charge carrier concentrations attained in these compounds are definitely low. Therefore, the law $\varepsilon(k) \propto k^{2.498}$, if it were implemented, for these compounds would be the best. On the contrary, the law described by the Fivaz model becomes efficient when the degree of band filling is increased. Therefore, it manifests itself in crystals with narrow allowed minibands in which the Fermi surface is not closed, as in cadmium and zinc antimonides, but transient or open [9].

Conclusion

1. Theoretical calculations based on the simulation of the temperature and concentration dependences of the mean free path of charge carriers have been used to optimize the thermoelectric material based on zinc antimonide for the concentration of charge carriers.
2. It has been found that if the band spectrum of zinc antimonide is considered parabolic, then at temperatures 300, 400 and 600K its thermoelectric figure of merit ZT can be brought to the values of 0.39, 0.61 and 1.21, respectively, at charge carrier concentrations of $6 \cdot 10^{18}$, $7.1 \cdot 10^{18}$ and 10^{19} sm^{-3}, respectively.
3. By simulation of the concentration dependence of the effective mass of charge carriers under the condition that the mean free path is independent of their concentration, it has been established that the experimental data on the mobility of charge carriers in zinc antimonide can be satisfactorily explained not only by the slow dependence of the "effective" dielectric constant of the material on the concentration of charge carriers, but also by the band spectrum nonparabolicity of the latter, which is of the form $\varepsilon(k) \propto k^{2.498}$. However, if such a nonparabolicity were implemented in zinc antimonide, then at charge carrier concentration equal to 1019 sm^{-3}, its thermoelectric figure of merit could be brought to 1.44, 2.01 and 3.09 at temperatures of 300, 400 and 600 K, respectively.

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Горський П.В., *докт. фіз.-мат. наук*

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна*, e-mail: anatych@gmail.com*

ОПТИМІЗАЦІЯ МАТЕРІАЛІВ НА ОСНОВІ АНТИМОНІДУ ЦИНКУ ДЛЯ ТЕРМОПАРНИХ ТЕРМОЕЛЕМЕНТІВ

У статті запропонований теоретичний підхід до оптимізації термоелектричних матеріалів, що ґрунтується не тільки на експериментальних даних «у чистому виді», але й на певних модельних виставах про фізичні механізми формування кінетичних коефіцієнтів матеріалу. Із числа характеристик, необхідних для визначення термоелектричної добротності матеріалу, аналізуються тільки термоЕДС, електропровідність і частина теплопровідності, обумовлена

вільними носіями заряду. Решеточная частина теплопровідності матеріалу вважається відомої й обернено пропорційній температурі. При цьому розглядаються й рівняються між собою кілька модельних підходів до опису розсіювання вільних носіїв заряду в матеріалі. Ефективність розробленого підходу ілюструється на прикладі оптимізації термоелектричного матеріалу для термопарних термоелементів на основі антимоніду цинку. Показане, що при забезпеченні належної концентрації вільних носіїв заряду в цьому матеріалі його термоелектрична ефективність ZT може бути доведено до 0.39 замість 0.2-0.35 при 300 ДО и до 1.21 замість 0.95 при 600 ДО. Бібл. 9, Рис. 4.

Ключові слова: оптимізація, термоелектрична добротність, термоелектрична ефективність, концентрація носіїв заряду, температурна й концентраційна залежність добротності, довжина вільного пробігу носіїв заряду, рухливість, домішки, екранування, непараболичность зонного спектра.

Горский П.В., *докт. физ.-мат. наук*

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина
e-mail: anatych@gmail.com

ОПТИМИЗАЦИЯ МАТЕРИАЛОВ НА ОСНОВЕ АНТИМОНИДА ЦИНКА ДЛЯ ТЕРМОПАРНЫХ ТЕРМОЭЛЕМЕНТОВ

В статье предложен теоретический подход к оптимизации термоэлектрических материалов, основывающийся не только на экспериментальных данных «в чистом виде», но и на определенных модельных представлениях о физических механизмах формирования кинетических коэффициентов материала. Из числа характеристик, необходимых для определения термоэлектрической добротности материала, анализируются только термоЭДС, электропроводность и часть теплопроводности, обусловленная свободными носителями заряда. Решеточная часть теплопроводности материала считается известной и обратно пропорциональной температуре. При этом рассматриваются и сравниваются между собой несколько модельных подходов к описанию рассеяния свободных носителей заряда в материале. Эффективность разработанного подхода иллюстрируется на примере оптимизации термоэлектрического материала для термопарных термоэлементов на основе антимонида цинка. Показано, что при обеспечении надлежащей концентрации свободных носителей заряда в этом материале его термоэлектрическая эффективность ZT может быть доведена до 0.39 вместо 0.2-0.35 при 300К и до 1.21 вместо 0.95 при 600К. Библ. 9, рис. 4.

Ключевые слова: оптимизация, термоэлектрическая добротность, термоэлектрическая эффективность, концентрация носителей заряда, температурная и концентрационная зависимость добротности, длина свободного пробега носителей заряда, подвижность, примеси, экранирование, непараболичность зонного спектра.

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O.M. Manik, *Candidate Phys.-math. Sciences,*
T.O. Manik, *Candidate Phys.-math. Sciences,*
V.R. Bilinsky-Slotylo, *Candidate Phys.-math. Sciences*

Institute of Thermoelectricity of the NAS and MES of Ukraine,
1, Nauky str, Chernivtsi, 58029, Ukraine; *e-mail: anatych@gmail.com*
Yurii Fedkovych Chenivtsi National University, 2, Kotsiubynskyi str.,
Chernivtsi, 58012, Ukraine*; e-mail: anatych@gmail.com*

PECULIARITIES OF ELECTRONIC STRUCTURE AND INTERATOMIC INTERACTION IN *ZnSb* CRYSTALS

A complex approach has been developed for calculating the electronic structure parameters of hybrid orbitals corresponding to nonequivalent interatomic distances in low-symmetry AIIBV, AIIBVI, AIIIBV crystals (binary compounds). 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) have been performed. The obtained results can be used in the development of technological modes for the production of new materials based on n- and p-type ZnSb, which possess high sensitivity, stability, and characteristics identity, especially necessary for thermal converters of metrological application. Bibl. 8, Fig. 3, Table 1.
Key words: nonequivalent hybrid orbitals, effective charges, effective radii, dissociation energy.

Introduction

The present work contributes to further research on the nature of chemical bonding in low-symmetry *ZnSb* crystals, begun in [1 – 5], using the approach we developed [6]. It is not by chance that *ZnSb* was chosen as the object of research. This is a promising material for use in thermoelectric devices. A detailed review of the works devoted to the study of physical properties, crystal structure and production technology is given in [7]. This material has high values of thermoelectric figure of merit. Its anisotropic properties are also of interest. However, this material is of the greatest interest from the point of view of constructing theoretical models for the synthesis of new artificial composite materials with predetermined properties. Specific features of this material, together with a high level of knowledge, allow the construction of various theoretical models by solving the inverse problems [8] reflecting the nature of the substance at all stages of the study and describing the dependence of the properties of the investigated material on the composition, crystal structure, and energy spectrum parameters.

However, it should also be noted that a number of issues related to the technology of obtaining high-quality materials based on zinc antimonide remain open and contradictory. Thus, the zinc-antimony state diagram given in [7] and being the most reasonable compromise between the available literature data does not explain the nature of phase transformations in this system both between solid phases and in the melting region. The thermodynamic constants of zinc antimonides are almost unexplored.

In this connection, it is particularly important and relevant to pursue research that makes it possible to quantitatively describe the interrelation between the macroscopic properties of material under study and their microscopic characteristics in terms of chemical bond nature. The combination of the principles of two different approaches – theoretical and experimental – is not a mechanical summation of any concepts or methods of calculation. The theoretical comprehension of numerous empirical dependencies is associated with a revision of the system of established views on the problem of interatomic interaction, with the appearance of qualitatively new, nonstandard concepts that not only do not result from the consistent development of various directions of existing theories, but also deny some of them. Therefore, the way to solving the problem lies through the analysis of empirical material and quantum-mechanical description of the relationship between the properties of elements and the compounds formed by them.

Quantum-mechanical models of electronic structure of *ZnSb*

In [6], analysis of empirical information on the properties of elements and electronic structure of the compounds formed by them was carried out in terms of ionic radii R_u.

Phenomenological equations were constructed relating the value R_u to the number of electrons n in the orbitals of atoms. The simplest relations were obtained by postulating the linear dependence of the number of electrons in the outer shell of the atom on the logarithm of its Fermi radius. The relationship between the slope of rectilinear dependences $\mathrm{tg}\alpha = \Delta \lg R_u / \Delta n$ and electronegativities excludes the possibility of arbitrary variation in compared values.

A good agreement of the experimental data set is given by the dependence postulated in [6]:

$$\lg R_u^x = \lg R_{uA}^0 - x\mathrm{tg}\alpha\,, \tag{1}$$

where R^0_{uA} is the radius of the atom in the unexcited state, and x is the valence.

As long as equation (1) describes the change in R_u of atoms A and B with a change in the number of electrons in the orbitals of each, then assuming the equality of the absolute values of charges of the interacting atoms, the dependence (1) takes on the form of a system of equations:

$$\lg R_{uA}^{+x} = \lg R_{uA}^0 - x\mathrm{tg}\alpha_A \tag{2}$$

$$\lg R_{uB}^{-x} = \lg R_{uB}^0 + x\mathrm{tg}\alpha_B \tag{3}$$

$$d_1 = R_{uA}^{+x} + R_{uB}^{-x} \tag{4}$$

In terms of the quantum-mechanical approach, the system of equations (2) – (4) formally considers the geometric conditions for the contact of spherical electron clouds with different density levels at the boundary. Therefore, additional criteria are needed that allow the system (2) – (4) to be translated into the language of quantum chemistry. For this purpose it is necessary to analyze the dependence of interatomic distances on the effective charges: $d_1 = f(z_{ef})$. It turned out that at any point of this dependence, apart from $d_1 = d_{min}$, the density of states at the ion boundary is different. To determine effective charges and effective radii in the bonds with $d_1 < d_{min}$, formation of (A-B) bond is accompanied by electron drift to other directions of interatomic interaction, i.e. the bond becomes of donor nature. In so doing, the removal of electrons ($+\Delta q$) or their localization ($-\Delta q$) in this bond direction equally changes the values of charges that this pair has at $d_1 = d_{min}$.

With such an approach, system (2) – (4) goes over to system:

$$d_1 = R_{uA}^{zA} + R_{uB}^{zB} \tag{5}$$

$$\lg R_{uA}^{zA} = \lg R_{uA}^{0} - \left(z_{\min_A} + \frac{\Delta q}{2} \right) \mathrm{tg}\alpha_A \tag{6}$$

$$\lg R_{uB}^{zB} = \lg R_{uB}^{0} - \left(z_{\min_B} + \frac{\Delta q}{2} \right) \mathrm{tg}\alpha_B \tag{7}$$

Function $d_1 = f(z_{ef})$, calculated in the crystallochemical approach ($x_A = x_B$), is correct from the quantum-mechanical standpoint only at $d_1 = d_{min}$, but this is enough for system (5) – (7) to be solved at known d_1.

Effective charges and effective radii of NHO atoms in *ZnSb* crystals

The specific feature of chemical bond in *Zn* crystals is the fact that each *Zn* atom in its immediate surrounding has three *Sb* atoms and one *Zn* atom, and each *Sb* atom has three nearest *Zn* atoms and one *Sb* atom. There are five NHO altogether, which differ both in the interatomic distances and in the composition of components.

To solve the formulated problem, system (5) – (7) was written for each *i*-th NHO, and then the inverse problem was solved to find $R^{(i)}_{uZn}$, $R^{(i)}_{uSb}$, Δq using known interatomic distances $d_1 (1 \le i \le 5)$. In so doing, the accuracy of calculations was restricted by the accuracy of experimental methods of finding interatomic distances. The error of such an approach for all NHO ($1 \le i \le 5$) did not exceed 0.01 %.

The values of R^0_{Zn}, R^0_{Sb}, $\mathrm{tg}\alpha_{Zn}$ and $\mathrm{tg}\alpha_{Sb}$ required for the calculations were found by the method of [6]. As a result of calculations, the following numerical values were obtained:

$$R^0_{Zn} = 1.37 \text{ Å}; \qquad R^0_{Sb} = 1.45 \text{ Å};$$
$$\mathrm{tg}\alpha_{Zn} = 0.135; \qquad \mathrm{tg}\alpha_{Sb} = 0.074. \tag{8}$$

Then, in the present paper the diagram $d_1 = f(z_{ieff})$ was constructed. Fig. 1 shows a dependence of interatomic distances d_1 of bonds φ_i ($Zn_x - Sb_{-x}$) (in angstroms) on the effective charges x in the range of $-4 \le i \le 4$. The minimum on this dependence is realized at $d_{\min} = 2.7233$ Å, which exceeds the real interatomic distances along φ_1 (*Zn – Sb*), φ_2 (*Zn – Sb*) and is less than d_3 for the bonds φ_3 (*Zn – Sb*). The results of calculations of the effective radii R_{ui}, interatomic distances d_i, redistribution of electronic density Δq are given in the table.

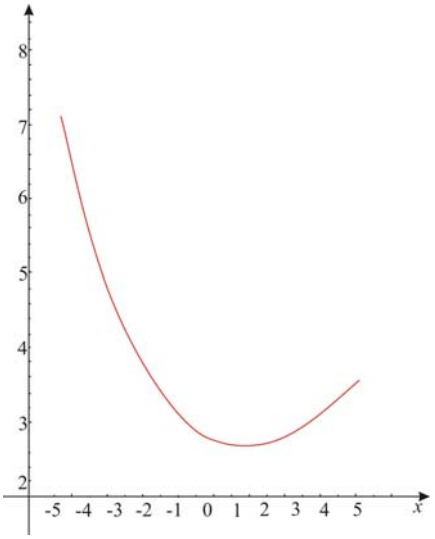

Fig. 1. Diagram of dependence $d_1 = f(x)$ of Zn_xSb_{1-x} system

Table 1

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

φ_j / $R_u, \Delta q, D_j$	φ_1 (*Zn-Sb*)	φ_2 (*Zn-Sb*)	φ_3 (*Zn-Sb*)	φ_4 (*Sb-Sb*)	φ_5 (*Zn-Zn*)
d_j^{exp} (Å)	2.64	2.64	2.76	2.80	2.82
d_j^{theor} (Å)	2.6455	2.644	2.766	2.7943	2.8203
R_u^{Zn} (Å)	0.98	0.975	1.021	–	1.41
R_u^{Sb} (Å)	1.664	1.669	1.745	1.3975	–
R_u^{Zn} / R_u^{Sb}	0.589	0.585	0.585	–	–
Δq bond q_j	0.0874	0.0279	-0.0169	0.0345	0.029
D_j (eV)	1.5544	1.5526	1.4808	2.3327	1.1955

Thus, as a result of taking into account the quantum-mechanical interpretation of the empirical material by combining the principles of different approaches- theoretical and experimental- in a uniform quantitative method for calculating the electronic structure of substance, the dependence of the NHO bond energies on their lengths and electron configurations of atoms in *ZnSb* crystals was obtained. In contrast to [6], in this paper the construction of the working formula is carried out with regard to the elements of the similarity theory, and the expression for the binding energy of NHO in *ZnSb* crystals takes on the form:

$$D_{A-B}^{(j)} = \frac{C_1\left(R_{uA}^0 + R_{uB}^0\right)}{\left(tg\alpha_A + tg\alpha_B\right)}\left(\frac{C_2 d_j}{d_j^2 - R_{uA}R_{uB}} - \frac{1}{d_j}\right), \tag{9}$$

where $R^0{}_{uA(B)}$ and $tg\alpha_{A(B)}$ are coefficients of Eqs. (2) – (4) for atoms A and B, and R_{uA} and R_{uB} are effective radii of their ions in ($A - B$) bond of length $d_i (1 \le i \le 5)$; C_1 and C_2 are constants:

C_1 is a coefficient which reflects the correlation between dimensional and energy characteristics of interatomic interaction, such as ionization potentials, screening effects, electronegativity with effective radii and interatomic distances. In the case of using non-system units, when the distance is measured in angstroms, C_1 is measured in volts.

C_2 is a coefficient which depends on the type of crystalline structure, chemical bond and reflects quantitatively the correlation between coefficients $tg\alpha_A$ and $tg\alpha_B$ from equations (2) – (4) and the values d_j and (R_{uA}/R_{uB}) – with regard to similarity theory elements, coefficient C_2 is selected dimensionless.

When solving a self-consistent variational problem, as a first approximation, coefficients C_1 and C_2 were chosen equal. The results of calculations of binding energies of individual NHO for $C_1 = C_2 = 1$ are also given in the table.

With a view to expand the possibilities of calculations using formula (9), Figs. 2–3 present the dependences of D_{ZnSb} as a function of C_1 and C_2. A characteristic feature of both dependences is that with increasing C_1 and C_2, the numerical value of D_j increases, which may reflect the dependence of D_j on the crystal structure of the substance, the nature of the chemical bond, the degrees of doping, the presence of polymorphous and phase transformations.

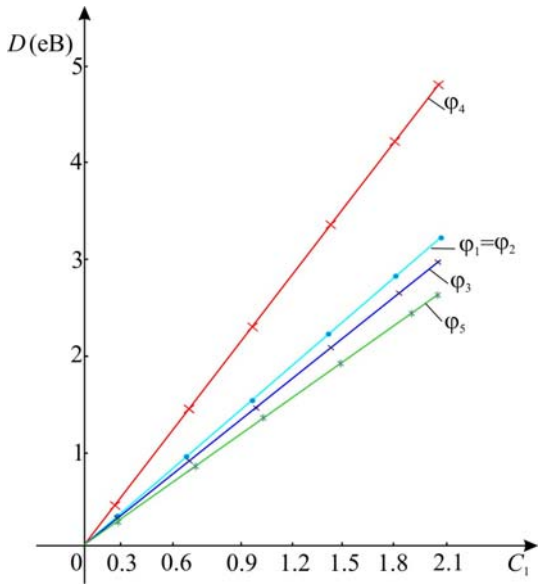

Fig. 2. Dependence of dissociation energy D_j of nonequivalent chemical bonds on the values of coefficient C_1

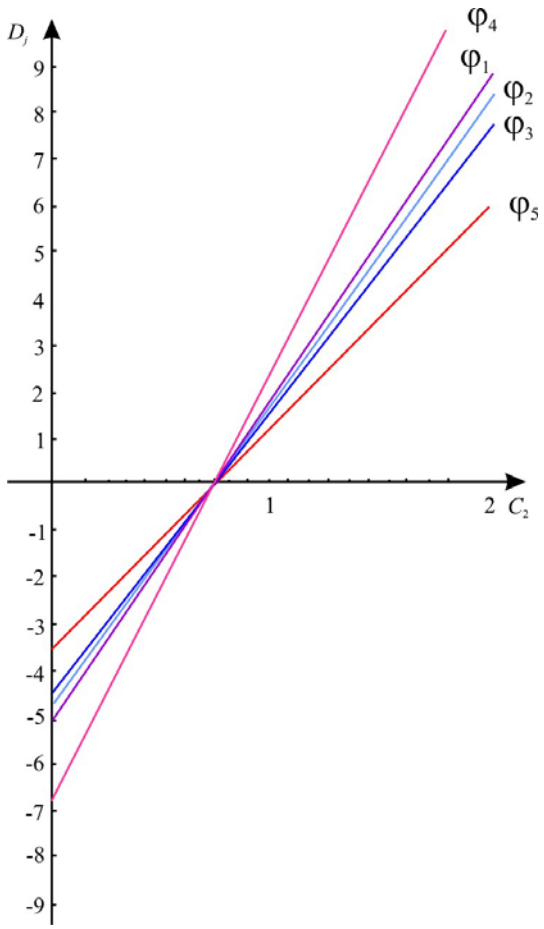

Fig. 3. Dependence of dissociation energy D_j of nonequivalent chemical bonds on the values of coefficient C_2

Of particular interest, in our opinion, is the region in the vicinity $C_2 = 0.75$, where the sign of the charge carriers is inversed. Such an approach can not only give an answer to the question of why this occurs, but it can also indicate a sequence of technological methods for obtaining *ZnSb* crystals with a certain type of conductivity and the necessary set of physicochemical properties.

Discussion of the results

Analysis of the results obtained in the present study showed that the semi-empirical relationships presented in this paper can be used not only for calculating the binding energies of individual NHO in *ZnSb* crystals, but also for developing technological modes for the production of new thermoelectric materials based on *ZnSb* with a certain type of conductivity and a set of physicochemical properties.

The possibilities of a uniform physical interpretation of the above equations make it possible to use the achievements in describing the interrelation of the individual characteristics of atoms in the study of interatomic interactions in compounds differing in stoichiometry, structure, type of chemical bonds, and physicochemical properties.

Conclusion

1. On the basis of quantum-mechanical approach a method of using nonequivalent hybrid orbitals has been developed for the calculation of interatomic interaction in *ZnSb* crystals.
2. Calculations have been made of charge redistribution in the nonequivalent hybrid orbitals characterizing formation of a donor or acceptor bond.
3. A method has been developed and calculations have been performed of the dissociation energy of nonequivalent chemical bonds in *ZnSb* crystals.
4. The results obtained in this paper agree with the results of chemical bond calculation by microscopic theory methods and can be used in the development of technological conditions for synthesis of new thermoelectric materials based on *n*- and *p*-type *ZnSb*.

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Маник О. М., *канд. фіз.-мат. наук*
Маник Т. О. *канд. фіз.-мат. наук.*,
Білинський-Слотило В. Р. *канд. фіз.-мат. наук*

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна, *e-mail: anatych@gmail.com*;
Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatych@gmail.com

ОСОБЛИВОСТІ ЕЛЕКТРОННОЇ БУДОВИ Й МІЖАТОМНОЇ ВЗАЄМОДІЇ В КРИСТАЛАХ *ZnSb*

Розроблено комплексний підхід для розрахунків параметрів електронної будови гібридних орбіталей, що відповідають нееквівалентним міжатомним відстаням у низькосиметричних кристалах $A^{II}B^{V}$, $A^{II}B^{VI}$, $A^{III}B^{V}$ (бінарних сполук). На основі квантовомеханічного та квантовостастичного підходів проведено розрахунки енергії Фермі, ефективних зарядів, ефективних радіусів, а також перерозподілу електронної густини, енергії дисоціації нееквівалентних гібридних орбіталей (НГО) ZnSb. Отримані результати можуть бути використані при розробці технологічних режимів одержання нових матеріалів на основі ZnSb n- та p- типу, що володіють високою чутливістю, стабільністю та ідентичністю характеристик, особливо необхідних для термоперетворювачів метрологічного призначення. Бібл.8, Рис. 3, Табл. 1.

Ключові слова: нееквівалентні гібридні орбиталі, ефективні заряди, ефективні радіуси, енергія дисоціації.

Маник О. Н. *канд. физ.-мат. наук*
Маник Т. О. *канд. фіз.-мат. наук,*
Билинский-Слотыло В. Р. *канд. физ.-мат. наук*

[1]Институт термоэлектричества НАН и МОН Украины, ул. Науки, 1,
Черновцы, 58029, Украина, *e-mail: anatych@gmail.com*;
[2]Черновицкий национальный университет имени Юрия Федьковича,
ул. Коцюбинского 2, Черновцы, 58012, Украина
e-mail: anatych@gmail.com

ОСОБЕННОСТИ ЭЛЕКТРОННОГО СТРОЕНИЯ И МЕЖАТОМНОГО ВЗАИМОДЕЙСТВИЯ В КРИСТАЛАХ *ZnSb*

Разработан комплексный подход для расчетов параметров электронного строения гибридных орбиталей, соответствующих неэквивалентным межатомным расстояниям в

низкосимметричных кристаллах $A^{II}B^{V}$, $A^{II}B^{VI}$, $A^{III}B^{V}$ (бинарных соединений). На основе квантовомиханического и квантовостатистического подходов проведены расчеты энергии Ферми, эффективных зарядов, эффективных радиусов, а также перераспределения электронной плотности, энергии диссоциации неэквивалентных гибридных орбиталей (НГО) ZnSb. Полученные результаты могут быть использованы при разработке технологических режимов получения новых материалов на основе ZnSb n- p типа, обладающих высокой чувствительностью, стабильностью и идентичностью характеристик, особенно необходимых для термопреобразователей метрологического назначения. Библ.8, Рис.3, Табл. 1.
Ключевые слова: неэквивалентные гибридные орбитали, эффективные заряды, эффективные радиусы, энергия диссоциации.

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L.M. Vikhor

L.M. Vikhor, *Doctor of Phys.-math. Sciences,*
M.V. Maksimuk

Institute of Thermoelectricity of the NAS and MES of Ukraine, 1, Nauky str, Chernivtsi, 58029, Ukraine;
e-mail: anatych@gmail.com

M.V. Maksimuk

DESIGN OF THERMOELECTRIC CASCADE MODULES FOR SOLID FUEL TEG

This paper presents the results of computer design of generator thermocouple cascade modules made of materials based on Bi_2Te_3-PbTe-TAGS to be used in solid fuel thermoelectric generators. Computer methods based on the optimal control theory were used to determine optimal conditions whereby the maximum power of modules and thermoelectric conversion efficiency is achieved. The comparative energy characteristics of such modules are given in the operating temperature range 30 – 500 °C. The design was performed with regard to the temperature dependences of material parameters, thermal and electrical losses on the contacts and interconnects of stages. Bibl. 15, Fig. 1, Table 2.

Key words: thermoelectric generator, cascade modules, computer design, optimal control theory, physical model, efficiency.

Introduction

Solid fuel heaters, running on firewood and pressed briquettes, are widely used for indoor heating and cooling, especially in rural areas and remote areas of residence. Such heaters become increasingly popular as a result of an increase in the cost of gas and liquid organic fuels. Promising is also their use as heat sources for thermoelectric generators (TEG). In addition to undeniable advantages in terms of cost-effectiveness, the use of heated surfaces of solid fuel furnaces in the TEG design allows creating universal thermoelectric combined heat and power systems that, in comparison with similar thermoelectric systems, working on diesel, gasoline or gas fuel, have a simpler and, at the same time, more reliable construction, are safer and easier to operate [1].

Nowadays, thermoelectric generators whose operation is based on the use of heat from solid fuel heaters are serially produced by a number of foreign enterprises. In particular, the Russian companies Kryotherm and Termofor created thermoelectric power heaters with an electric power of 25 and 50 W designed for lighting, powering low-power household appliances, charging laptop batteriess, mobile phoness,navigators, and heating rooms up to 50 m^2 [2, 3]. Analogues of Russian power heaters are the developments of the Chinese firm Thermonamic Electronics (Jiangxi) Corp., Ltd. with a power of 15 W, 30 W, 45 W [4]. Research on the creation and refinement of existing constructions of solid fuel TEG is pursued in virtually all leading countries of the world, so they are represented by a large number of patents and other scientific literature.

The common weak point of most solid fuel thermoelectric generators is the use as a thermoelectric converter of thermoelectric modules made of materials based on bismuth telluride with the limiting hot temperature 300 °C. However, the temperature of surfaces of solid fuel heat sources on which TEG is installed can be significantly higher, which will reduce service life and, as a result, lead to a rapid generator failure. In this connection, the research aimed at development of

thermoelectric modules with higher operating temperatures and, accordingly, higher efficiency, becomes currently central.

Particularly promising in this respect, in our opinion, is the use of two-stage thermoelectric generator modules optimized for the hot temperature level 500 °C [5].

The purpose of this work is to design a cascade module for thermoelectric generators working from the heat of heated surfaces of solid fuel furnaces wherein thermoelements of the low-temperature stage are made of traditional materials based on *BiTe*, and the high-temperature stage employs the most efficient for temperature range 300°C – 600 °C *PbTe* materials for *n*-type legs and *GeTe-AgSbTe* (TAGS) compounds for *p*-type legs.

Physical model of a cascade thermoelectric module and its mathematical description

Physical model for designing a two-stage generator module for TEG is shown in Fig. 1. Numbering of stages is from the cold to hot stage, electrically connected in series.

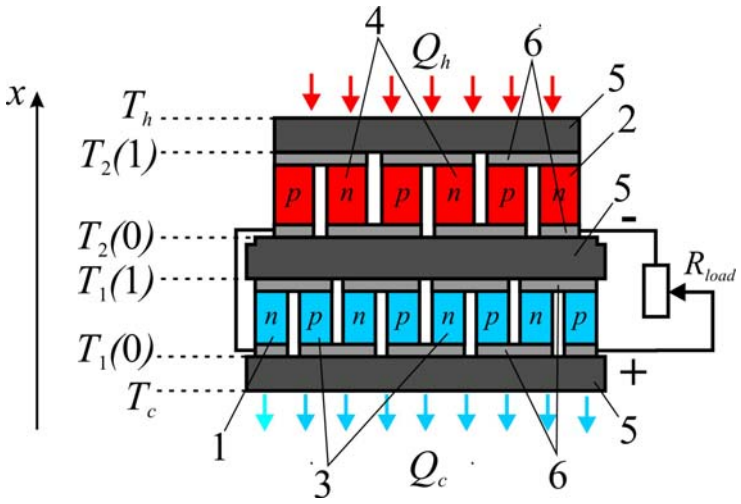

Fig. 1. Physical model of a two-stage module: 1 – low-temperature stage; 2 – high-temperature stage, 3 – thermoelement legs of the low-temperature stage of materials based on n- and p-type BiTe; 4 – thermoelement legs of the high-temperature stage of materials based on n-type PbTe and p-type TAGS; 5 –heat-conducting electrically insulating plates; 6 –connecting plates

Thermocouple elements of the cold stage are made of classical materials based on *n*-type *BiTe*. In the hot stage for *p*-type legs use is made of *PbTe*, and for *p*-type legs – *GeTe-AgSbTe* (TAGS) alloy. The thermocouples of each stage are connected electrically in series and thermally in parallel.

The approximate methods of calculation of cascade thermocouple modules for generators are described in monographs [6 – 8]. The main requirement for the design of cascade generator modules is optimal thermal and electric matching of stages [8]. The most precise optimization of stages is achieved by methods of optimal control theory [9, 10]. In [11], such methods were used for designing two-stage modules of *BiTe* and *PbTe* – TAGS, however, the method of calculation of the optimal design of modules did not take into account thermal and electrical losses in the connecting and insulating plates. Under conditions of high temperatures the impact of thermal resistances of the insulating and connecting plates, as well as electrical resistances of contacts and interconnects in thermoelements on module efficiency is rather significant [9]. Therefore, let us write the basic relations for the design and

optimization of construction of a two-stage generator module with regard to thermal and electrical losses on thermoelement junctions.

Optimization of thermoelectric module lies in the achievement of maximum efficiency, the expression for which is written as

$$\eta = \frac{Q_h - Q_c}{Q_h}\ , \tag{1}$$

where Q_c, Q_h are external heat fluxes on the cold and hot modules surfaces, respectively. To maximum value of η corresponds minimum of functional

$$J = \sum_{k=1}^{2} \left(\ln q_0^k - \ln q_1^k \right), \tag{2}$$

where $q_1^k = Q_1^k / n_k I$, $q_0^k = Q_0^k / n_k I$, k = 1,2 are specific (related to current strength I) heat fluxes on the junctions of thermocouples of k-th stage, n_k is the number of thermocouples in the k-th stage, Q_0^k, Q_1^k are heat fluxes on the cold and hot surfaces of k-th stage which satisfy the conditions of thermal matching on the surfaces of each stage, namely $Q_0^1 = -Q_c$, $Q_0^2 = Q_1^1$, $Q_1^2 = -Q_h$.

To calculate heat fluxes q_1^k, q_0^k, which appear in (2), a system of differential equations of nonequilibrium thermodynamics is used that can be represented as

$$\left.\begin{aligned} \frac{dT}{dx} &= -\frac{\alpha_k^{n,p}(T) j_k^{n,p}}{\kappa_k^{n,p}(T)} T - \frac{j_k^{n,p}}{\kappa_k^{n,p}(T)} q \\ \frac{dq}{dx} &= \frac{(\alpha_k^{n,p}(T))^2 j_k}{\kappa_k^{n,p}(T)} T + \frac{\alpha_k^{n,p}(T) j_k^{n,p}}{\kappa_k^{n,p}(T)} q + \frac{j_k^{n,p}}{\sigma_k^{n,p}(T)} \end{aligned}\right\}_{n,p}, \quad k = 1,2\ , \tag{3}$$

where $x = x/l$ is dimensionless coordinate, l is leg height, $0 \le x \le 1$, $j_k^{n,p} = Il/s_k^{n,p}$ is specific current density in the legs of thermoelements of k-th stage. Characteristics of thermoelectric materials, namely the Seebeck coefficient α, electric conductivity σ and thermal conductivity κ are temperature dependent. The boundary conditions for system (3) are of the form

$$\begin{aligned} &T_n^k(0) = T_p^k(0) \equiv T_k(0), \qquad T_n^k(1) = T_p^k(1) \equiv T_k(1), \qquad k = 1,2, \\ &T_1(0) = T_c + \delta T_1, \quad T_2(1) = T_h - \delta T_3, \quad T_2(0) = T_1(1) + \delta T_2, \end{aligned} \tag{4}$$

The losses in temperature difference on the insulating and connecting plates are found by the formulae:

$$\begin{aligned} \delta T_1 &= T_1(0) - T_c = -q_0^1 \frac{1}{l\left(\frac{1}{j_1^n} + \frac{1}{j_1^p}\right)} \left(\frac{R_{cer} l_{cer}}{K_{cer}} + \frac{R_{con} l_{con}}{K_{con}} \right), \\ \delta T_2 &= T_2(0) - T_1(1) = -\left(\frac{q_0^2}{l\left(\frac{1}{j_2^n} + \frac{1}{j_2^p}\right)} + \frac{q_1^1}{l\left(\frac{1}{j_1^n} + \frac{1}{j_1^p}\right)} \right) \left(\frac{R_{cer} l_{cer}/2}{K_{cer}} + \frac{R_{con} l_{con}}{K_{con}} \right), \\ \delta T_3 &= T_h - T_2(1) = -\frac{q_1^2}{l\left(\frac{1}{j_2^n} + \frac{1}{j_2^p}\right)} \left(\frac{R_{cer} l_{cer}}{K_{cer}} + \frac{R_{con} l_{con}}{K_{con}} \right). \end{aligned} \tag{5}$$

where R_{cer}, R_{con} are specific thermal resistances of insulating and connecting plates, l_{cer}, l_{con} – the thicknesses of insulating and connecting plates, K_{cer}, K_{con} – fill factors of insulating and connecting plates the values of which must be preset in order to take into account the losses in temperature difference on the insulating and connecting plates in the design of a generator module.

Specific heat fluxes q_1^k, q_0^k on the hot and cold junctions of thermocouples are related to heat fluxes at the boundaries of thermoelement legs by relationships

$$\left.\begin{aligned} q_1^k &= \sum_{n,p}\left[q_k^{n,p}(1) + \frac{j_k^{n,p}}{l} r_0 \right] + q_{com} \\ q_0^k &= \sum_{n,p}\left[q_k^{n,p}(0) - \frac{j_k^{n,p}}{l} r_0 \right] - q_{com} \end{aligned}\right\},\ k = 1,2\,, \tag{6}$$

which take into account the Joule heat release on the contact resistances r_0 and connecting plates. To calculate the specific Joule heat which is released in connecting plate q_{con}, one can use the following expression [12]

$$q_{com} = \frac{2 r_{com} I}{l_{com}}\left(K_{com} - \frac{2}{3} \right), \tag{7}$$

Heat fluxes q_1^k, q_0^k depend on the parameters of specific current density in stages $j_k^{n,p}$. The problem of optimization of thermoelectric generator module is to find such optimal values of current density $j_k^{n,p}$ for each stage which impart minimum to functional J (2).

Such problem is solved by methods of optimal control theory [13], according to which to find the optimal values of current density $j_k^{n,p}$, we get the following recurrence relations:

$$j_k^{n,p} = \left(\frac{I_1^k}{2 I_2^k - \partial J / \partial j_k} \right)_{n,p}, \qquad k=1,2, \tag{8}$$

where

$$\left.\begin{aligned} I_1^k &= \psi_2 q\big|_0^1 + \int_0^1 \frac{\alpha_k j_k}{\kappa_k}\left(\psi_1 T - \psi_2 q \right) dx, \\ I_2^k &= \int_0^1 \frac{\psi_2}{\sigma_k}\left(1 + \frac{\alpha_k^2 \sigma_k}{\kappa_k} T \right) dx, \end{aligned}\right\}_{n,p} \qquad k=1,2,$$

$$\frac{\partial J}{\partial (j_k^{n,p})} = -\frac{r_0}{l}\left(\frac{1}{q_0^k} + \frac{1}{q_1^k} \right).$$

The temperature at the boundary of stages $T_1(1)$ must satisfy the condition

$$\sum_{n,p} \psi_1^{(2)_{n,p}}(0) = \sum_{n,p} \psi_1^{(1)_{n,p}}, \tag{9}$$

and the temperature $T_2(0)$ – the equality (5). In optimal control theory, functions $\Psi_1^{(k)n,p}(x)$, $\Psi_2^{(k)n,p}(x)$, which appear in relations (8) and (9), are called pulses and are solutions of the linear boundary problem conjugate to problem (3) – (4) of finding phase variables $T_k^{n,p}(x)$, $q_k^{n,p}(x)$ [13].

The solution of the problem of optimization of a cascade thermoelectric module is realized by the method of successive approximations. As a result, for given temperatures of generator surfaces T_c and T_h, the temperature dependences of material parameters of thermoelement legs $\alpha(T)$, $\sigma(T)$ and $\kappa(T)$ and parameters which characterize contacts, insulating and connecting plates, the optimal values of current density $j_k^{n,p}$ in the legs of thermoelements and the corresponding distributions of temperature $T(x)$ and heat flux $q(x)$ are determined, which provides the minimum value of $J_{\max}$ functional.

The resulting data are then used to calculate the optimal design of thermoelectric generator module, which must provide the present values of generated power W and voltage U on the external load. In the case of a series electrical connection of stages and thermoelements in stages, the value of current in the thermocouple legs is defined as I = W/U. Then, at given values of thermoelement leg height l and current I, the optimal cross-sectional areas of legs are found from conditions of electric matching of stages

$$\left(\frac{j_n S_n}{l}\right)_k = \left(\frac{j_p S_p}{l}\right)_k = I, \quad k = 1,2. \tag{10}$$

Maximum module efficiency is calculated by the formula

$$\eta = 1 - \exp(J). \tag{11}$$

Thermal power on the hot surface of module, necessary for the generation of preset electric power W, is determined as

$$Q_h = \frac{W}{\eta}. \tag{12}$$

Optimal number of thermocouples n_1 anda n_2 in the low-temperature and high-temperature stages, respectively, is found from the conditions of their thermal matching

$$Q_h = -q_1^2 n_2, \qquad q_1^1 n_1 = q_0^2 n_2. \tag{13}$$

Such a problem of designing thermoelectric generator modules with maximum efficiency is solved by computer methods. For this purpose, the appropriate computer tools have been developed at the Institute of Thermoelectricity [14].

Results of design of a two-stage module for TEG

The above described method was used for the calculation of optimal design parameters of a two-stage module for thermoelectric solid fuel generators with the operating temperature range 30 °C – 500 °C. It was assumed that thermoelements of the low-temperature stage are made of materials based on *BiTe*, and the high-temperature stage employs *PbTe* materials for *n*-type legs and *GeTe-AgSbTe* (TAGS) compounds for *p*-type legs. The experimental temperature dependences of characteristics $\alpha(T)$, $\sigma(T)$ i $\kappa(T)$ of these materials that were approximated by polynomials were used for the calculations and given in [15]. The design of the module was performed to obtain power W = 20 W and voltage U = 6 V on the external load. Other parameter values of insulating and connecting plates, necessary for the calculations, are given in Table 1.

Table 1

Input data for the design of cascade module for TEG

Parameter	Designation	Value
Contact resistance	r_0	$10^{-5}\,\Omega\cdot\text{sm}^2$
Height of thermoelement legs	L	0.55 sm
Thickness of insulating plates	l_{cer}	0.063 sm
Thickness of connecting plates	l_{con}	0.025 sm
Thermal conductivity of material of insulating plates	κ_{cer}	0.24 W/(sm·K)
Thermal conductivity of material of connecting plates	κ_{con}	4 W/(sm·K)
Electric conductivity of material of connecting plates	σ_{con}	$58.1\cdot10^4\ \Omega^{-1}\cdot\text{sm}^{-1}$

Table 2 shows the obtained values of design parameters of a two-stage module from *BiTe* and *PbTe* and TAGS materials for TEG.

Table 2

Calculated values of design parameters of a two-stage module

Parameter	Designation	Value
The number of thermoelements of the low-temperature stage	n_1	82 couples
The number of thermoelements of the high-temperature stage	n_2	64 couples
Cross-sectional area of the low-temperature stage legs	S_1	0.4x0.4 sm^2
Cross-sectional area of the high-temperature stage legs	S_2	0.36x0.36 sm^2

According to the calculation results, the expected efficiency value of such a module in the operating temperature range 30 °C – 500 °C can reach 12 %. The required amount of heat from combustion of solid fuel is about 160 W. Accordingly, thermal energy of power 140 W must be removed from the heat releasing surface of module in order to assure the necessary operating temperature range.

Thus, the efficiency of a two-stage module exceeds by a factor of 1.5 – 2 the efficiency of traditional single-stage modules of materials based on *BiTe*. Practical application of such modules in solid fuel generators can significantly improve the efficiency of heat into electricity conversion.

Conclusion

1. Technique for computer design of cascade thermoelectric generator modules by methods of optimal control theory is improved. The effect of thermal and electrical losses in the insulating and connecting plates is additionally taken into account.
2. The optimal values of design parameters of a two-stage thermoelectric module of power 20 W of materials based on *BiTe* in the low-temperature stage and *PbTe* and TAGS in the high-temperature stage were calculated. The expected value of module efficiency 12 % was obtained. Practical application of such a module in solid fuel generators will help to improve the efficiency of thermal into electric energy conversion by a factor of 1.5 – 2.

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Вихор Л.М., *докт. фіз.-мат. наук*,
Максимук М.В.

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна*, e-mail: anatych@gmail.com*

ПРОЕКТУВАННЯ ТЕРМОЕЛЕКТРИЧНИХ КАСКАДНИХ МОДУЛІВ ДЛЯ ТЕГ НА ТВЕРДОМУ ПАЛИВІ

Наведено результати комп'ютерного проектування генераторних термопарних каскадних модулів з матеріалів на основі Bi_2Te_3-PbTe-TAGS для використання в термоелектричних генераторах на твердому паливі. Шляхом застосування комп'ютерних методів, що ґрунтуються на теорії оптимального керування визначено оптимальні умови, за яких

досягається максимальна потужність модулів та ККД термоелектричного перетворення. Подано порівняльні енергетичні характеристики таких модулів у діапазоні робочих температур 30 – 500 °С. Проектування здійснено з урахуванням температурних залежностей параметрів матеріалів, теплових і електричних втрат на контактах і комутаціях каскадів. Бібл. 15, Рис. 1, Табл. 2.
Ключові слова: термоелектричний генератор, каскадні модулі, комп'ютерне проектування, теорія оптимального керування, фізична модель, ефективність.

Вихор Л.Н., *докт. физ.-мат. наук,*
Максимук Н.В.

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина
e-mail: anatych@gmail.com

ПРОЕКТИРОВАНИЕ ТЕРМОЭЛЕКТРИЧЕСКИХ КАСКАДНЫХ МОДУЛЕЙ ДЛЯ ТЭГ НА ТВЕРДОМ ТОПЛИВЕ

Приведены результаты компьютерного проектирования генераторных термопарных каскадных модулей из материалов на основе Bi_2Te_3-PbTe-TAGS для использования в термоэлектрических генераторах на твердом топливе. Путем применения компьютерных методов, которые основываются на теории оптимального управления, определены оптимальные условия, при которых достигается максимальная мощность модулей и КПД термоэлектрического преобразования. Представлены сравнительные энергетические характеристики таких модулей в диапазоне рабочих температур 30 – 500 °С. Проектирование осуществлено с учетом температурных зависимостей параметров материалов, тепловых и электрических потерь на контактах и коммутациях каскадов. Библ. 15, Рис. 1, Табл. 2.
Ключевые слова: термоэлектрический генератор, каскадные модули, компьютерное проектирование, теория оптимального управления, физическая модель, эффективность.

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L.I.Anatychuk

L.I.Anatychuk[1,2] *acad. National Academy of Sciences of Ukraine*,
A.V.Prybyla [1,2], *Candidate Phys.-math. Sciences*

Institute of Thermoelectricity of the NAS and MES of Ukraine, 1, Nauky str, Chernivtsi, 58029, Ukraine;
e-mail: anatych@gmail.com
[2]Yu.Fedkovych Chernivtsi National University, 2, Kotsiubynskyi str., Chernivtsi, 58000, Ukraine


A.V.Prybyla

LIMITING POSSIBILITIES OF THERMOELECTRIC LIQUID-LIQUID HEAT PUMPS

The paper presents the results of calculations of the limiting possibilities of thermoelectric liquid-liquid heat pumps, in particular, for their use as a high-performance heater for a space-purpose water purifying device. Bibl. 9, Fig. 2.
Key words: thermoelectric heat pump, efficiency, distiller.

Introduction

General characterization of the problem. The use of thermoelectric heat pumps (THP) in air conditioning systems is due to their unique properties [1 – 5]: environmental friendliness (such equipment does not contain toxic refrigerants); reliability (resistance to mechanical influences, long service life); independence from orientation in space (the possibility of work in the absence of gravity) [6, 7].

An example of efficient use of thermoelectric heat pumps is systems of water recovery from liquid biowaste aboard manned spacecrafts (urine, atmospheric condensate, sanitary and hygienic water). Testing their efficiency on NASA stand has shown that in the most important characteristics, such as specific energy consumption, dimensions, weight and quality of the distillate obtained, water purifying devices with a thermoelectric heat pump outperform known space-purpose analogs [4, 5].

However, new, higher demands are put on such devices due to the possibilities of their new applications (manned missions of mastering Mars and other planets). This mainly concerns the reduction of their weight, dimensions, as well as energy costs for the operation of thermoelectric heat pump. The task of further improving the quality of such devices is very complicated, since the achieved values of their efficiency are close to the limit.

The purpose of our work is to determine the limiting possibilities of thermoelectric liquid-liquid heat pump in order to understand further steps to improve its efficiency.

Physical model of THP

To determine the limiting possibilities of thermoelectric heat pump, its simplified physical model is used (Fig. 1). It comprises heat exchangers 1 assuring passage of heat flux Q_h through the hot side of thermoelectric modules, thermoelectric modules 3, heat exchangers 2 assuring passage of heat flux Q_c through the cold side of thermoelectric modules and a system of hydraulically bound channels 4 providing for circulation of liquid in the thermoelectric heat pump.

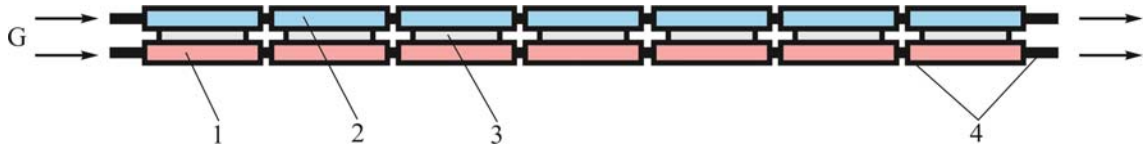

Fig. 1. The simplest physical model of thermoelectric heat pump

In the simplest case this model represents series-connected hot 1 and cold 2 heat exchangers with thermoelectric modules arranged between them. In so doing, in order to determine maximum possible values of the efficiency of thermoelectric heat pump, we neglect the losses of energy on pumping of heat carrier in the heat exchangers and the losses of temperature difference in them.

To assure optimal operation of thermoelectric modules, each of them has individual power supply.

Mathematical and computer description of the model

To describe heat and electric current fluxes, we will use the laws of conservation of energy

$$div\vec{E} = 0 \tag{1}$$

and electric charge

$$div\vec{j} = 0, \tag{2}$$

where

$$\vec{E} = \vec{q} + U\vec{j}, \tag{3}$$

$$\vec{q} = \kappa\nabla T + \alpha T\vec{j}, \tag{4}$$

$$\vec{j} = -\sigma\nabla U - \sigma\alpha\nabla T. \tag{5}$$

Here, $\vec{E}$ is energy flux density, $\vec{q}$ is thermal flux density, $\vec{j}$ is electric current density, U is electric potential, T is temperature, α, σ, κ are the Seebeck coefficient, electric conductivity and thermal conductivity.

With regard to (3) – (5), one can obtain

$$\vec{E} = -(\kappa + \alpha^2\sigma T + \alpha U\sigma)\nabla T - (\alpha\sigma T + U\sigma)\nabla U. \tag{6}$$

Then the laws of conservation (1), (2) will acquire the form:

$$-\nabla\left[(\kappa + \alpha^2\sigma T + \alpha U\sigma)\nabla T\right] - \nabla\left[(\alpha\sigma T + U\sigma)\nabla U\right] = 0, \tag{7}$$

$$-\nabla(\sigma\alpha\nabla T) - \nabla(\sigma\nabla U) = 0. \tag{8}$$

Nonlinear differential equations of second order in partial derivatives (7) and (8) determine the distribution of temperature T and potential U in thermoelements.

An equation describing the process of heat transport in the walls of heat exchangers in the steady-state case is written as follows:

$$\nabla(-k_1 \cdot \nabla T_1) = Q_1, \tag{9}$$

where k_1 is thermal conductivity of heat exchanger walls, ∇T_1 is temperature gradient, Q_1 is heat flux.

The processes of heat-and-mass transfer of heat carriers in heat exchanger channels in the steady-state case are described by equations [8]

$$-\Delta p - f_D \frac{\rho}{2d_h} v|\vec{v}| + \vec{F} = 0, \tag{10}$$

$$\nabla(A\rho\vec{v}) = 0, \tag{11}$$

$$\rho AC_p\vec{v} \cdot \nabla T_2 = \nabla \cdot Ak_2\nabla T_2 + f_D \frac{\rho A}{d_h}|\vec{v}|^3 + Q_2 + Q_{wall}, \tag{12}$$

where p is pressure, ρ is heat carrier density, A is cross-section of the tube, $\vec{F}$ is the sum of all forces, C_p is heat carrier heat capacity, T_2 is temperature, $\vec{v}$ is velocity vector, k_2 is heat carrier thermal conductivity, f_D is the Darcy coefficient, $d = 4A/Z$ is effective diameter, Z is perimeter of tube wall, Q_2 is heat which is released due to viscous friction [W/m] per unit length of heat exchanger, Q_{wall} is heat flux coming from the heat carrier to the tube walls [W/m]

$$Q_{wall} = h \cdot Z \cdot (T_1 - T_2), \tag{13}$$

where h is heat exchange coefficient which is found from equation

$$h = \frac{Nu \cdot k_2}{d}. \tag{14}$$

Here, Nu is the Nusselt number found from equation:

$$Nu = \frac{\left(\frac{f_d}{8}\right)(Re - 1000)\,Pr}{1 + 12.7\left(\frac{f_d}{8}\right)^{\frac{1}{2}}\left(Pr^{\frac{2}{3}} - 1\right)}, \tag{15}$$

where $Pr = C_p \cdot \mu / k_2$ is the Prandtl number, μ is dynamic viscosity, $Re = \rho v d/\mu$ is the Reynolds number, $3000 < Re < 6 \cdot 10^6$, $0.5 < Pr < 2000$.

The Darcy coefficient f_D is found with the use of the Churchill equation for the entire spectrum of the Reynolds number and all the values of e/d (e is roughness of wall surface)

$$f_D = 8\left[\left(\frac{8}{Re}\right)^{12} + (A + B)^{-1.5}\right]^{1/12}. \tag{16}$$

where $A = \left[-2.457 \cdot \ln\left(\left(\frac{7}{Re}\right)^{0.9} + 0.27(e/d)\right)\right]^{16}$, $B = \left(\frac{37530}{Re}\right)^{16}$.

Solving Eqs.(7) – (12), we obtain the distributions of temperatures, electric potential (for thermoelements), velocities and pressure (for heat carrier).

The above differential equations with the respective limiting conditions were solved using Comsol Multiphysics package of applied programs.

Computer simulation results

Below are given the results of calculations of the parameters of thermoelectric pump with respect to physical model shown in Fig.1. The optimal number of thermoelectric modules N was determined to assure the required cooling capacity Q_0, as well as the optimal supply current I_{opt} of each module to assure the highest integral coefficient of performance ε^{int}.

The initial data for calculations:

cooling capacity – 600 W;

heat carrier temperature at inlet to hot heat transfer loop – 36 ºC;

heat carrier temperature at inlet to cold heat transfer loop – 31 ºC;

heat carrier flow rate in each loop – 22 ml/s.

Thus, as a result of the simulation, the number of thermoelectric modules was determined to provide the required cooling capacity Q_0 = 600 W, which is 110 pieces. In so doing, all thermoelectric modules work at optimal power supply which provides for achievement of the highest value of integral coefficient of performance of thermoelectric heat pump at the level of $\varepsilon^{int} = 2.5$.

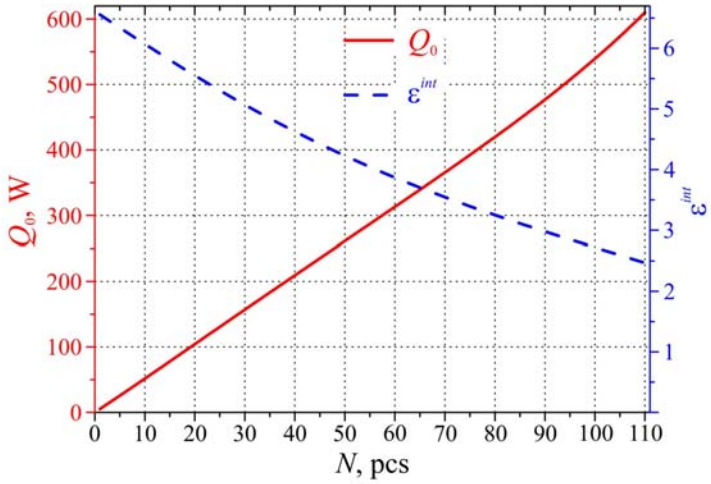

Fig. 2.Dependence of cumulative cooling capacity and integral coefficient of performance of thermoelectric heat pump on the number of thermoelectric modules

Comparison of the results obtained to the results of previous investigations of thermoelectric heat pump [9] testifies that the limit value of coefficient of performance of THP exceeds the level reached for today (ε = 1.85) by 26 %. This allows us to conclude that there is a need for further research on THP in order to bring its efficiency closer to the maximum possible values.

Conclusion

1. The dependence of cooling capacity of thermoelectric heat pump on the number of thermoelectric modules each working at optimal supply current was calculated. To achieve cooling capacity Q = 600 W, it is necessary to have 110 thermoelectric modules.
2. It was established that the limit values of the integral coefficient of performance of thermoelectric heat pump, provided optimal electric current is supplied to each of thermoelectric modules and cooling capacity Q_0 = 600 W is achieved, are ε^{int} = 2.5.
3. Comparison of the results obtained to the results of previous investigations of thermoelectric heat pump testifies that the limit value of coefficient of performance of THP exceeds the level reached for today by 26 %.

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Анатичук Л.І. *ак. НАН України*,[1,2]
Прибила А.В. *кандидат фіз.-мат. наук*[1,2]

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна*, e-mail: anatych@gmail.com*
Чернівецький національний університетім. Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58000, Україна,
e-mail: anatych@gmail.com

ПРО ГРАНИЧНІ МОЖЛИВОСТІ ТЕРМОЕЛЕКТРИЧНИХ ТЕПЛОВИХ НАСОСІВ РІДИНА-РІДИНА

У роботі наводяться результати розрахунків граничних можливостей термоелектричних теплових насосів рідина-рідина, зокрема для їх використання у якості високоефективного нагрівника для приладу очистки води космічного призначення. Бібл. 9, Рис. 2.
Ключові слова: термоелектричний тепловий насос, ефективність, дистилятор.

Анатычук Л.И.[1,2] *ак. НАН Украины*,
Прибыла А.В.[1,2] *канд.физ.-мат. наук*

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина
e-mail: anatych@gmail.com
Черновицкий национальный университет им. Юрия Федьковича,
ул. Коцюбинського 2, Черновцы, 58000, Украина
e-mail: anatych@gmail.com

О ПРЕДЕЛЬНЫХ ВОЗМОЖНОСТЯХ ТЕРМОЭЛЕКТРИЧЕСКИХ ТЕПЛОВЫХ НАСОСОВ ЖИДКОСТЬ-ЖИДКОСТЬ

В работе приводятся результаты расчетов предельных возможностей термоэлектрических тепловых насосов жидкость-жидкость, в частности для них использование в качестве высокоэффективного нагревателя для прибора очистки воды космического назначения. Библ. 9, Рис. 2.

Ключевые слова: термоэлектрический тепловой насос, эффективность, дистиллятор.

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P.D.Mykytiuk, *Candidate Phys.-math. Sciences*

P.D.Mykytiuk

Institute of Thermoelectricity of the NAS and MES of Ukraine, 1, Nauky str, Chernivtsi, 58029, Ukraine; *e-mail: anatych@gmail.com*
Yurii Fedkovych Chenivtsi National University, 2, Kotsiubynskyi str., Chernivtsi, 58012, Ukraine; e-mail: anatych@gmail.com

ON THE STABILITY OF PARAMETERS OF THERMOELECTRIC CONVERTERS

The results of experimental studies of the change with time in the main parameters and characteristics of thermoelectric converters are presented.
The results of the studies confirmed the high stability of thermal converters after 20 and more years of their storage and can be used in assessing the reliability criteria of different types of thermoelectric converters. Bibl. 9, Fig. 2, Tables 2.
Key words: thermocouple, heater, thermal converters, sensitivity, stability, reliability.

Introduction

The sphere of application of metrological-purpose thermoelectric converters is constantly expanding due to their unique properties [1 – 2].

Studies in the field of semiconductor physics, electromagnetic fields of lightning and static discharges, as well as nuclear, seismic, ballistic, some biological processes, contact processes of electric welding are often accompanied by the emergence of single electrical signals. A large area of occurrence of such signals causes a wide dynamic range of their values. The voltage range of single pulses encountered in the measurement practice ranges from a few microvolts to hundreds of kilovolts, and the range of duration ranges from a fraction of a second to several seconds.

Determination of the energy of single and rarely encountered electrical pulses is relevant in radar, telemetry, electrical and radio communication, digital technology, automatic control and regulation, and so on [3, 4].

One of the most effective means for recording the integral parameters of single current pulses are pulsed thermoelectric converters [5 – 8].

The pulsed thermoelectric converters, created at the Institute of Thermoelectricity, are optimized for the study of pulsed processes by the method of replacing the investigated element of the circuit by a thermal converter (integrator). Such pulsed thermoelectric converters are characterized by high sensitivity (10/50 V/J), small dimensions and improved reliability. The reliability of pulsed thermoelectric converters in many cases becomes a decisive criterion for their application, since the price of failure can be too high.

Using the modern theory of reliability of thermoelectric devices created at the Institute of Thermoelectricity [9], it is possible to calculate the reliability of pulsed thermoelectric converters. However, no theoretical assessment method can compare in the completeness and reliability of the information obtained with the results of actual verification of the main parameters of pulsed thermoelectric converters after a considerable period of time from the moment of their manufacture.

Therefore, it is relevant to study actual changes with time in the main parameters of pulsed thermoelectric converters in order to evaluate their stability and reliability.

The purpose of the work is to analyze the change in parameters of thermal converters with a storage life of 20 years or more to evaluate their operating stability.

Method of studying the main parameters of pulsed thermoelectric converters

For the object of investigation, 94 pulsed thermoelectric converters of different types were taken, that had been manufactured in the Special Design and Technological Bureau "Phonon" in the period from 1987 to 1990 and at the Institute of Thermoelectricity in 1991.

The investigated pulsed thermoelectric converters were manufactured in conformity with Technical Specifications ТУ АЮЖ 3.369.018.ТУ ГК-1987 by the technology developed in the Special Design and Technological Bureau "Phonon". These pulsed thermoelectric converters were selected at random from different lots of thermal converters as the samples of external appearance, as was required by the state standards that regulated the output of such products.

It should be noted that pulsed thermoelectric converters with not the best electric parameters were selected as the samples of external appearance, since the appearance and quality of pulsed thermoelectric converters labeling were decisive in this case.

In Technical Specifications ТУ АЮЖ 3.369.018. ТУ ГК-1987 the main characteristics and parameters of pulsed thermoelectric converters of different ratings are determined (heater resistance R_H, thermocouple resistance R_T, volt-joule sensitivity S_Q, thermocouple thermoEMF E_T, capacity between the heater and thermocouple, C) and their nominal values are set. Also provided is a complete list of all types of electrical, mechanical, climatic tests according to the results of which the quality of pulsed thermoelectric converters was evaluated.

The above mentioned R_H, R_T, E_T, S_Q, C were selected as the main characteristics in the study of experimental lot of pulsed thermoelectric converters in the amount of 94 pcs. It is the assessment of the deviation of their values from the nominal values established by the technical specifications that will determine the level of stability of the pulsed thermoelectric converters which had been stored from 21 to 25 years.

The method chosen for studying the specified parameters and characteristics is based on the preliminary direct measurement of the heater and thermocouple resistances with the meter L C R MCP BR2820. This approach allows estimating the state of pulsed thermoelectric converters already at the initial research step.

The next research step lies in passing through the heater of an electric current pulse with known energy and registering the thermoEMF value of thermocouple. This allows one to determine the volt-joule sensitivity of pulsed thermoelectric converters S_Q which is found by the formula

$$S_Q = \frac{E_T}{Q}, \tag{1}$$

where E_T is amplitude value of the output signal (thermoEMF) when pulsed thermoelectric converters input is exposed to current pulse, Q is pulse energy. For such investigation a measuring circuit was used which is shown in Fig. 1.

To determine the volt-joule sensitivity of a pulsed thermoelectric converter at given energy (Q = 150 μJ), pulse generator is transferred into manual start mode. The necessary pulse duration is set ($\tau = 10^{-4}$ s). Voltage 5 – 10 V is applied from the power supply unit to power amplifier. Current pulses are fed to the bank of resistors, on which the pre-measured resistance is set, the value of which is equivalent to the resistance of the heater. Then, pulse generator is transferred to the mode of generation of rectangular pulses that can be observed on the oscilloscope. By the formula

$$U_H = \sqrt{\frac{Q \cdot R_H}{\tau}}, \qquad (2)$$

where U_H is voltage supplied to the heater, τ is pulse duration, voltage U_H is determined which corresponds to energy Q = 150 μJ at known τ and R_H.

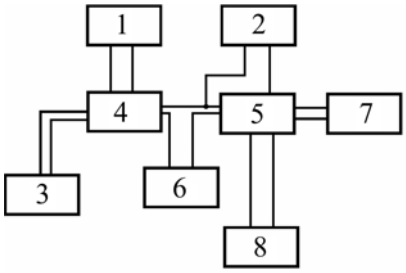

Fig. 1. Structural circuit for measuring parameters of pulsed thermoelectric converters
1 – pulse generator; 2 – R_{equiv} (equivalent resistance); 3 – power supply unit;
4 – power amplifier; 5 – measuring pad with investigated pulsed thermoelectric converter;
6 – R_{lim} (limiting resistance); 7, 8 – memory oscilloscope.

The next research stage is to use limiting resistance R_{lim} and oscilloscope in order to set the necessary voltage U_H which is supplied to the equivalent resistance R_{equiv}. The pulse generator is transferred to the manual start mode, and the measuring pad switches to the position of the converter. Through the pulsed thermoelectric converter using the T5-63 generator the energy pulse of given value is triggered. The oscilloscope connected to the output of pulsed thermoelectric converter registers the output signal – thermocouple thermoEMF E_T. Further, formula (1) is used to calculate the volt-joule sensitivity S_Q.

The final step in the chosen research method is direct measurement of the capacity between the heater and the thermocouple with the help of a high-frequency meter L C R MCP BR2820.

Results of experimental investigations of pulsed thermoelectric converters

As structural elements of the measuring circuit shown in Fig. 1 there were selected serial, checked in the established order electrical measuring instruments: oscilloscope Fluke 199C, meter L C R MCP BR2820, pulse generator G5-63, etc. However, due to the lack of a standard power amplifier, the power amplifier was created and manufactured on the IRF 3808 transistor.

Fig. 2. The picture of a bench for measuring parameters of pulsed thermoelectric converters

Investigations of pulsed thermoelectric converters were performed on a bench the appearance of which is shown in Fig. 2.

Parameters of investigated pulsed thermoelectric converters averaged by the number of each of thermal converter ratings are given in Tables 1 and 2.

Table 1

Averaged parameters of pulsed thermal converters

Year made	Rated value	n, pcs	Averaged values					
			R_H, Ω		R_T, Ω		C, pF	
			specs	fact	Specs	fact	specs	fact
1987	0101	42	0.4 – 0.6	0.543	10 – 200	20.73	5	1.7
	0104	11	0.8 – 1.2	1.104		27.1		1.57
	0116	2	8 – 11	10.578		20.2		1.55
1988	0101	6	0.4 – 0.6	0.584	10 – 200	31.23		1.67
	0104	27	0.8 – 1.2	1.091		19.66		1.57
	0119	2	15 – 17	15.867		16.16		1.6
1989	0116	2	8 – 11	10.117	10 – 200	36.3		1.6
1991	0101	2	0.4 – 0.6	0.6		19.91		1.65

Table 2

Averaged electrical characteristics of pulsed thermal converters

Year made	Rated value	n, pcs	Averaged values			
			$E_{T\min}$, mV, specs	E_T, mV Fact	$S_{Q\min}$, V/J, Specs	S_Q, V/J fact
1987	0101	42	0.1	1.64	10	11
	0104	11		2.27		15
	0116	2		4.25		29
1988	0101	6		1.7		11
	0104	27		2.04		14
	0119	2		4.05		27
1989	0116	2		3.5		23
1991	0101	2		1.7		11

where n is the number of integral thermal converters.

From Tables 1 and 2 it is seen that heater resistance value R_H, thermocouple resistance value R_T, capacity C and volt-joule sensitivity S_Q are within the limits established by specifications.

The above data shows that even after 20 – 25 years of storage, the values of the parameters of the investigated pulsed thermoelectric converters did not deviate from their nominal values specified in the Technical Specifications, while Technical Specifications ТУ АЮЖ 3.369.018. ТУ ГК-1987 allow deviation of the parameters by up to 15 % of their rated values.

Considerable part of the investigated pulsed thermoelectric converters fully meets the requirements of technical specifications, which points to the high stability of parameters of pulsed thermoelectric converters and their reliability.

Constructions of different types of thermal converters, both single-element type TP-2 and TP-4,

pulsed type TI, and multi-element differential type DTPT, are developed using unified structural elements and base members, which provide high reliability and resistance of thermal converters to mechanical and climatic effects. While well-developed perfect technique for manufacturing thermocouples and thermopiles for thermal converters with the use of highly effective thermoelectric materials, which little degrade over time, provide stability and characteristics identity of thermal converters created at the Institute of Thermoelectricity.

In view of the foregoing, the results of the work can be used to select and evaluate the reliability criteria of pulsed thermoelectric converters and other types of thermal converters created at the Institute of Thermoelectricity.

Conclusion

1. Semiconductor thermoelectric converters of pulsed type, created in the Scientific Design and Technological Bureau "Phonon" and at the Institute of Thermoelectricity are characterized by high reliability, maintain stability of their parameters even after 20 – 25 years of storage and are one of the most efficient means in the investigation of single or rarely encountered electric current pulses.
2. In order to determine the critical uptimes of the investigated pulsed thermoelectric converters, it is expedient to continue their research until complete failure

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Микитюк П.Д., *канд. фіз.-мат. наук*

[1]Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна, *e-mail: anatych@gmail.com*;
[2]Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatych@gmail.com

ПРО СТАБІЛЬНІСТЬ ПАРАМЕТРІВ ТЕРМОЕЛЕКТРИЧНИХ ПЕРЕТВОРЮВАЧІВ

Наведено результати експериментальних досліджень зміни з часом основних параметрів і характеристик термоелектричних перетворювачів.
Результати досліджень підтвердили високу стабільність термоперетворювачів після 20 і більше років їх збереження і можуть бути використані при оцінці критеріїв надійності різних типів термоелектричних перетворювачів. Бібл. 9, Рис. 2, Табл. 2.
Ключові слова: термопара, нагрівник, термоперетворювач, чутливість, стабільність, надійність.

Микитюк П.Д., *канд. физ.-мат. наук*

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина;
e-mail: anatych@gmail.com;
Черновицкий национальный университет им. Ю.Федьковича,
ул. Коцюбинского, 2, Черновцы, 58000, Украина
e-mail: anatych@gmail.com

О СТАБИЛЬНОСТИ ПАРАМЕТРОВ ТЕРМОЭЛЕКТРИЧЕСКИХ ПРЕОБРАЗОВАТЕЛЕЙ

Приведены результаты экспериментальных исследований изменения со временем основных параметров и характеристик термоэлектрических преобразователей.
Результаты исследований подтвердили высокую стабильность термопреобразователей после 20 и больше лет их хранения и могут быть использованы при оценке критериев надежности разных типов термоэлектрических преобразователей. Библ. 9, Рис. 2, Табл. 2.
Ключевые слова: термопара, отопитель, термопреобразователь, чувствительность, стабильность, надежность.

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L.I.Anatychuk

L.I. Anatychuk, *acad. National Academy of Sciences of Ukraine*,
O.J. Luste, *Doctor Phys.-math. Sciences*

Institute of Thermoelectricity of the NAS
and MES of Ukraine, 1, Nauky str,
Chernivtsi, 58029, Ukraine;
e-mail: anatych@gmail.com
Yu.Fedkovych Chernivtsi National University, 2,
Kotsiubynskyi str., Chernivtsi, 58012, Ukraine,
e-mail: anatych@gmail.com


O.J.Luste

MODEL STUDIES OF DEGRADATION MECHANISMS OF THERMOELECTRIC MATERIALS AND NEAR-CONTACT STRUCTURES

Analysis of current status and prospects of physical and computer models of degradation of thermoelectric materials and near-contact structures is carried out. Classification of available computer technologies is developed, the relevant lines of their use for the research and development of reliable thermoelectric modules are considered. Bibl. 102, Fig. 16.
Key words: reliability, degradation, thermoelectric materials

Introduction

The rapid improvement of computer technology and software opens up new possibilities for the study of physical processes in thermoelectric materials, instruments and devices. Computer technologies find expanding applications in thermoelectricity [1]. However, their available arsenal is much wider than the methods that have already found application in this field, such as finite-element methods and program complexes on their basis [2, 3].

Numerical experiment has become of the main research tools [4]. Development and use of modern computer technologies is one of the topical problems of simulation in thermoelectricity.

One of classifications of computer simulation methods is given in [5], which deals with:

- finite-difference methods [6, 7],
- finite-element methods [8 – 11],
- finite-volume methods [12, 13],
- particle simulation method [5, 14, 15].

When solving the main problems of thermoelectricity [16], namely electric energy generation, cooling/heating and creation of sensors, one has to study several fields of different nature on the basis of the law of thermoelectric induction [1], consider nonlinear models, optimize models for many parameters and investigate reliability [17]. For such a complex analysis, solely numerical methods and modern computer technologies on their basis can be used.

The purpose of this work is to analyze modern numerical methods and computer technologies on their basis, to identify promising methods of simulation and numerical analysis for solving thermoelectricity problems.

General classification of methods of simulation of thermoelectric devices and materials

The main methods of simulation of physical fields are grid methods. They are mostly used for computer simulation of macro objects. For a complete and comprehensive analysis of thermoelectric materials and devices based on them, universal and integrated methods of computer simulation are required.

Fig. 1 gives a general approach to computer simulation of thermoelectric objects of any complexity at different stages of research, which clearly illustrates the relationship of characteristic lengths and times considered in computer models of physical processes.

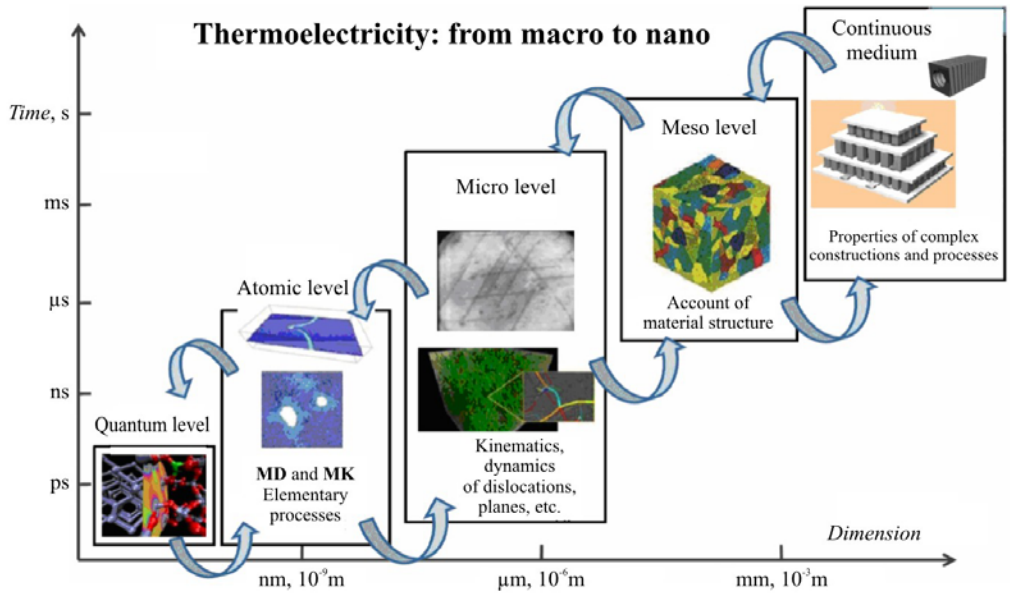

Fig. 1. Computer simulation in thermoelectricity from macro to nano.

General principles of constructing physical models on different levels can be found in [18]. The hierarchy of multi-scale modelling, simulation methods that are used in thermoelectricity [19] on the basis of object-oriented programming [20], with different characteristic times and lengths are given in Fig. 2.

Today, the *ab initio* simulation of particle system is possible, when the number of particles does not exceed 100. Works [21 – 23] are devoted to application of Green's functions, as well as other nanodevice modelling methods [21 – 23]. A review of quantum and classical methods of molecular dynamics can be found in [24 – 26]. Classical Monte Carlo methods are described in [27 – 28], a review of quantum Monte Carlo methods is given in [29].

Deterministic simulation of semiconductors on the basis of the Boltzmann equation is described in monographs [30 – 32]. Phenomenological models of thermoelectric devices are dealt with in a lot of works, such as [16, 33].

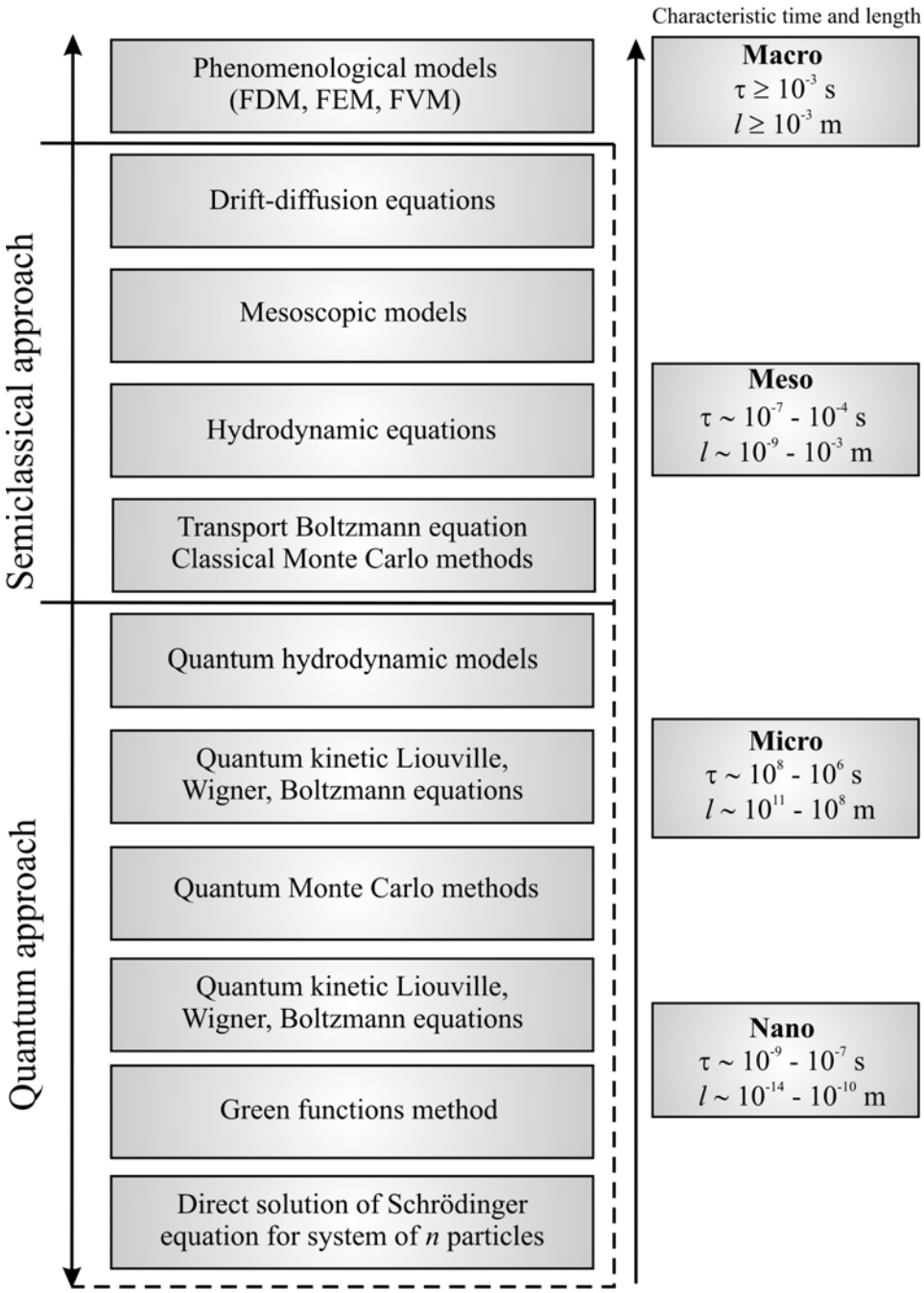

Fig. 2. Hierarchy of simulation methods.

Structural-functional simulation

Traditionally, computer simulation methods are divided into two large groups presented in Fig. 3.

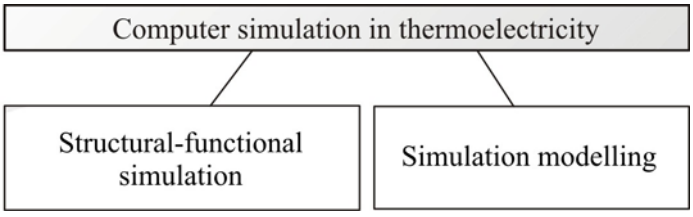

Fig. 3. The main groups of computer simulation methods in thermoelectricity.

The first group is structural-functional simulation of objects described by means of systems of differential or integro-differential equations.

Classification of structural-functional simulation methods is presented in Fig. 4.

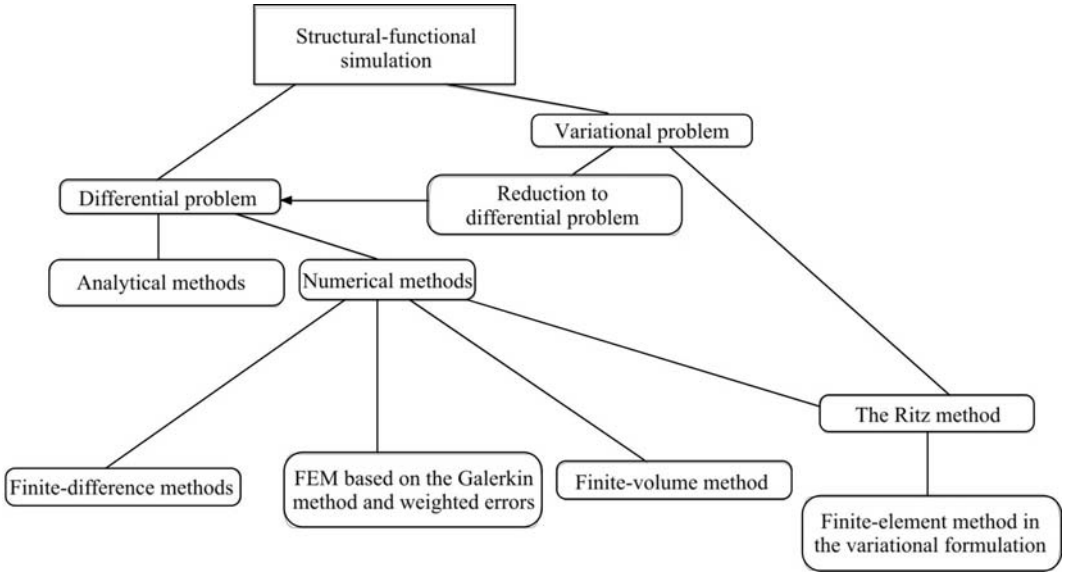

Fig. 4. Classification of structural-functional simulation methods.

The second group – simulation modelling methods for many-body systems will be considered below.

In the majority of cases, thermoelectric models reduce to differential equations (integro-differential). Also, the problem can be stated in the variational formulation of search for functional optimum, which in turn reduces to system of differential equations (if possible). With the aid of analytical methods one can solve a narrow class of problems that are mostly artificial and labour-intensive.

Numerical methods are characterized by universality, making it possible to solve problems for which analytical solution is impossible or too laborious. Finite-difference methods are most common, and to this group of methods one can refer the majority of known numerical methods. Finite-element methods are widely used for solving the problems of simulation of physical fields in geometric areas of arbitrary shape. Fig. 4 shows only the best known, namely the Ritz method and the Galerkin method. Finite-volume method is used rarely, mostly in fluid dynamics and sometimes it is not singled out as a separate group.

Finite-difference methods (FDM)

Finite-difference method is the simplest interpolation method, most studied and known. Its principle lies in the replacement of infinitesimal values in the differential equation by the finite differences between the desired functions and variables.

The basic idea of the method is that the desired continuous function is replaced by a set of approximate values at some points of the domain – nodes. The set of nodes forms a grid. To take into account the boundary conditions, a system of linear/nonlinear (in the case of coefficients depending on independent variables) algebraic equations is formed for the values of function at the grid nodes. The created system is solved by one of the numerical methods of solving systems of equations (Gauss,

relaxation, simple iteration, rotational methods, Jacobi, Seidel, runoff, etc.) [34]. The stability of such schemes is discussed in [35].

In the case of models of thermoelectric devices, in particular, generators based on thermocouple thermoelement [36], several numerical solution procedures were used: precise, iterative and averaging methods. Single-dimensional stationary equations for heat flux and electrical current were used. As an example of thermoelement, the authors chose a thermocouple thermoelement in the temperature range of 0 ÷ 900 K. The results of simulation agree with classical analytical theory of thermocouple element [37]. FDM were also used to study the model of thermoelectric cooler [38], for the optimization of charge carrier concentration of single-valley semiconductor [39]. On the basis of FDM, studied were roll-type thermoelectric generator [40], the models of microprobe for measuring potential in non-isothermal semiconductor [41] and the models of thermoelectric cooler [42, 43]. A program for solving phenomenological equations describing the Seebeck, Hall, Nernst, Peltier, Ettinshausen and Righi-Leduc effects for objects of different geometric shape was developed [44]. FDM were used to study sectional thermoelements [45 – 46].

Finite-difference methods are used almost in all theoretical studies as an auxiliary and basic tool.

Finite-element methods (FEM)

Principle of method

Finite-element analysis became the main research method in many physical and engineering problems, including thermoelectricity. The properties of thermoelectric devices are in many respects dependent on the geometrical shape of device components. For simulation of physical fields of various complexity, FEM analysis provides a versatile and well-developed approach for solving applied problems of thermoelectric instrument making.

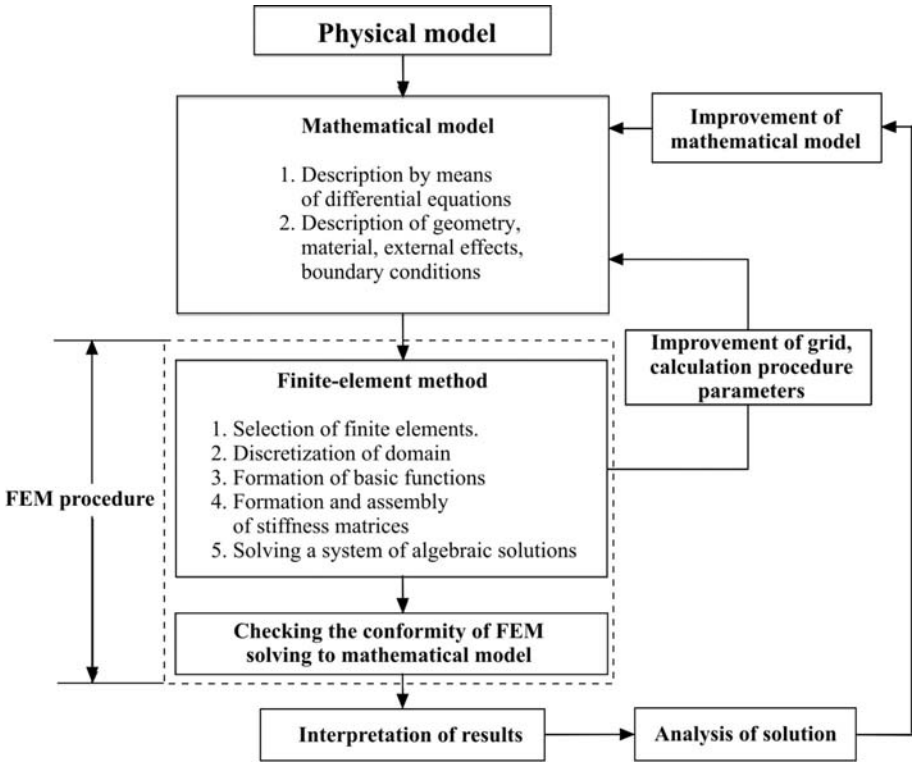

Fig. 5. General diagram of problem solution by finite element methods.

General diagram of the algorithm of solving the problem of physical field simulation by finite-element method consists of the following stages [11]:

- discretization of solution domain;
- selection of solution interpolation on the finite element;
- formation of basic functions;
- calculation of differential problem error with the use of approximate solution in the form of rows;
- formation of stiffness matrices for elements, orthogonalization of error;
- assembly of stiffness matrices according to elements;
- account of boundary conditions;
- solving a system of algebraic equations [47, 48].

Fig. 5 shows a general diagram of simulation of thermoelectric devices by means of FEM algorithms.

Generation of finite-element grid is discussed in [49]. A review of the Delaunay triangulation methods is done in [50]. The Rappert algorithm, specially developed for FEM, is dealt in [51]. The possibilities of constructing finite-element grid for any geometrical area, in case 2*D*-triangles/3*D*-tetrahedrons are chosen as elements, are discussed in [52]. The technological aspects of using vector finite elements for solving the Maxwell equations are dealt in [53].

Finite-element methods have proven themselves as a universal tool for the study of physical objects and are most developed and most versatile.

Use of FEM for research on thermoelectric models

Finite element methods are widely used for research on thermoelectric models. In [54], FEM is considered with one-dimensional elements without regard to contact resistance with few iterations because of low power of computer technology of that time, whereas in [55], three-dimensional stationary and non-stationary simulation of single-stage and multi-stage Peltier cooler by means of program complex ANSYS 9.0 is considered. Even under such conditions, in [54], a comparative analysis of FEM with averaging methods is carried out. The authors of the work conclude that FEM is more precise and gives better optimization. It can be argued that FEM is the most versatile, precise and promising simulation method for thermoelectricity. In 2009, a new ANSYS 12 version was created, which includes a separate thermoelectric module, the package also included new modules, creation of model geometry became much easier, and a number of new improvements appeared. In particular, in [56], for simulation of thermoelectric ice makers for domestic refrigerators use was made of ANSYS FLUENT module, destined for solving the problems of computational fluid and gas dynamics. High efficiency and precision of this module enabled one to take into account the effects that had been ignored before, and to simulate the device as a whole. The experimental data are in good agreement with the model. Examples of using a new version of ANSYS package can be found on the WEB-site [57], including the thermoelectric module.

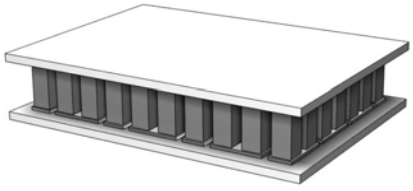

Fig. 6. Cooler model.

FEM has found application in many fields, such as mechanics of deformable solids, heat exchange, fluid dynamics and electromagnetic fields, and thermoelectricity in recent years as well. By the example of the Peltier cooler and on the basis of classical equations of thermoelectricity, a finite-element diagram was built to find the temperature distribution and electric potential distribution profile [55]. The authors emphasize that ANSYS makes it possible to simulate conjugate fields and that ANSYS has already filled the gap that had been thermoelectric simulation. Fig. 6 shows a model of the cooler. Simulation of thermoelectric devices requires taking into account not only electromagnetic and temperature fields, but also the effects of thermal elasticity and piezoelectric effect caused by them. Ref. [58] is devoted to simulation of thermoelectric field in SP-100 device and minimization of all kinds of deformation with the aid of FEM and ANSYS program complex.

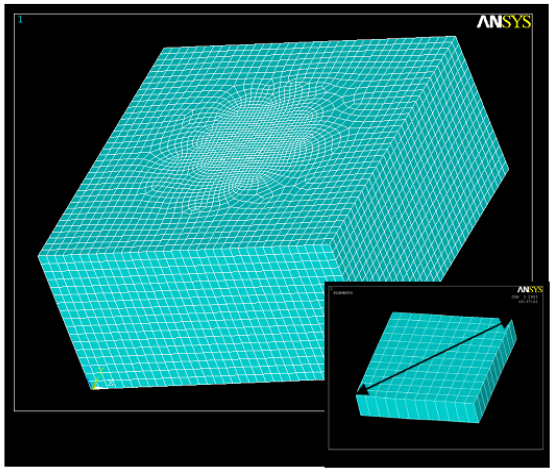

Fig. 7. Finite-element grid for contact.

Ref. [59] is a review of functionally graded materials (FGM) – another promising line for improving the thermoelectric figure of merit. The author emphasizes the need for numerical simulation of FGM properties and their optimization. The experimental data are in a very good agreement with the model given by the phenomenological heat balance equations. Emphasis is made on the need to take into account the volumetric Peltier, Thomson effects and on the possibility of approximation of the Seebeck coefficients using splines. Splines were also used for calculation by collocation method (one of the types of FEM) of the thermoEMF of various thermoelectric devices [60]. The author points to high precision of FEM and the consistency of theoretical calculations with the experiment. Therefore, for solving the problems of thermoelectricity in the case of phenomenological formulation of the problem it is necessary to use finite-difference methods and finite-element methods.

Ref.[61] considers a micro matrix thermoelement simulated with the use of 3*D* FEM. Based on the laws of conservation of energy and charge, an algorithm for solving is built to find temperature profile. With the help of FEM a matrix-type thermoelement is studied, each of its legs being separated from the others by glass, and, finally, an unclear conclusion is made that thermal conductivity of such structure is lower, but power output is not increased.

Another application of three-dimensional FEM and ANSYS is discussed in [62], where the subject of investigation is one-coil Peltier thermoelement based on Bi_2Te_3. The contact effect is investigated. The authors make a comparative analysis of 3*D*-model and one-dimensional model. The contact area of cooled surface in the former case is smaller, and the results of simulation coincide with one-dimensional simulation. Thus, reduction of contact area of even uniform voltage distribution yields no gain in cooling temperature. Only uniform current distribution along contact area provides a rise of cooling temperature by 21 %. The authors emphasize that technical implementation of this

condition requires the use of matrix structure of point contacts, and this can achieve arbitrary potential distribution in each cell and assure maximum cooling of some areas.

Fig. 7 shows a finite-element grid of contact model. This work once again confirms the necessity of using exactly three-dimensional modeling for an adequate, most complete description and taking into account thermoelectric effects.

The widespread use of ANSYS has shadowed other finite-element software. Comsol Multiphysics, in contrast to ANSYS, makes possible simulation and study without a detailed knowledge of FEM features. An intuitive interface gives the researcher the ability to focus on the physical task without thinking of algorithmic-programming problems. Relative nonoccurrence of Comsol Multiphysics resulted in the absence of articles, manuals and descriptions of this software package, with the exception of Institute of Thermoelectricity, where systematic research has been pursued on rectangular spiral anisotropic thermoelement [62], short-circuited thermoelements [63] with the help of FEM and Comsol Multiphysics software package for several years already. On the basis of simulation results, the theory of zone-inhomogeneous thermoelement was developed [3].

The possibilities of Comsol Multiphysics for thermoelectricity are described in [64], where 4 examples are given of using FEM for different thermoelectric devices – cooler and generator. For simulation of temperature and electrical fields, the PDE (partial differential equation) form of thermoelectricity equations is used. The article describes various possibilities of FEM for simulation of thermoelectric objects, as well the possibility of creating both stationary and non-stationary models of different geometry and fields of different nature. Examples of using object-oriented programming and FEM for creating the models of thermoelectric generators and heat exchangers are given in [65, 66].

The use of FEM in microelectronics, the study of thermoelectric effects in MEMS is dealt with in [67 – 70], a specialized module more4ANSYS based on algorithms was developed [71]. FEM was also used for simulation of technological processes, specifically for powder sintering technology [72].

Although simulation and use of computer technologies based on FEM is widely used in thermoelectricity, it is non-systematic or auxiliary, rather than the main research method. In addition, there is no specialized software today for simulation of thermoelectric effects and devices.

Thus, the use of finite-element methods and computer technologies on their basis opens up wide opportunities for research on new properties of thermoelectric materials, models, technologies. FEM is one of the main simulation methods which has proven itself well, and is one of the most promising computer simulation methods for thermoelectric instrument making.

Finite-volume methods

Finite-volume method is widely used in fluid dynamics. In thermoelectricity, for cells with an arbitrary number of faces (edges) the algebraic relations are formed, sometimes strongly non-linear and more similar to hydraulic formulae. Unlike FEM and FED, they have no node governing medium parameters, with preference given to parameters on edges and faces.

The presence of three-dimensional effects necessitates the use of finite-volume method, the algorithm of which can be divided into the following stages [36].

1. Definition of control equations:

$$\nabla\left(\chi * \nabla T\right) = p\vec{J}^2 - T\vec{J}\left[\frac{\partial \alpha}{\partial T}\nabla T + \left(\nabla \alpha\right)_T\right] = 0, \tag{1}$$

$$\nabla \vec{J} = 0, \tag{2}$$

$$\vec{J} = -\delta\left[\nabla\left(\frac{M}{e} + V\right) + \alpha\nabla T\right], \tag{3}$$

$$\vec{q} = \alpha T\vec{J} - \alpha\nabla T, \tag{4}$$

$$\alpha = \alpha(T), \chi = \chi(T), \delta = \delta(T), p = p(T), \tag{5}$$

with the boundary conditions

$$\begin{aligned} &T = T_0, \vec{q} = \vec{q}_0, \\ &V = V_0, \vec{J} = \vec{J}_0. \end{aligned} \tag{6}$$

To find a stationary solution, it is proposed to consider a non-stationary system of differential equations

$$\begin{aligned} &\frac{1}{\gamma_T}\frac{\partial T}{\partial t} = \nabla(\chi\nabla T) + f(T,U), \\ &f(T,U) = p\overline{\vec{J}^2} - T\vec{J}\left[\frac{\partial\alpha}{\partial T}\nabla T + (\nabla\alpha)_T\right], \\ &\frac{1}{\gamma_U}\frac{\partial U}{\partial t} = -\nabla\vec{J}, \end{aligned} \tag{7}$$

where γ_T and γ_U are parameters.

2. Discretization of domain. The area of parallelepiped is divided into cubes.
3. Replacement of differential equations in partial derivatives by algebraic equations.
4. Algorithm of solving a system of algebraic equations.

Derived variables are replaced by finite differences and boundary conditions are also taken into account. Separately, a difference scheme is constructed at the boundary of the domain, which leads to a system of nonlinear algebraic equations of triple-diagonal form. In so doing, it is desirable to use the implicit methods of solving a system of differential equations, which in this case give absolute convergence, in contrast to the explicit Adams or Runge-Kutta methods [7]. It is concluded that 3D modeling by the finite volume method enables one to establish new effects and reproduce the true picture of the process, in contrast to classical methods of numerical solution of differential equations.

It may be deduced that finite-volume methods hold much promise, but are not adapted yet to thermoelectricity by simulation methods. There is a need in development of specialized algorithms and software for solving the problems of thermoelectricity.

Simulation modelling

Simulation modelling is a study of a mathematical model in the form of algorithms that reproduce the functioning of the system by successively executing a large number of elementary operations. Classification of simulation modelling methods for many-body systems is given in Fig. 8. Another way to improve the properties of thermoelectric devices is to improve the parameters of materials and to devise new ones. Monte Carlo and molecular dynamics methods are used to simulate the properties of materials [73, 74].

The stages of multilevel design of new materials based on computer simulation are shown in Fig. 8. Such an integrated approach makes it possible to design new materials with given properties.

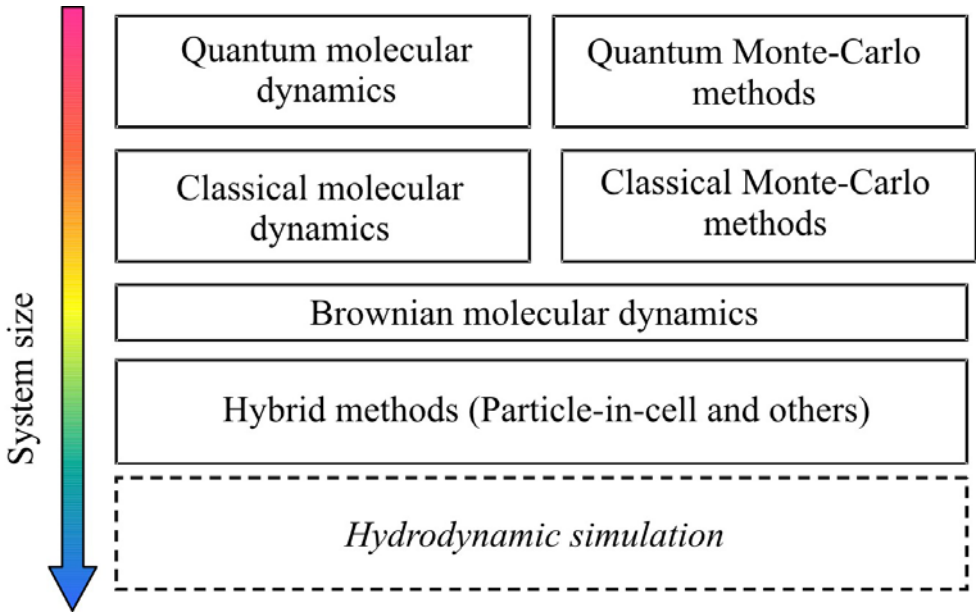

Fig. 8. Classification of simulation modelling methods.

Traditionally, simulation methods are divided into main groups depending on the size of the simulated system. Methods of molecular dynamics, Brownian molecular dynamics, hybrid methods, and hydrodynamic simulation can be denoted by one term - particle simulation.

Monte Carlo methods. General properties and classification

There is no single definition of Monte Carlo methods, but it can be argued that Monte Carlo methods are numerical procedures for solving mathematical problems (systems of algebraic, differential, integral equations) and direct statistical modelling (physical, chemical, biological, economic, social processes) by means of obtaining and transforming random numbers.

The first work in which Monte Carlo method was systematically taught was published in 1949 by Metropolis and Ulam [75], where Monte Carlo method was used to solve linear integral equations. Works on Monte Carlo methods began to be actively published after the International Geneva Conference on the Peaceful Uses of Atomic Energy. One of the first was the article by Vladimirov and Sobol [76]. Monograph [77] is the first systematic work devoted to the consideration of the statistical theory of non-ideal systems, based on the study of many-particle systems.

Monte Carlo methods are divided into classical and quantum ones. There is also a diffusion Monte-Carlo method [78].

The classical Monte Carlo methods for the system of particles are based on the stochastic search of points in phase space with a prevalent sampling of those domains that make a significant contribution to the integral

$$\langle A\rangle = \frac{1}{Z}\int_{\Omega} A(\mathbf{R})\, p\big(H(\mathbf{R})\big), \tag{8}$$

where A is system state function, $H(\mathbf{R})$ is system Hamiltonian, $\mathbf{R} = (\mathbf{r}_1,\ldots,\mathbf{r}_N)$ specifies one state of the system, $\mathbf{r}_i$, $i = 1,N$ specifies all degrees of freedom of one particle, p is distribution function, $Z = \int_{\Omega} p\big(H(\mathbf{R})\big)d\mathbf{R}$ is statistical sum. In accordance with the distribution function, a chain of states is generated in the phase space along which the integral (8) is calculated. When the number of elements

in the chain tends to infinity, one can obtain the exact mean. In the case of finite number of chain elements, the integral (8) can be obtained more precisely than by the usual integration techniques.

Quantum Monte-Carlo methods are used for simulation of quantum many-body system, for instance, for solving the Boltzmann equation for phonon system [79]. The group of these methods is mainly used for integration of multi-dimensional integrals that arise when solving the Schrödinger equation –

$$i\hbar\frac{\partial}{\partial\tau}\varphi(\mathbf{R},\tau)=\hat{H}\varphi(\mathbf{R},\tau). \qquad (9)$$

Various aspects of using quantum Monte-Carlo methods are considered in [31, 80].

Simulation of thermoelectric nanodevices and materials

Recently, the theme of nanotechnology has become very popular, including in thermoelectricity [81 – 83], and Monte Carlo methods are one of the tools for simulation and studying the properties of such devices and materials.

As noted above, another approach to simulation of thermoelectric objects are statistical methods, or Monte Carlo methods. In [84], Monte Carlo algorithm is proposed for simulation of thermoelectric properties of nanocomposites. Both two-dimensional and three-dimensional models for studying phonon transport are considered. Three-dimensional simulation gave high figures of effective thermal conductivity. The authors note that randomly placed nanoparticles provide thermal conductivity very close to the case when the particles are arranged periodically. Three-dimensional simulation reveals new effects and determines other thermoelectric properties. Monte-Carlo method is also used to calculate the nonlinear Peltier coefficient [85] for *InGaAs*. Numerical values agree well with the analytical expressions. Monte Carlo method is one of the powerful means for solving the Boltzmann equation.

In [86], a comparative analysis is given for two models: approximation of relaxation time for the kinetic Boltzmann equation and solution of this equation by means of spherical harmonics. As a result of research with regard to effective mass anisotropy, it is concluded that in the model of electron gas scattering on ionized impurities the influence of effective mass anisotropy on the value of the Seebeck coefficient is insignificant. Even with relaxation time increase, the figure of merit of material is not increased either.

Several works are dedicated to theoretical research of thermoelectric effects of molecular electronics [87 – 90]; the possibility of creating nanostructured thermoelectric devices [91] and new materials [92] is investigated; new thermoelectric effects [93, 94]; the outlook for development of nanotechnologies in thermoelectricity is considered, in particular, research is performed on the thermoelectric properties of nanocontact of two nanotubes of Bi_2Te_3 and Sb_2Te_3 [95]. In [96], irreversible effects in thermoelectric nanomaterials are simulated by the example of quantum dot lattice.

In [90], the thermoelectric effect in molecular compounds is considered. The metal contact-molecule-metal contact model is investigated. Based on the analytical presentation and numerical simulation, it is shown that the thermoelectric potential gives important information about the mechanisms of electron motion control, including weak electron-electron interaction and thermal dissipation. It is shown that at high temperatures, the Fermi energy position relative to the molecular states can be deduced from the thermoelectric potential. The thermoelectric power does not depend on the material of which the contacts are made.

Monte Carlo methods are attractive for computer simulation in thermoelectricity. Their use leads to a better understanding of the origin of thermoelectric phenomena, which opens up possibilities for creation and prediction of properties of new thermoelectric materials.

Particle simulation method

Particle simulation – a relatively new and little developed method compared to the FEM – was practically not used in thermoelectricity. Particle method simulates the constituents of the physical object. Description of particle models in a cell for thermoelectric effects is given in [97] for the simplest geometries (two wires). As thermoelectric materials, metals are selected. Thermoelectric phenomena are considered as an ensemble of particles, namely electron gas. In the equilibrium state, the distribution satisfies the Fermi-Dirac law. The Seebeck, Peltier and Thomson effects are considered. The computational model and the developed program are absent. One-dimensional Hubbard model [98, 99] is investigated in several papers based on the Kubo formalism. The basic kinetic coefficients are calculated, namely electric conductivity, thermal conductivity and the Seebeck coefficient. Although particle simulation is mainly used to study the physical and chemical properties of continuous media, it also finds its application for solving mechanical problems of strong inelastic deformation and fracture [100]. This paper is a review of simulation of high-speed destruction of solids by the particle method. Specific problems are considered: penetration of obstacles by a striker which is deformed, destruction of a layer under the action of a spherical stretching wave, spalling failure in case of a plane impact interaction of plates (Fig. 9). The main provisions of this method are given. In the case of particle simulation, it is not necessary to consider physical particles (electrons, ions, molecules), but virtual macroparticles whose interaction is described by certain potential can be considered [101]. Each particle has its specific features. The use of the particle method does not require the description of a complex theory, many effects appear automatically. This is a significant advantage of simulation modelling. But the particle method requires high power computers, since a great many particles are necessary for adequate simulation (~10^8). Implementation of such simulation program already requires multiprocessor mainframes. Research on deformations is a promising direction for studying the reliability of thermoelectric devices.

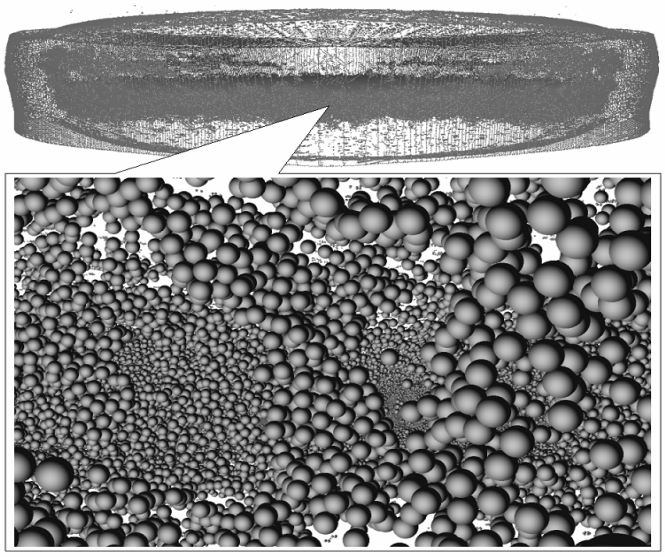

Fig. 9. Three-dimensional model of spalling failure of the body. Comprises 100 mln particles.

The subject of review in [102] is nanoscale heat transfer. The thermal conductivity of many solid interfaces has been studied experimentally, but the range of observed properties is much smaller than theoretically predicted. The rapid development of microelectronics according to Moore's law has led to the necessity of studying the properties of nanomaterials. The microelectronic devices are too large for direct simulation at the atomic level, so the main simulation method is the Boltzmann kinetic equation [103].

$$\frac{\partial f}{\partial t}+\frac{\partial f}{\partial \mathbf{x}}\cdot\frac{\mathbf{p}}{m}+\frac{\partial f}{\partial \mathbf{p}}\mathbf{F}(\mathbf{x},t)=\left.\frac{\partial f}{\partial t}\right|_{coll}, \tag{10}$$

where $\mathbf{F}(\mathbf{x},t)$ is field of external forces, $f(\mathbf{x},\mathbf{p},t)$ is density distribution function in one-particle phase space, $\mathbf{p}$ is pulse, $\mathbf{x}$ is coordinate, m is mass, $\left.\frac{\partial f}{\partial t}\right|_{coll}$ is repulsive term.

Particle simulation method is another promising computer simulation method that opens up the possibilities for revealing new thermoelectric effects and for creating materials with given properties.

Simulation of failure rate of thermoelectric modules in generation mode

As an effective example of using FEM and Comsol Multiphysics software package, we give the results of studying failure rate of thermoelectric modules of 3 types *TEC1 7107, TEC1 12715* and *TEC1 12704* in the temperature range of 80 – 280 ^{0}C.

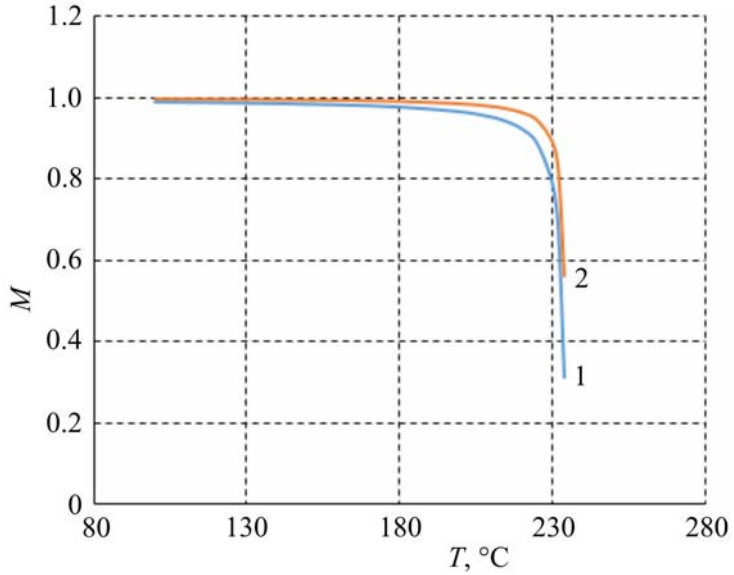

Fig. 10. Temperature dependence of failure rate according to reliability theory.
1 – type TEC1 7107 and TEC1 12715; 2 – type TEC1 12704

Temperature dependence of failure rate M, according to reliability theory, satisfies with confidence probability P = 0.9 the Arrhenius law with Curie points for solder melting temperature. For three types of modules these dependences are given in Fig. 10.

With regard to the above temperature dependence of failure rate, the dependences of electrical power drop and efficiency of modules on the number of hours worked were obtained (Fig.11 – 16).

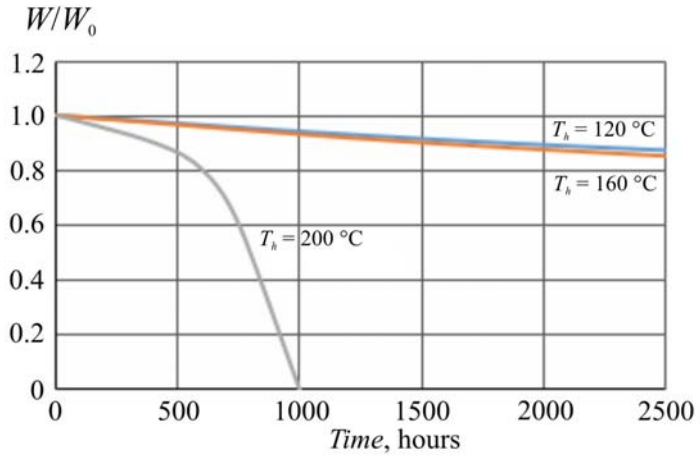

Fig. 11. The electrical power of modules TEC1 7107 versus the number of hours worked.

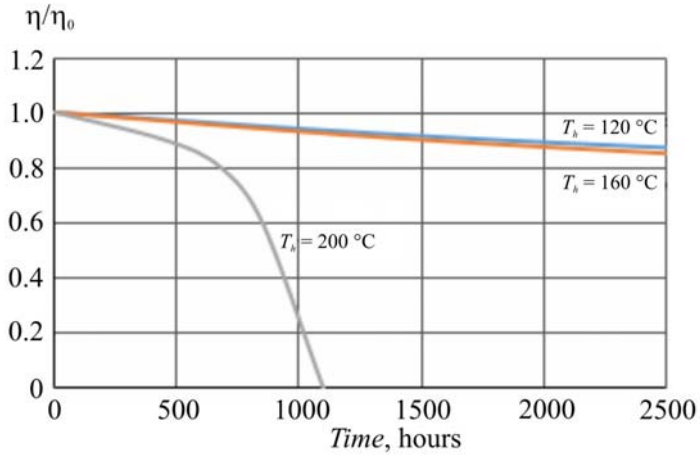

Fig. 12. The efficiency of modules TEC1 7107 versus the number of hours worked.

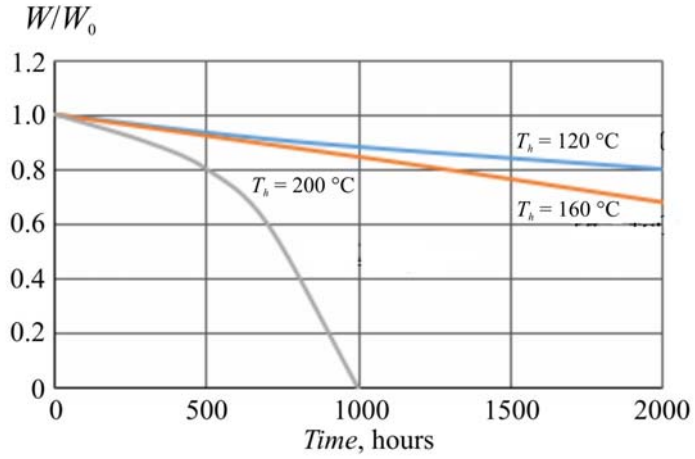

Fig. 13. The electrical power of modules TEC1 12704 versus the number of hours worked.

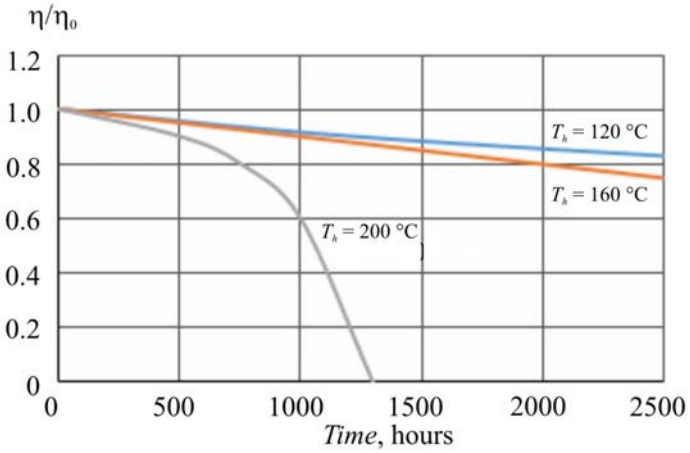

Fig. 14.The efficiency of modules TEC1 12704 versus the number of hours worked.

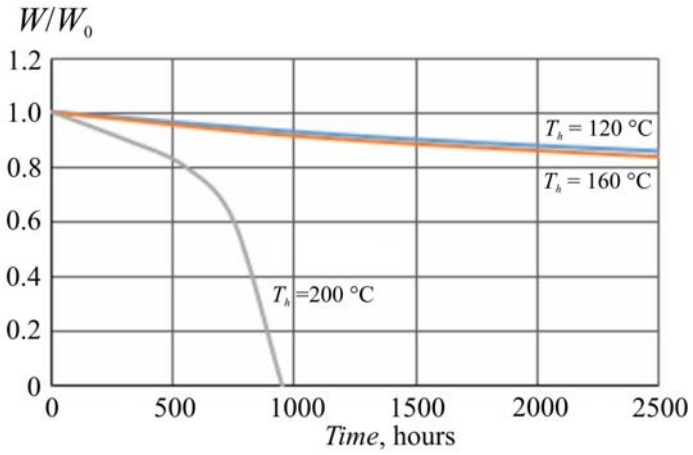

Fig. 15. The electrical power of modules TEC1 12715 versus the number of hours worked.

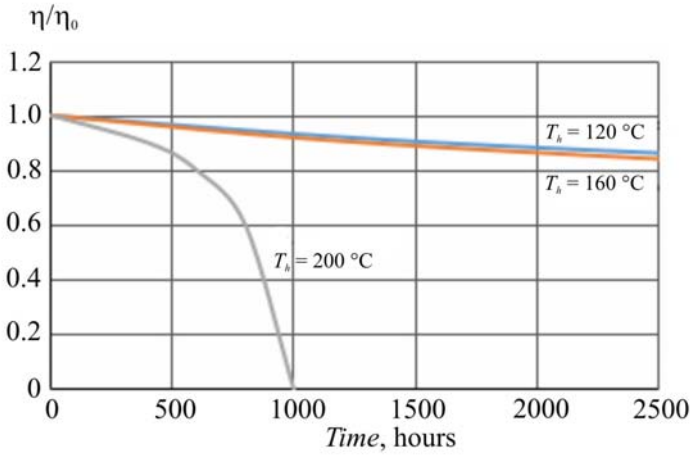

Fig. 16. The efficiency of modules TEC1 12715 versus the number of hours worked.

Conclusion

1. Computer technologies and computational experiments are the main tool for theoretical study of thermoelectric models.
2. It is shown that finite element methods are the most developed and universal procedures for the creation and research on phenomenological models of thermoelements and thermoelectric devices.
3. It is necessary to develop the algorithms of finite element method for thermoelectric effects, in particular, vector finite element method and specialized software for simulation of thermoelectric devices.
4. Finite volume method is a promising tool for simulation of physical fields, but it is not used in thermoelectricity today. It is necessary to develop the algorithms of finite volume method and the software which implement this method.
5. Particle simulation method and other statistical simulation methods are promising for the study, modeling and detection of new thermoelectric effects and investigation of already known ones.
6. Particle method, Monte Carlo and molecular dynamics methods open up the opportunities for the design of new thermoelectric materials with given properties. It is necessary to develop the algorithms, the appropriate software and models which implement particle method. Large computational difficulties in the case of using particle method necessitate the use of algorithms of parallel computations.
7. The main conclusion is that all of the described models of thermoelectric modules are deterministic, and that the possibilities of computer simulation of random failures of thermoelectric modules have not been considered yet. All computers are equipped with generators of pseudorandom numbers, which is a powerful means of studying random processes by the deterministic non-random computers. The operation algorithms of generators of pseudo-random numbers are a trade secret, except for compilers of programs written in high-level languages. The high efficiency of research on random processes with the help of generators of pseudo-random numbers has already been proved. It is time to use such computer programs for the needs of thermoelectricity.

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Анатичук Л.І. *ак. НАН України*,
Лусте О.Я. *доктор фіз.-мат. наук*

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна, *e-mail: anatych@gmail.com*
Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatych@gmail.com

МОДЕЛЬНІ ДОСЛІДЖЕННЯ МЕХАНІЗМІВ ДЕГРАДАЦІЇ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ І ПРИКОНТАКТНИХ СТРУКТУР

Проведено аналіз сучасного стану і перспектив фізичних і комп'ютерних моделей деградації термоелектричних матеріалів і приконтактних структур. Розроблено класифікацію наявних комп'ютерних технологій, розглянуто актуальні напрямки їх використання для дослідження і розробки надійних термоелектричних модулів. Бібл. 102, Рис. 16.
Ключові слова: надійність, деградація, термоелектричні матеріали.

Анатычук Л.И. *ак. НАН Украины*,
Лусте О.Я. *доктор физ.-мат. наук*

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина
e-mail: anatych@gmail.com
Черновицкий национальный университет имени Юрия Федьковича,
ул. Коцюбинского 2, Черновцы, 58012, Украина
e-mail: anatych@gmail.com

МОДЕЛЬНЫЕ ИССЛЕДОВАНИЯ МЕХАНИЗМОВ ДЕГРАДАЦИИ ТЕРМОЭЛЕКТРИЧЕСКИХ МАТЕРИАЛОВ И ПРИКОНТАКТНЫХ СТРУКТУР

Проведен анализ современного состояния и перспектив физических и компьютерных моделей деградации термоэлектрических материалов и приконтактных структур. Разработана классификация имеющихся компьютерных технологий, рассмотрены актуальные направления их использования для исследования и разработки надежных термоэлектрических модулей. Библ. 102, Рис. 16.

Ключевые слова: надежность, деградация, термоэлектрические материалы.

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L.I.Anatychuk

L.I. Anatychuk, *acad. National Academy of Sciences of Ukraine*,
V.V. Lysko, *Candidate Phys.-math. Sciences*

Institute of Thermoelectricity of the NAS and MES of Ukraine, 1, Nauky str, Chernivtsi, 58029, Ukraine;
e-mail: anatych@gmail.com
[2]Yu.Fedkovych Chernivtsi National University, 2, Kotsiubynskyi str., Chernivtsi, 58012, Ukraine, *e-mail: anatych@gmail.com*

V.V.Lysko

METHOD FOR COMPENSATION OF THE INFLUENCE OF THE PELTIER EFFECT WHEN MEASURING THE ELECTRICAL CONDUCTIVITY BY TWO-PROBE METHOD

This paper describes the method for elimination of the influence of the Peltier effect when measuring the electrical conductivity of thermoelectric materials by two-probe method by compensation of the Peltier cooling effect by the heat of electric heater. The results of computer studies of the effectiveness of using such method and possible errors in this case are presented. The method for determining the Seebeck coefficient of material based on the Thomson relation is proposed. Bibl. 9, Fig. 6.
Key words: electric conductivity, the Peltier effect, error, thermoelectric material.

Introduction

General characterization of the problem.

An important role in the development and manufacture of thermoelectric power converters, as well as devices on their basis, is played by quality control of the source thermoelectric material. It is carried out by determining the thermoelectric parameters of material, namely electrical conductivity, thermal conductivity, thermoEMF and figure of merit. In so doing, the best in terms of measurement accuracy are comprehensive measurements of all these parameters on the same sample. Such measurements can be implemented using the absolute method [1].

The basis for determination of electrical conductivity is two-probe measurement method, whereby current is passed through sample faces, and electrical potential on its surface is measured by two probes with a known distance between them [2, 3]. The electrical conductivity is calculated by the values of current and potential difference between the probes with regard to geometrical dimensions (sample cross-sectional area and the distance between the probes). This method is generally accepted for the research on semiconductor material (international standard SEMI MF397-02 “Test Method for Resistivity of Silicon Bars Using a Two-Point Probe”).

Analysis of the literature.

Refs. [4, 5] are concerned with the main sources of errors of two-probe method for the case of long rods (ingots) of thermoelectric material:

- inhomogeneity of current density in the ingot due to current supply solely at points of contact with current leads, rather than uniformly across its surface;

- nonisothermal conditions caused by the influence of the Peltier and Joule effects, and by the

heat exchange with the environment.

Current density inhomogeneity is controlled by locating the measuring probes possibly far from the current contacts, where the electric field is most one-dimensional.

It is more difficult to satisfy the isothermality condition of the samples. When current flows, its violation leads to the appearance on the probes of thermoEMF in addition to potential difference. In this caseg, nonisothermality is primarily caused by the influence of the Peltier effect at points of electrical connections of the sample with current contacts. In so doing, potential difference between the probes due to current flow and thermoEMF due to sample nonisothermality can be quantities of the same order, which leads to rather rude errors. In order to reduce this error, it is recommended to pass through a sample an alternating current of sufficiently high frequency, which should prevent the influence of the Peltier effect [6]. However, in this case there are difficulties in measuring the alternating current potential difference due to insufficient accuracy of measuring equipment and all kinds of pickup.

Measurements of the voltage drop at the moment of switching on the current are also used, when the influence of the Peltier effect will be insignificant due to material heat capacity [7]. In [8], it was proposed to use the recording of the time dependence of transient process when the current is disconnected from the sample and the finding of the ohmic component of the voltage $U\sigma$ as the difference between the stationary voltage value ($U\alpha + U\sigma$) and thermoEMF $U\alpha$. Such methods require high-speed measuring devices and automation of measuring equipment to eliminate human factor.

The purpose of this work is to study the effectiveness of method for eliminating the influence of the Peltier effect under steady-state conditions by compensation of the Peltier cooling effect by the heat of electric heater.

Physical and computer models of the method for compensation of the influence of the Peltier effect by the heat of electric heater

A physical model of two-probe method for the electrical conductivity measurement with compensation of the influence of the Peltier effect by the heat of electric heater is shown in Fig. 1. It comprises a sample of thermoelectric material arranged between the electric heater and the thermostat. Located on the lateral surface of the sample are two measuring potential probes and two thermocouples for control of temperature difference between the probes. As the measuring probes, identical thermocouple legs can be used, in which case two additional potential probes can be dropped.

A constant electric current I is passed through the sample. The direction of the current is chosen so that the Peltier cooling effect manifests itself on the contact of the sample with the heater, and the heating effect – on the contact with the thermostat. The equality of temperatures between thermocouples is achieved by passing the current through the electric heater. Following that, the voltage drop U between the probes is measured. The electrical conductivity of the sample material is determined by the formula

$$\sigma = \frac{I}{U}\frac{l}{S}, \tag{1}$$

where S is cross-sectional area of the sample, l is the distance between measuring probes.

The physical model takes into account heats Q1 – Q13 which occur in measuring. They include the Peltier heat on the contacts of the sample with the thermostat and the heater; the Joule heat released in the sample; the Joule heat released on the contact electric resistances; heat exchange between the heater and the thermostat due to radiation; heat exchange between the sample and the

thermostat due to radiation; heat exchange due to thermal conductivity through thermocouple conductors, current conductors, pressure mechanism, etc.

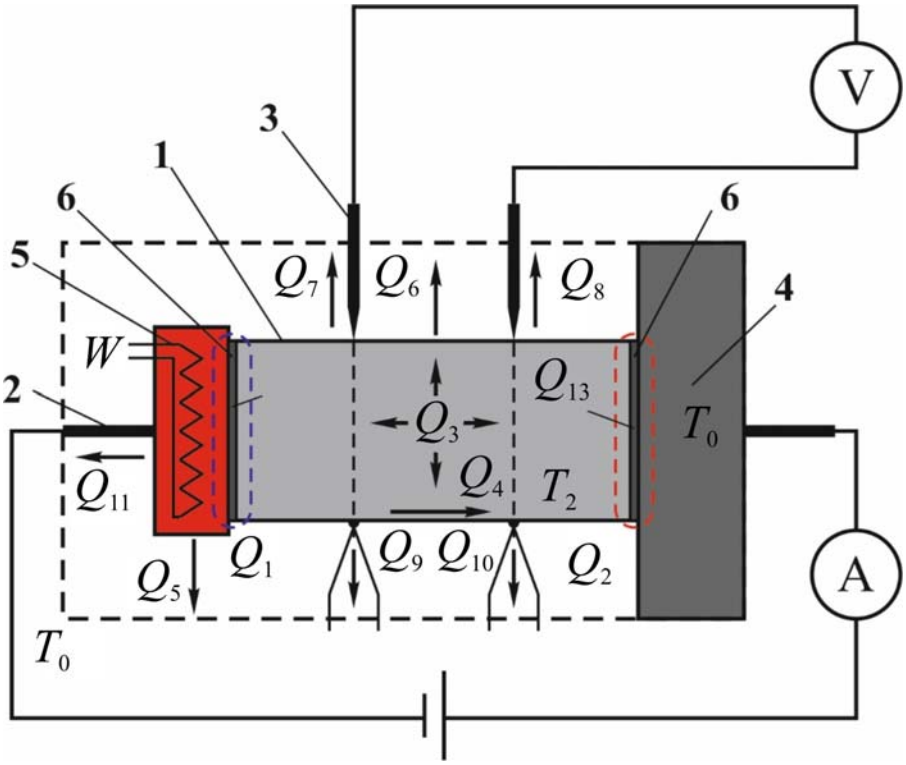

Fig. 1. Physical model of two-probe method for measuring the electrical conductivity of thermoelectric material with compensation of the Peltier effect by the heat of electric heater. 1 – sample of thermoelectric material under study; 2 – current conductors; 3 – measuring probes; 4 – thermostat; 5 – electric heater; 6 – contact resistances.

To study the effectiveness of this measurement method, one should find the distributions of electric potential φ and temperature T in the sample, which can be done based on the laws of conservation of electrical charge

$$\operatorname{div} \boldsymbol{j} = 0, \tag{2}$$

and energy

$$\operatorname{div} \boldsymbol{w} = 0, \tag{3}$$

where $\boldsymbol{w}$ is energy flux density

$$\boldsymbol{w} = \boldsymbol{q} + \varphi \boldsymbol{j}, \tag{4}$$

$\boldsymbol{q}$ is heat flux density

$$\boldsymbol{q} = -\kappa \nabla T + \alpha T \boldsymbol{j}, \tag{5}$$

$\boldsymbol{j}$ is electric current density

$$\boldsymbol{j} = -\sigma \nabla \varphi - \sigma \alpha \nabla T. \tag{6}$$

α, σ, κ are the Seebeck coefficients, electric conductivity and thermal conductivity.

Substituting (5) and (6) into (4), we obtain

$$\boldsymbol{w} = -(\kappa + \alpha^2\sigma T + \alpha\sigma\varphi)\nabla T - (\alpha\sigma T + \sigma\varphi)\nabla\varphi\,. \tag{7}$$

After taking into account (6), (7) in (2), (3), the laws of conservation of electric charge and energy will take on the form:

$$\begin{cases} -\nabla\left(\left(\kappa + \alpha^2\sigma T + \alpha\varphi\sigma\right)\nabla T\right) - \nabla\left(\left(\alpha\sigma T + \varphi\sigma\right)\nabla\varphi\right) = 0, \\ -\nabla\left(\sigma\nabla\varphi\right) - \nabla\left(\sigma\alpha\nabla T\right) = 0. \end{cases} \tag{8}$$

Having solved the system (8) with the corresponding boundary conditions, we obtain the distributions of the electric potential and temperature in the sample. For the calculations, computer methods of object-oriented simulation were used, in particular, COMSOL Multiphysics software package [9].

Results of computer calculations of the electric potential and temperature distributions in the sample. Measurement errors.

To test the effectiveness of the proposed method for eliminating the influence of the Peltier effect, computer calculations of the distributions of temperature and electric potential in the sample were carried out. A sample of thermoelectric material based on *Bi-Te* of diameter 6 and length 12 mm was considered. Measuring probes are arranged on the lateral surface of the sample at a distance of 5 mm from each other and symmetrically with respect to the sample ends.

Fig. 2 shows a dependence of temperature difference between measuring probes on the value of current passed through the sample, for the case when a reference heater is switched off. The electrical conductivity measurement error can reach 40 %.

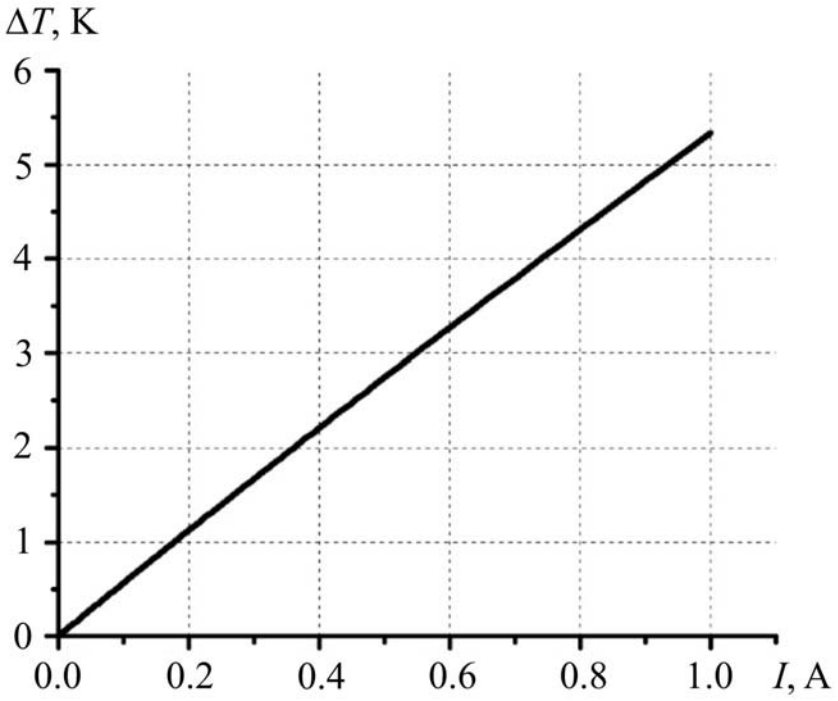

Fig. 2. Dependence of temperature difference between measuring probes on the value of current passed through the sample.

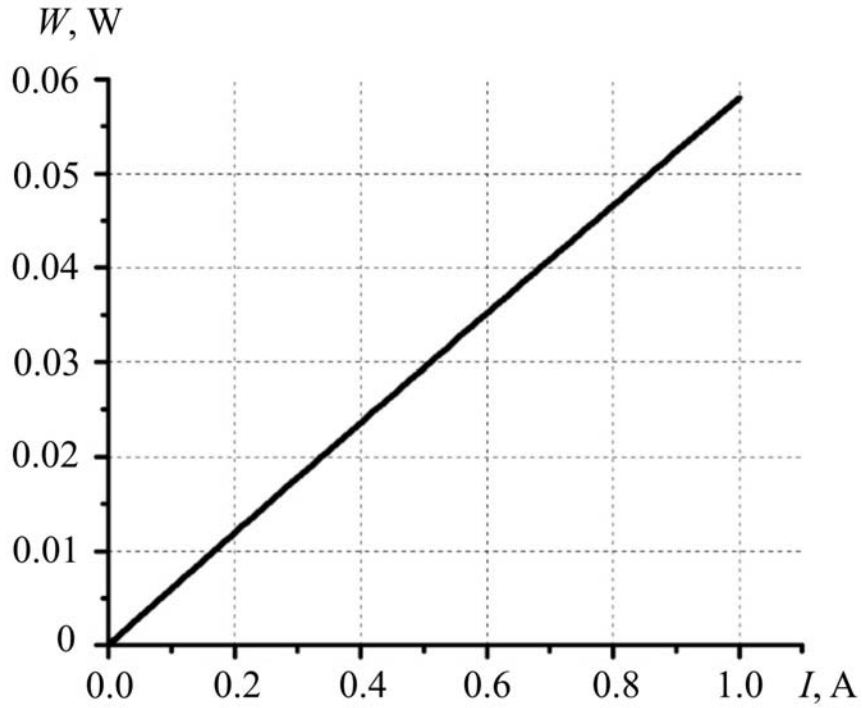

Fig. 3. Dependence of electric heater power necessary for compensation of the Peltier effect influence on the value of current passed through the sample.

To eliminate this error, the cooling influence of the Peltier effect is compensated by the heat of electric heater. Dependence of the necessary heater power on the value of current passed through the sample is shown in Fig. 3. The distributions of electric potential and temperature along the sample for different values of current through the sample are shown in Fig. 4.

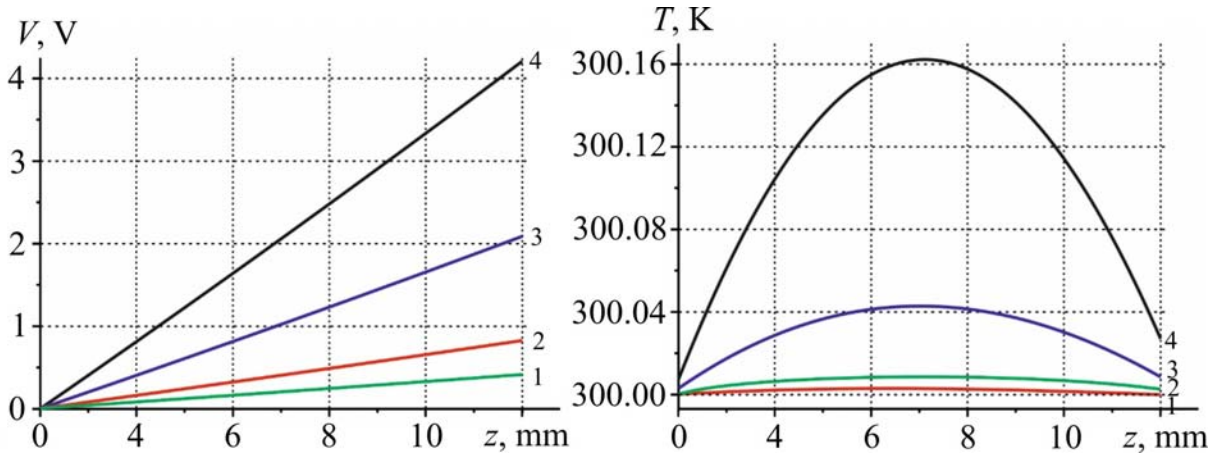

Fig. 4. Distributions of electric potential (a) and temperature (b) along the sample when using the Peltier heat compensation by the heat of reference heater for different values of current passed through the sample. 1 – I = 0.1A; 2 – I = 0.2A; 3 – I = 0.5A; 4 – I = 1A;

An important factor that influences the accuracy of measurements when using the Peltier effect compensation by the heat of reference heater is the accuracy of temperature equalization between the

probes. Fig. 5 shows the dependence of the electrical conductivity measurement error on the value of current through the sample for different levels of temperature equalization between the probes. As is seen, to reach a decrease in measurement error below 1 – 1.5 %, it is necessary to assure temperature equality between the probes at a level at least 0.05 – 0.1 K.

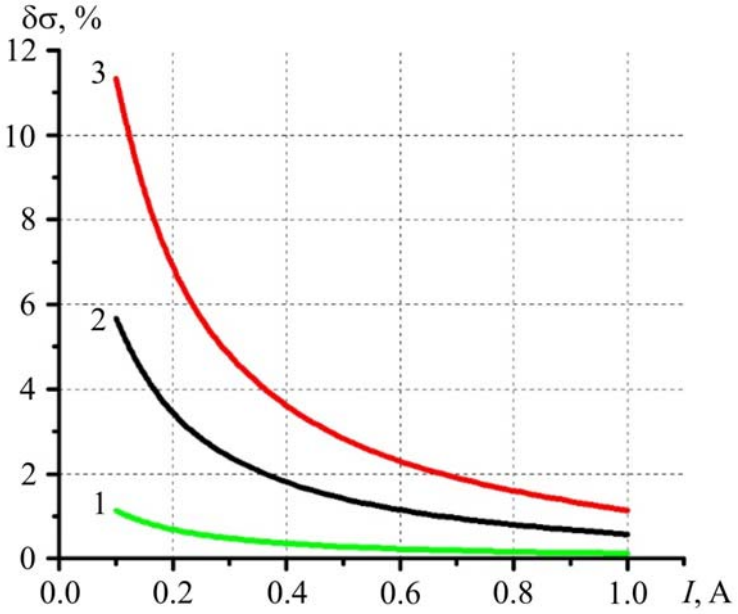

Fig. 5. Dependence of the electrical conductivity measurement error on the value of current passed through the sample for different values of temperature equalization accuracy between the probes: 1 – 0.01K; 2 – 0.02K; 3 – 0.05K.

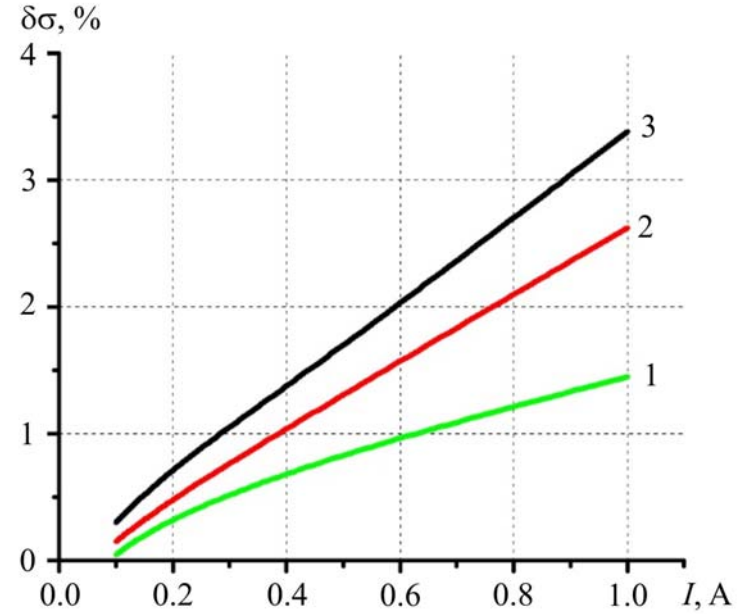

Fig. 6. Dependence of the Seebeck coefficient measurement error on the value of current passed through the sample for different thermostat temperature values. 1 – T_0 = 300K; 2 – T_0 = 500K; 3 – T_0 = 700K

The method for compensation of the influence of the Peltier effect considered above allows also determination of the Seebeck coefficient of the sample based on the Thomson relation

$$Q_{\Pi} = \alpha IT = W \,, \tag{9}$$

$$\alpha = \frac{IT}{W} \,. \tag{10}$$

The accuracy of this method for determination of the Seebeck coefficient will be governed by the ratio of heat flows in the sample and the heat exchange of the sample and the reference heater with the thermostat. The dependences of thermoEMF measurement error on current through the sample for different values of thermostat temperatures are presented in Fig. 6. It is seen that for a rather wide temperature interval and the range of currents used the accuracy of thermoEMF measurement by this method can be 1 – 2 %. Therefore, this method can be useful as another independent method for determination of the Seebeck coefficient jointly with the electrical conductivity measurements.

Conclusion

1. The possibility of eliminating the influence of the Peltier effect through compensation of the Peltier cooling effect by the heat of electric heater was considered. The effectiveness of using this method was proved by means of computer simulation. It was established that to achieve a decrease in measurement error below 1 – 1.5 %, it is necessary to ensure temperature equality between the probes at a level at least 0.05 – 0.1 K.
2. It is shown that the method of compensation of the influence of the Peltier effect by the heat of electric heater also allows determination of the Seebeck coefficient of the sample based on the Thomson relation. The accuracy of thermoEMF measurement using this method is at the level of 1 – 2 % for the temperature range from room temperature to 700 K.

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Анатичук Л.І. *ак. НАН України*,
Лисько В.В. *канд. фіз.-мат. наук*

Інститут термоелектрики НАН і МОН України, вул. Науки, 1,
Чернівці, 58029, Україна*, e-mail: anatych@gmail.com*
Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна
e-mail: anatych@gmail.com

МЕТОД КОМПЕНСАЦІЇ ВПЛИВУ ЕФЕКТУ ПЕЛЬТЬЄ ПРИ ВИМІРЮВАННІ ЕЛЕКТРОПРОВІДНОСТІ ДВОЗОНДОВИМ МЕТОДОМ

Наведено опис методу усунення впливу ефекту Пельтьє при вимірюванні електропровідності термоелектричних матеріалів двозондовим методом шляхом компенсації охолоджуючої дії ефекту Пельтьє теплом електричного нагрівника. Представлено результати комп'ютерних досліджень ефективності застосування такого методу та можливих при цьому величин похибок.
Запропоновано методику визначення коефіцієнту термоЕРС матеріалу, виходячи із співвідношення Томсона. Бібл. 9, Рис. 6.
Ключові слова: електропровідність, ефект Пельтьє, похибка, термоелектричний матеріал.

Анатычук Л.И. *ак. НАН Украины*,
Лысько В.В. *канд. физ.-мат. наук*

Институт термоэлектричества, ул. Науки, 1, Черновцы, 58029, Украина
e-mail: anatych@gmail.com
Черновицкий национальный университет им. Юрия Федьковича,
ул. Коцюбинського 2, Черновцы, 58000, Украина
e-mail: anatych@gmail.com

МЕТОД КОМПЕНСАЦИИ ВЛИЯНИЯ ЭФФЕКТА ПЕЛЬТЬЕ ПРИ ИЗМЕРЕНИИ ЭЛЕКТРОПРОВОДНОСТИ ДВУХЗОНДОВЫМ МЕТОДОМ

Приведено описание метода устранения влияния эффекта Пельтье при измерении электропроводности термоэлектрических материалов двухзондовым методом путем

компенсации охлаждающего действия эффекта Пельтье теплом электрического нагревателя. Представлены результаты компьютерных исследований эффективности применения такого метода и возможных при этом величин погрешностей.

Предложена методика определения коэффициента термоЭДС материала, исходя из соотношения Томсона. Библ. 9, Рис. 6.

Ключевые слова: электропроводность, эффект Пельтье, погрешность, термоэлектрический материал.

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Examples of LITERATURE CITED

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