Belarusian State University

Department of Energy Physics

TEMPUS program of the European Union

Project 530379-TEMPUS-1-2012-1-LVTEMPUS-JPCR "Energy"

Study of thermoelectric materials

The goal of this work is to study theoretical bases of thermoelectric energy conversion, as well as the methods of investigation of thermoelectric materials and their practical implementation.

Theoretical bases

Physical basis of thermoelectric energy conversion. Thermoelectric converter is a heat engine and, like any heat engine, obeys the laws of thermodynamics. Consider a converter as a thermoelement consisting of branches A (n-type semiconductor) and B (p-type semiconductor), Fig. 1. Efficiency η of such thermoelement is defined as the ratio of the electric energy W_{load} transmitted to load to heat Q_{hot} absorbed at the hot end of branches:

$$\eta = \frac{W_{\text{load}}}{Q_{\text{hot}}}. \tag{1}$$
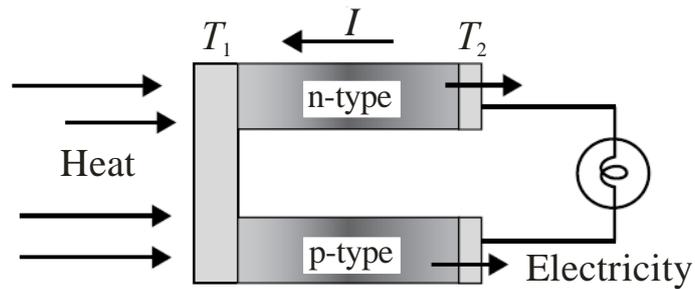

Fig. 1 – Thermoelectric generator based on the Seebeck effect

It can be shown that the efficiency η at maximum output power is equal to

$$\eta = \frac{T_1 - T_2}{\dfrac{3T_1}{2} + \dfrac{T_2}{2} + \dfrac{4}{Z}}, \tag{2}$$

and maximum efficiency

$$\eta_{\max} = \eta_c \cdot \chi, \tag{3}$$

where

$$\eta_C = \frac{T_1 - T_2}{T_1} \tag{4}$$

is the Carnot efficiency and

$$\chi = \frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + \dfrac{T_1}{T_2}} \cdot \tag{5}$$

In equation (5)

$$\bar{T} = \frac{T_1 + T_2}{2} \tag{6}$$

is the average temperature of the converter and a physical quantity Z is determined by the parameters of the materials from which thermoelectric converter is made:

$$Z = \frac{\alpha_{AB}^2}{\left[\left(\dfrac{\lambda_A}{\sigma_A} \right)^{\frac{1}{2}} + \left(\dfrac{\lambda_B}{\sigma_B} \right)^{\frac{1}{2}} \right]^2}, \tag{7}$$

where α_{AB} is Seebeck coefficient of materials of A and B branches,
λ_A and λ_B are coefficients of thermal conductivity of these materials,
σ_A and σ_B are their electrical conductivities.

Thus, the maximum efficiency of a thermoelectric generator (TEG) depends on the Carnot efficiency η_c and the coefficient χ, which is determined by the material parameters.

Since the materials of both converter branches often have about the same characteristics, the efficiency of a material for thermoelectric conversion is often given by the Ioffe relation

$$Z = \frac{\sigma \alpha^2}{\lambda}, \tag{8}$$

where product

$$P = \sigma \alpha^2 \tag{9}$$

is called the electric power factor. As follows from (8), parameter Z called thermoelectric figure of merit depends on the physical properties of the thermoelectric material (TEM) and has a dimension of inverse temperature. As a characteristic of the thermoelectric efficiency of TEM one use often the dimensionless quantity

$$Z\bar{T} = \frac{\sigma \alpha^2 \bar{T}}{\lambda}, \tag{10}$$

where $\bar{T}$ is working or average converter temperature. Equations (8) – (10) reflect the fact that for a given temperature difference, the generation of electric power will be more effective, the greater the thermopower of thermoelement and the lower unproductive ohmic heat loss in TEM (due to the low conductivity σ) and the power loss due to high thermal conductivity λ (due to the inability to create a high temperature difference ΔT between the branches of TEG). To minimize these losses, TEM should have a high Seebeck coefficient, as well as a high electrical and a low thermal conductivity.

Since the thermoelectric figure of merit is directly related to the efficiency of TEG by relations (2) and (3), it makes it very convenient parameter to compare the potential effectiveness of converters, which use different materials. Values about $ZT = 1$ at room temperature are now considered as a good and allow to achieve efficiency of the order 8 %. Increasing of the figure-of-merit up to 2-3 would increase the efficiency of thermoelectric converters to about 20 % and dramatically expansion of their applications. ZT values about $3 - 4$ seems to be sufficient in order to the thermoelectric device can compete in efficiency with electric generators and cooling units of conventional design.

Conversion efficiency as a function of the working temperature difference ΔT and the Carnot eficiency η_c is given in Fig. 2. It is assumed here that the parameters in the relations (8) – (10) defining the thermoelectric figure-of-merit do not depend on the temperature (which is actually not the case).
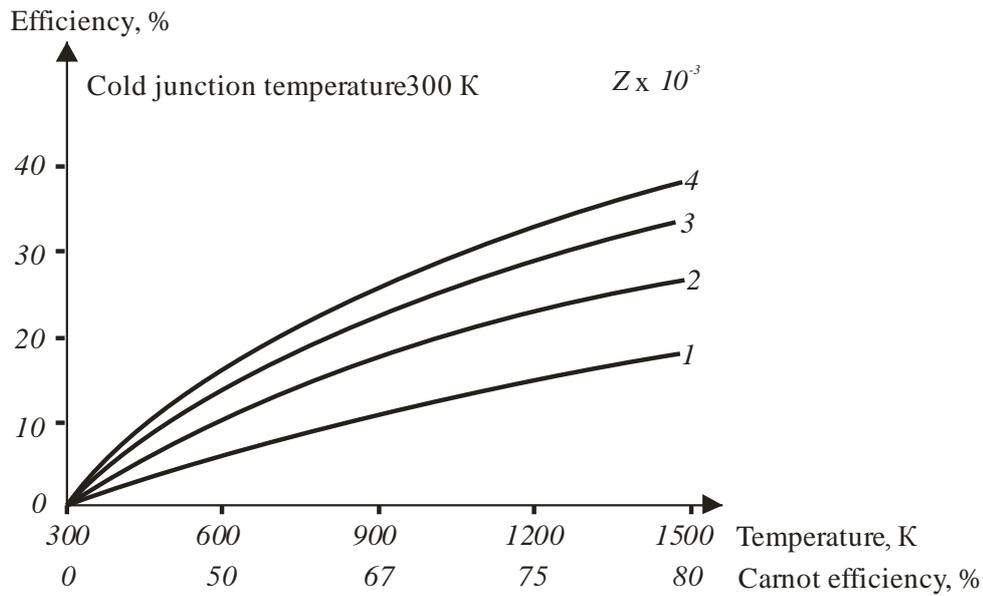

Fig. 2 – Conversion efficiency depending on the temperature of the hot junction and the Carnot efficiency for $Z=10^{-3}$ (curve 1), $Z=2 \cdot 10^{-3}$ (curve 2), $Z=3 \cdot 10^{-3}$ (curve 3), $Z=4 \cdot 10^{-3}$ (curve 4)

The achieved level of thermoelectric figure of merit. The achieved level of thermoelectric figure of merit is determined by parameters of the best materials used at the moment for these purposes. Since the fundamental physical limits of thermoelectric conversion efficiency are unknown, a lot of attention is now being paid the search for new TEM with improved parameters. The question is, however, how an increase the conversion efficiency can be achieved.

It is seen from the above relations (8) – (10) that high-quality TEM must simultaneously have high values of electrical conductivity and thermoEMF, and low thermal conductivity. Thermoelectric power and conductivity are determined mainly by the electronic properties of the material, and so they are often combined into a single value - the power factor, defined by relation (9). As can be seen, the power factor increases with increasing conductivity and Seebeck coefficient of TEM. The thermal conductivity of TEM is determined by the sum of an electron λ_e and a lattice (phonon) λ_l contributions:

$$\lambda = \lambda_e + \lambda_l. \tag{11}$$

It should be noted that the growth of σ which is required to increase the power factor (9) is usually accompanied by an increase of the λ_e value in (11) in accordance with the Wiedemann – Franz law

$$\frac{\lambda_e}{\sigma} = L_0 T, \tag{12}$$

where L_0 is the Lorentz constant. For a degenerate electron gas, it has a value

$$L_0 = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.44 \cdot 10^{-8} \frac{V^2}{K^2}, \tag{13}$$

and for non-degenerate one

$$L_0 = 2\left(\frac{k_B}{e}\right)^2 = 1.48 \cdot 10^{-8} \frac{V^2}{K^2} \tag{14}$$

where k_B is the Boltzmann constant,
and e is the electron charge.

Furthermore, an increase in conductivity is accompanied not only by electron conductivity growth, but usually by thermoEMF fall so that it is not easy to optimize ZT value. Sometimes it is possible to increase the power factor by tuning the concentration of charge carriers in the material. At the same time, the possibility to reduce λ_e and especially λ_l (which is determined by the structure, the strength (hardness) of interatomic bonds, atomic mass and other characteristics of the crystal lattice) of a material of a particular type is much more limited.

Metals have a high electrical conductivity, but at the same time a low Seebeck coefficient and a large heat conductivity. Semiconductors and insulators have, on the contrary, high values of Seebeck coefficient and a small electronic contribution to the thermal conductivity, but the concentration of charge carriers and the electrical conductivity of them are small that leads to a low thermoelectric power factor. Therefore, the best known thermoelectric materials are heavily doped semiconductors or semimetals with carrier concentrations of the order of 10^{19} cm^{-3}.

Over the past half-century it has not been achieved any significant improvement in the thermoelectric performance of homogeneous materials used for energy conversion. Typical figure-of-merit values of known TEMs operating at different temperature ranges are shown in Figs. 3 and 4. It follows from the analysis of these figures that all for presented materials the thermoelectric figure-of-merit lies in the region $ZT < 2$ even at elevated temperatures. As can be seen, $(Bi_{1-x}Sb_x)_2(Se_{1-y}Te_y)_3$ based semiconductor alloys with ZT close to unity at room temperature remain the best commercially produced TEMs widely used for creation of TEGs.

Note that for the laboratory samples ZT values ~2–3 are achieved at room temperature.

Methods to improve the thermoelectric figure-of-merit. Possible ways to improve thermoelectric figure-of-merit and physical ideas, on which they are based, are discussed below.

Applied to homogeneous semiconductors, the main way to improve their thermoelectric properties is a combination of their composition changes and selection of the appropriate band structure.

Important way to improve the thermoelectric properties currently is connected with creation of spatially inhomogeneous materials and structures in which the dimensions of the inhomogeneities are comparable to the characteristic wavelength of electrons or phonons, i.e. lie in the nanometer range.

Consider the advantages and disadvantages of these methods to change the performance of thermoelectric materials.
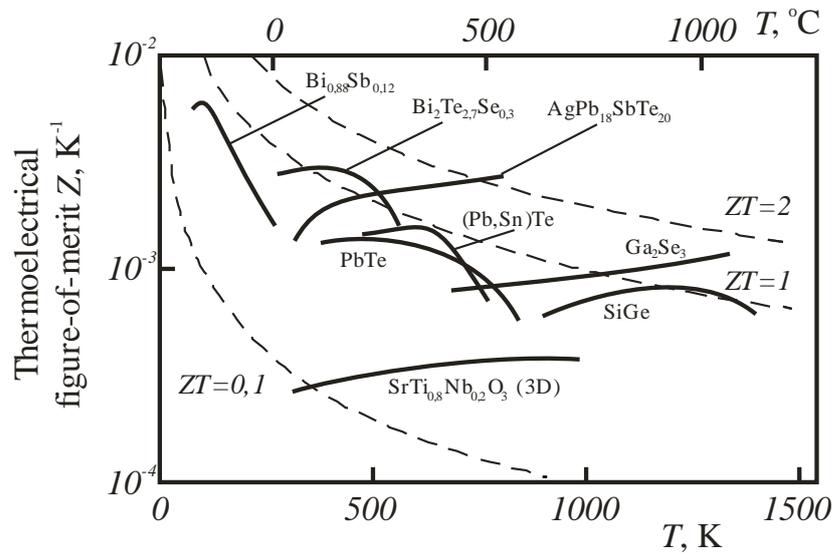
Fig. 3 – Thermoelectric figure-of-merit of number of used and promising materials
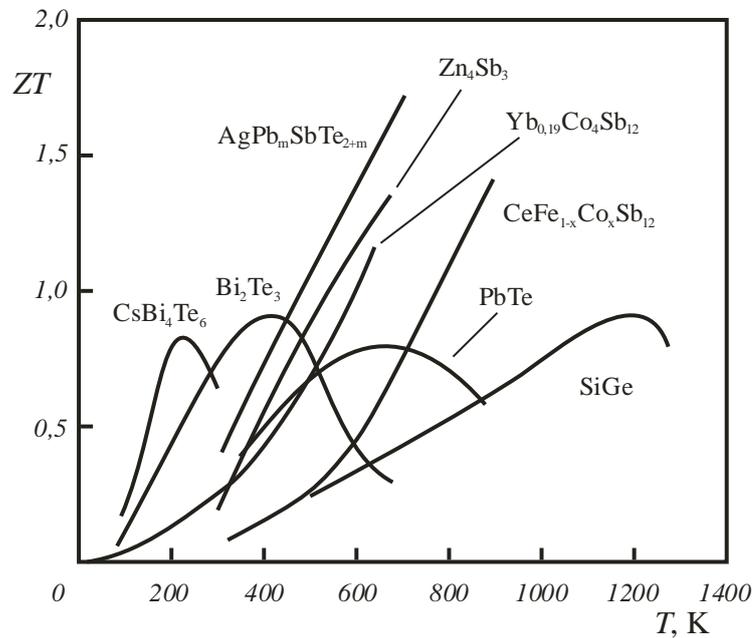

Fig. 4 – The dimensionless thermoelectric figure-of-merit
of some common and promising materials depending on the temperature

Conductivity is one of parameters used for classification of the thermoelectric material from the viewpoint of their thermoelectric figure-of-merit. From this viewpoint, semiconductors with intermediate (between metals and dielectrics) values of electrical conductivity are most suitable. Note that it just the concentration of charge carriers determines the other two parameters (the Seebeck coefficient and the thermal conductivity) occurring in relation Ioffe for thermoelectric figure-of-merit.

As can be seen from the diagram in Figure 5, electrical conductivity increases and Seebeck coefficient decreases with increasing carrier concentration. As a result, the power factor P in (9) has a maximum in the vicinity of the concentration of $1 \cdot 10^{19}$ cm^{-3}. The electronic contribution to the thermal conductivity in (11), which does not exceed one third of the total thermal conductivity also increases with the concentration of charge carriers. This means that the optimization of the thermoelectric figure-of-merit according to the Ioffe formula corresponds to the concentration of carriers in semiconductors, Fig. 5. For this reason, until now semiconductors are most studied materials from the viewpoint of thermoelectric properties. Among semiconductors, compounds and alloys based on bismuth (in combination with antimony,

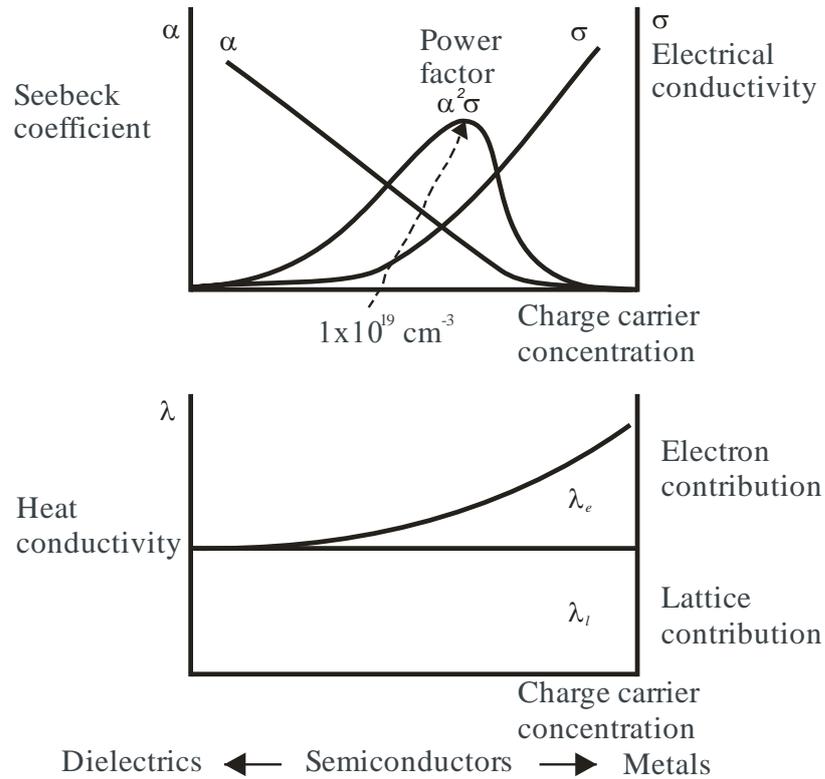tellurium and selenium) have been most popular industrial TEM with operating temperatures below 750 K.

Fig. 5 – Schematic representation of the dependence of the electrical conductivity, Seebeck coefficient, power factor and the thermal conductivity on the carrier concentration

Selection of an optimal concentration of carriers. Selection of the optimal doping level providing the maximum value of thermoelectric figure-of-merit is one of the most simple from a technological point of view and, therefore, almost always used for semiconductor TEM. As noted above, the need to select the optimal charge carriers concentration is due to the fact that its increase enhances the conductivity and usually reduces the Seebeck coefficient of a semiconductor. This decrease in the α value can be understood on the basis of the mechanism of the Seebeck effect.

If there is a temperature difference in a semiconductor sample with electron conductivity, the electrons at the hot edge have higher energies and speeds than at the cold one. This results in more rapidly electron diffusion from the hot to the cold junction than in the opposite direction. As a result of the preferential electron flow from the hot to the cold junction occurs, the negative charge is formed at the cold and uncompensated positive remains on the hot. Thereby the bulk thermoelectric power arises.

If the material contains charge carriers of opposite signs, their contributions to the thermoelectric power will be subtracted because both electrons and holes diffuse from the hot end of the sample to the cold, but bring with them the charges of opposite signs. For this reason, a good thermoelectric material should possess a monopolar conductivity.

We now turn to the dependence of the thermoelectric power on the charge carriers concentration. With increasing of the charge carriers concentration, gas of carriers (electrons, for definiteness) becomes degenerate, when the Fermi level E_F (chemical potential per 1 electron) is adjudged to the conduction band and the Fermi energy, i.e. distance from the Fermi level to the bottom of this band exceeds $k_B T$. Energy and velocity of particles are determined in this case by the E_F value and are practically independent of temperature (due to small smearing of the Fermi

– Dirac distribution). Therefore, flows of electrons from hot and cold ends of the sample differ not significantly, and Seebeck coefficient is small.

This conclusion can be reached in a different way. When the electron distribution becomes degenerate, the role of states, which lie below Fermi level, is reduced. In this case the electron transport is determined mainly by the states, which are distributed near the Fermi level in an energy layer with a width of the order of the crystal lattice energy $k_B T$. Seebeck coefficient α is related to the Peltier energy E_P (energy carried by one electron) by the Kelvin ratio

$$\alpha = E_P/k_B T \ . \tag{15}$$

The Peltier energy is obtained by summing the $(E–E_F)$ contributions of electrons with energies E close to the Fermi level E_F. The contributions of electron states with $E > E_F$ and hole states with $E < E_F$ have opposite signs and may have different values due to dependence of the density of states and the relaxation time on the energy. In the case of strong degeneracy, for example, in metals, the relative changes in the density of states are small and decrease with the Fermi level growth. Therefore, the thermoelectric power of metals is small and decreases with increasing carrier concentration.

Significantly higher values of Seebeck coefficient and figure-of-merit are obtained in the case of semiconductors and semimetals when the concentration is not too low, but there is no strong degeneracy. In Fig. 6 the results of the conductivity, Seebeck coefficient and power factor calculations are given for semiconductor compound PbTe as one of the most common TEMs. It can be seen that the maximum value of the power factor in n-type material is obtained in the case when the Fermi level of electrons lies near the conduction band edge. Then there is no strong degeneracy yet, but the asymmetry in density of states and contributions of the charge carriers with $E > E_F$ and $E < E_F$ is significant. In addition, the concentration of holes reducing the thermoelectric power of n-type material is very small for such a position of the Fermi level.
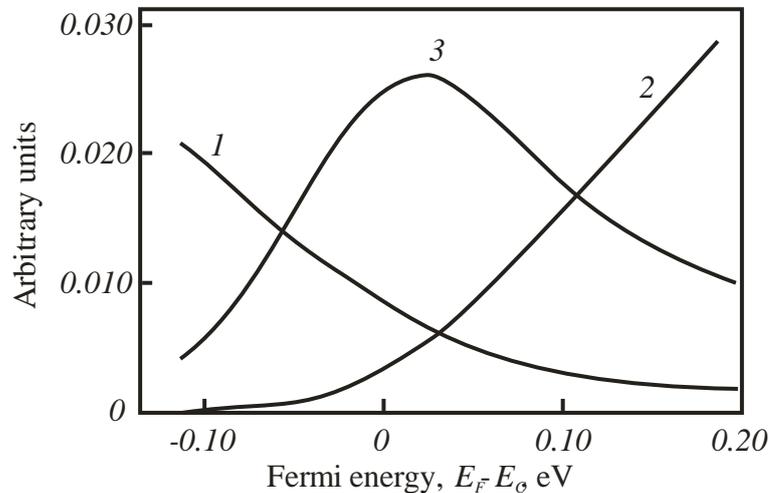

Fig. 6 – ThermoEMF (curve 1), electrical conductivity (curve 2) and power factor (curve 3) in PbTe as a function of the Fermi energy measured from the conduction band bottom

Selection of the optimal energy gap. Many semiconductor TEMs represent solid solutions that enables one to control their properties only by changing the alloy composition. In particular, the change in the composition of such materials makes it possible to vary parameters of band structure (for example, the energy gap) in order to optimize their thermoelectric properties by controlling the charge carriers concentration and the Seebeck coefficient.

Calculations show that in a good thermoelectric material the energy gap should be approximately an order of magnitude larger than the thermal energy $k_B T$, and the Fermi level

should be located near the edge of the majority charge carriers' band. The reason for this is that at such energy gap and the Fermi level lying near the conduction band bottom (or the valence band top), the concentration of minority carriers and their contribution to a charge transport become negligible, and as explained above, it promotes an increase of thermoelectric power.

Modification of the chemical composition. Another standard method to improve the thermoelectric properties of the material is to modify its chemical composition by preparing solid solutions and alloys or by growing new chemical compounds on its basis. The changes arising in this case are not reduced only to variation in energy gap.

One of the main advantages of the solid solutions compared to pure substances is their lower lattice thermal conductivity due to the scattering of phonons by structural defects. The presence of crystal lattice defects has much less effect on reduction of the electronic conductivity, since due to greater (compared with phonons) velocity of electrons their wavelength is much larger than that of the phonons.

At a sufficiently high level of semiconductor doping an impurity band located either below the valence band or above the conduction band can be formed. A sharp change in the electronic density of states occurring in vicinity of the impurity band may lead to a substantial increase in the thermopower compared to a material in which there is no such band. This follows, for example, from the known Mott equation applicable in the case of a degenerate electron gas

$$\textrm{б} = \frac{\textrm{p}^2 T}{3e} \frac{d \ln(v^2 g\phi)}{dE}\bigg|_{E=E_F} \tag{16}$$

where v is velocity of charge carriers,
τ is the relaxation time,
g is the density of electronic states.

Spatially inhomogeneous semiconductor systems. Nanostructured systems are of considerable interest for thermoelectric applications. They include:

- polycrystalline materials (metal and semiconductor alloys), including those with nano-sized grains;
- composites representing a matrix with regular or irregular inclusions (particles) of nanometer size;
- ordered and unordered arrays (grids) of the quantum zero- and one-dimensional objects (wells dots, wires, rods);
- superlattice of alternating nanolayers, etc.

Currently, spatially inhomogeneous nanostructured systems with a disordered arrangement of the components are regarded as the most promising nanothermoelectrical materials. They are simpler to manufacture and therefore are cheaper. Here we are talking primarily about heterogeneous composite systems, in which nanoparticles, nanowires or nanoposts are randomly distributed in a homogeneous matrix.

The transition to nonuniform (heterogeneous) systems and the introduction of the size of the system components as an additional parameter makes it easier solution of the problem of improving the thermoelectric figure-of-merit. One of the major changes in the physical properties of heterogeneous systems of reduced dimensionality, which leads to an increase of their thermoelectrical figure-of-merit, is a reduction of their thermal conductivity due to an additional phonon scattering on the inner interphase surfaces. It was mentioned above that the substitutional atoms in alloys scatter phonons effectively, thereby reducing the thermal conductivity of the crystalline substances to a so-called limit value in the alloy. A similar role, and even more effectively, can be performed by inhomogeneities of nanometer size (comparable to the wavelength of a phonon).

Of course, in the nanocomposites containing such inhomogeneities not only phonon, but also electronic properties can be changed, and the changes of the latter also affect the thermoelectric characteristics of the materials.

Consider first the impact of the introduction of nano-inhomogeneities (nanoparticles) on the thermal conductivity of thermoelectric materials.

Is is seen from the Rayleigh formula for the cross section of phonon scattering

$$s \sim a^2/\lambda^4, \tag{17}$$

(where a is the size of the scatterer, λ is the phonon wavelength) that whereas the point defects in a homogeneous alloy scatter effectively short-wavelength phonons, then nanoparticles entered into it will scatter additionally the phonons with medium and long wavelengths resulting in significantly reduced thermal conductivity. It is important that the ordered arrangement nanoinclusions is not required to reduce the lattice thermal conductivity.

Reduction of the crystal lattice thermal conductivity is not the only consequence of the introduction of nanoprecipitates into thermoelectric material. The processes of propagation and scattering not only of phonons but also electrons can vary in nanocomposites. Additional scattering of electrons at the intergrain or interphase boundaries in nanostructured material is an important mechanism of increase of its thermopower compared with a homogeneous material. The reasons for this increase are as follows. If charge carriers are approaching the potential barrier at the boundary, the energy distribution of the carriers crossed the barrier differs substantially from the initial: fraction of particles with increased energy grows that leads to an increase of the thermopower. However, this increase is local. When the carriers with increased energy fall into other grains, their non-equilibrium energy distribution gradually relaxes to the equilibrium one due to scattering on phonons on the length equal to the mean free path in the energy l_E. ThermoEMF thus returns to its "normal" value.

Hence, the equivalent circuit for description of the granular material with a size of grains (granules) $d > l_E$ can be represented as a system of series-connected regions with different values of Seebeck coefficient corresponding to the grain (granules) and intergrain (intergranular) boundaries. In so doing, the grains have the same value of the thermopower α_g as the material without grain boundaries (single crystal), whereas thermopower of grain boundary regions α_{gb} with a thickness of about l_E is enhanced due to non-equilibrium electron gas in them. Considering the material as an effective medium, the thermopower of granular material can be estimated using the expression

$$\alpha_{\text{eff}} = \alpha_g + (\alpha_{gb} - \alpha_g)\frac{l_E}{d}, \tag{18}$$

где $\alpha_{gb} > \alpha_g$. It can be seen from this relation that the thermoelectric power of a granular material increases with decreasing of grain size d.

Methods of study of thermoelectric materials. Obviously, the thermoelectric figure of merit can be calculated on the basis of independently determined Seebeck coefficient, the electrical conductivity and the thermal conductivity in accordance with (8). Along with such approach, the method of direct determination of thermoelectric figure of merit proposed in 1958 by Harman is realized in this lab.

Harman method based on the following. When a direct current is passing through the sample, some Peltier heat is released at one of its contacts and absorbed at the other. As a result, some temperature difference ΔT occurs between the contacts. This temperature difference is increased until the compensation of Peltier heat by the heat flow through the sample due to its thermal conductivity. A voltage V_{DC} between the sample faces by passing a constant electric current I consists of two components

$$V_{DC} = IR + \alpha\Delta T \,, \tag{19}$$

where R is ohmic resistance of the sample,
$\alpha\Delta T$ is thermoelectric power due to the temperature difference between the sample faces.

When an alternating current is passing, due to a thermal inertia of heat processes the temperature difference between the sample faces will be zero and therefore the potential difference will be equal $V_{AC} = IR$. Then

$$\frac{V_{DC}}{V_{AC}} = 1 + \frac{\alpha\Delta T}{IR} \,. \tag{20}$$

In the steady state, the Peltier power is compensated by heat flow through the sample due to its thermal conductivity, and hence it is possible to write:

$$\Pi I = \alpha T I = \lambda \frac{\Delta T}{l} S \,, \tag{21}$$

where $\Pi = \alpha T$ is Peltier coefficient,
T – temperature,
λ – the thermal conductivity of material,
l – sample length,
S – cross-section area of the sample.

Expressing ΔT from the last relation and substituting it into (20), we obtain

$$\frac{V_{DC}}{V_{AC}} = 1 + \frac{\alpha^2 T I l}{\lambda S I R} = 1 + \frac{\alpha^2 \sigma}{\lambda} T = 1 + ZT \,, \tag{22}$$

where we took into account that

$$R = \frac{l}{\sigma S} \,, \tag{23}$$

σ is the electrical conductivity of the sample.

Thus, in accordance with (22), for determination of the thermoelectric figure-of-merit it is sufficient to measure the voltage across the sample when direct and alternating currents are passing.

It is known that the accuracy of measurement of DC voltage is higher than in the case of AC voltage. Therefore, in the implementation of the Harman method, different measurement algorithm is often used. Through the sample a direct current is passed. After reaching of steady-state temperature difference between the sample faces, the I, U_{DC} and ΔT values are measured. After that, the current is turned off and the voltage across the sample is measured immediately. This voltage is obviously equal to

$$V\big|_{I=0} = \alpha\Delta T \,. \tag{24}$$

Hence, according to (22),

$$ZT = \frac{V_{DC}}{V_{AC}} - 1 = \frac{V\big|_{I=0}}{V_{DC} - V\big|_{I=0}} \,. \tag{25}$$

In accordance with (24), Seebeck coefficient is defined as

$$\alpha = \frac{V|_{I=0}}{\Delta T}. \tag{26}$$

According to (19), (23) and (24), electrical conductivity is

$$\sigma = \frac{lI}{S\left(U_{DC} - U|_{I=0}\right)}. \tag{27}$$

Finally, the thermal conductivity in accordance with (21) can be calculated as

$$\lambda = \frac{\alpha T l I}{\Delta T S}. \tag{28}$$

Thus, Harman method requires a smaller number of measurements than in the case when the figure-of-merit is calculated from α, σ and λ parameters measured separately.

However, it is obvious that the Harman method is poorly applicable to study thermoelectric materials with low values of figure-of-merit. Indeed, the temperature gradient necessary for a reliable determination of the Seebeck coefficient and thermal conductivity is created by the Peltier heat; for small α and large λ values, temperature difference will small leading to a sharp increase in the inaccuracy. In the case of low electrical conductivity, the passing of high currents will lead to a significant release of Joule heat, against which the Peltier heat will be noticeable.

When implementing the Harman method, six contacts to the sample are typically used (Fig. 7). Two of them are used for current passing through the sample, whereas other four form two thermocouples and may serve both to measure the temperatures at the hot and cold faces of the sample and for measurement the potential difference between the faces.
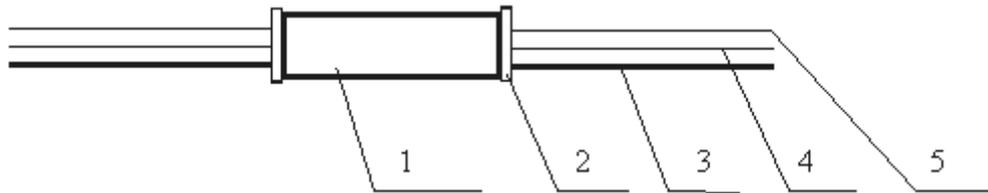
1 – sample, 2 – copper plate, 3 – constantan wire,
4 – potential copper wire, 5 – current copper wire
Fig. 7 – Scheme of the Harman method implementation

It is necessary to consider that efficient thermoelectric materials have typically high electrical conductivity. For example, if the specific electrical resistance is equal to 10^{-5} $\Omega\cdot$cm, for the sample with dimensions of 5 x 5 x 10 mm^3 the resistance will equal 40 $\mu\Omega$. Determination of such small resistances with an acceptable inaccuracy using the scheme shown in Fig. 7 is not possible due to the influence of contact resistances. Therefore, during experimental investigation of such samples it is necessary to use the four-probe method of the resistivity determination. For this purpose on the lateral sample surface two potential probes are placed and the voltage between them is measured when a current is passing, as is shown in Fig. 8.
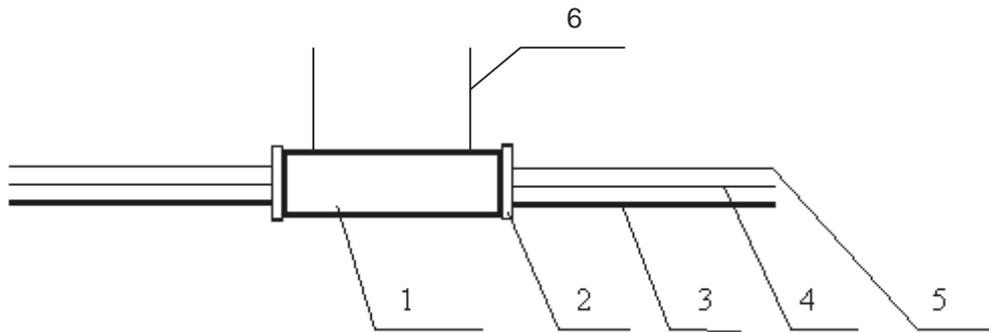
1 – sample, 2 – copper plate, 3 – constantan wire,
4 – potential copper wire, 5 – current copper wire, 6 – potential probes
Fig. 8. – Scheme of the Harman method implementation
using additional potential probes

Description of the laboratory setup

General information. For the experimental investigation of thermoelectric materials by the Harman method in this lab an automated measurement system (AMS) is used. This AMS allows to determine the thermoelectric figure of merit, the Seebeck coefficient, the electrical conductivity and the thermal conductivity in the temperature range 300–700 K.

Main technical characteristics of AMS are presented below:

- range of the thermal conductivity determination: 0.5–10 W/m·K;
- range of the electrical resistivity determination: 10^{-5}–10^3 Ω·cm;
- range of the Seebeck coefficient determination: 10–1000 µV/K;
- range of the temperature measurement: 300–700 K;
- temperature measurement error: less than 0.1 ^{o}C;
- error of voltage measurement by a Agilent 34420A nanovoltmeter (when 100 mV measurement range is used): less than 0.0002 % of a measured value + 0.1 µV;
- error of the current measurement: less than 0.15 %;
- stabilization of temperature within the range 300–700 K with accuracy of 1 %.
- the vacuum level in the measurement chamber: 1 Pa;
- permissible dimensions of the test samples:
  length: from 5 mm to 60 mm;
  width: from 4 mm to 20 mm;
  высота – от 4 мм до 20 мм.

AMS includes the following main elements:

- measurement unit;
- measurement control unit (including computer);
- evacuation unit;
- soldering station;
- soft.

Description of AMS

The measurement unit is the basis of AMS. It represents a hermetic chamber in which the thermoelectric sample under study is placed. The measurement unit consists of a body, cover, measuring cell, vacuum gauge, eight sealed feedthrough, and connection terminals. Cover of the measurement unit has two handles and four slots for mounting it on the shelf of the measurement unit using clamping nuts. Dial gauge is used for visual inspection of the vacuum breaking.

The measuring cell of the measurement unit is situated under the lid. The sample holder and the test sample of the thermoelectric material which is sandwiched between two flat copper contacts are placed in the cell.

Two copper and one constantan wires are welded to each of two copper contacts. One of the copper wires is used as a current lead; other copper wire with a constantan one form the thermocouple for determining the temperature of the copper contact. Two additional copper wires are attached to the clamping potential probes and are used to determine the sample resistance by the four-probe method. Using a special retainer it is possible to vary the distance between the copper clamping contacts to test the samples of different lengths.

The lid of the measurement unit has a system of three mirror reflectors that is necessary to reflect the thermal radiation at high measurement temperatures. The lid has a protrusion, which is pressed to the vacuum pad by four clamping screws.

Evacuation unit

Evacuation unit is intended to create and maintain the necessary degree of vacuum in the measuring cell. It is designed as a mobile unit on the rollers and consists of a carriage, a vacuum pump, a flexible vacuum hose, a clamp for vacuum connection, a vacuum valve and fitting.

To provide a vacuum in AMS a Varian TriScroll PTS-300 oil-free vacuum pump of spiral type used. The vacuum valve is designed for sealing of the vacuum chamber during heating when the vacuum pump is temporarily switched off.

If it is necessary to perform the measurement in an inert gas (e.g., argon) medium, an additional input into the vacuum circuit is provided. Such necessity occurs, for example, in the case of testing of bismuth telluride, which evaporates rapidly in vacuum at a temperature above 300 °C.

Measurement control unit

The measurement control unit provides the automation of the measurement process for determination of the thermoelectric characteristics of the sample studied. It consists of control computer, measuring devices, control panel, where the main switch, the switch of the evacuation unit, the switch of TRM148 regulator, and the TPM148 regulator are located.

Measuring instruments include an Agilent 34420A nanovoltmeter, an Agilent 34970A multimeter, an Agilent U3606A multimeter, which also is used for current passing through the sample.

Software. The measurement control unit is controlled by the measurement software AMS-v.4.0, which is part of AMS and installed on the control computer. The main window of AMS-v.4.0 program is shown in Fig. 9. The AMS-v.4.0 software is the LabView 8.6 executive file.
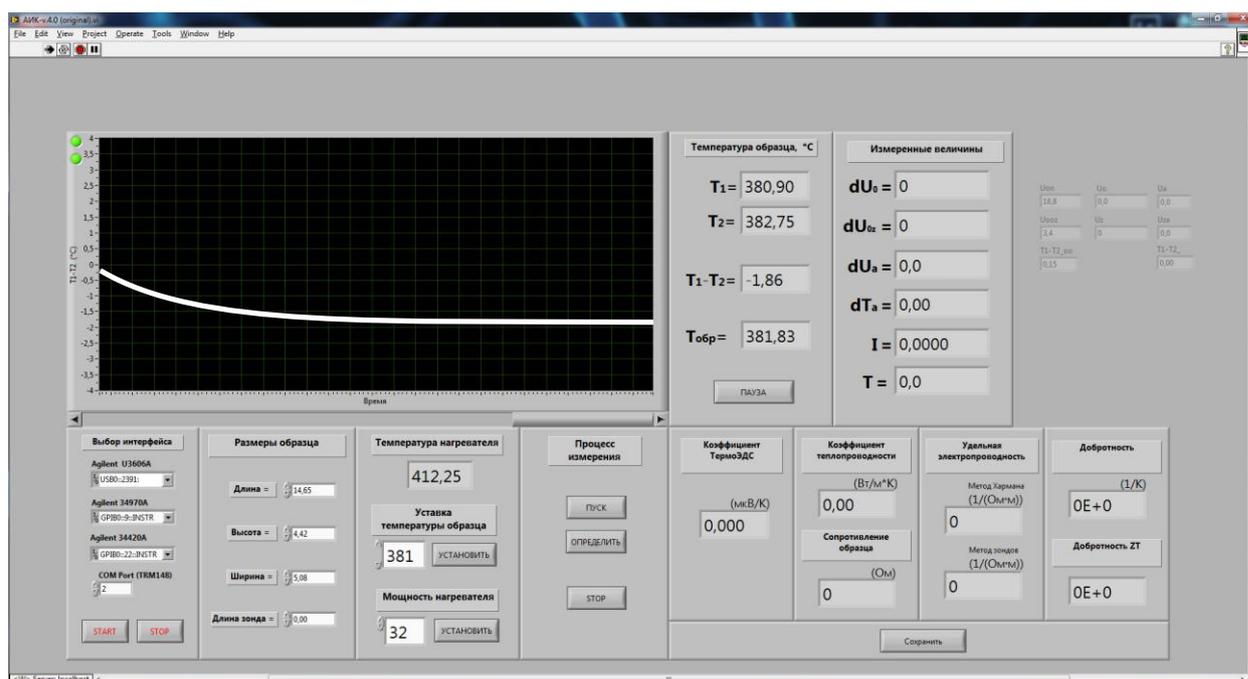

Fig. 9 – The main window of the AMS-v.4.0 program

14

The AMS-v.4.0 program allows to automate the measurement process and save the experimental data to a file for further analysis.

Principle of AMS operation. Principle of determination of the thermoelectric characteristics by the Harman method consists in the following:
– Constant current of the known value is passed through the sample;
– When the steady-state temperature difference ΔT is reached (due to the Peltier effect), the voltage UDC between "hot" and "cold" face of the sample U_{DC} and the voltage between the potential contacts U_z are measured;
– DC current is switched off and the voltage $V|_{I=0}$ between "hot" and "cold" faces of the sample and the voltage U_z between the potential contacts caused only by the Seebeck effect are measured immediately;

Thermoelectric figure-of-merit, Seebeck coefficient, electrical conductivity, and thermal conductivity of the test material are calculated from the measurement results using the formulas (25) – (28).

A heater placed in the housing of the measurement unit allows to do measurements at elevated (up to 400 °C) temperatures.

Work with AMS
Match of AMS to the following requirements must be established during the visual inspection:
- Absence of mechanical damage of AMS blocks (absence of visible defects);
- Absence of broken thermocouple, current and potential wires;
- Absence of foreign objects on the measurement unit and control unit;
- Presence of ground of AMS;
- Presence of a good contact of connecting cables between the measurement devices and compute.

Before placing the test sample of thermoelectric material, it is necessary to control its look and measure its dimensions (length, width, height, distance between the potential probes) for further input into the AMS-v.4.0 software.

Preparing of the measurement unit is performed in the following sequence:

1. Place test sample in the vacuum chamber of the measurement unit. To do this, install on the side faces of the specimen the potential contacts. Then take away the presser contact of the sample holder with a clip. Arrange the sample along the axis of the holder and press to the end copper contacts releasing the latch.

2. Close the lid of the vacuum chamber and press it tightly to the body of the measurement unit with four clamping nuts.

3. Turn on the main switch.

4. Start the process of evacuating the vacuum chamber with a switch and then open the vacuum valve.

5. After evacuating the chamber, close the vacuum valve and turn off the vacuum pump.

After preparing of the measurement unit, the preparing of the control units for work is carried out. It is necessary for this purpose:

1. Turn on the TPM148 regulator.

2. Turn on the measuring devices: Agilent 34420A nanovoltmeter, Agilent 34970A multimeter, Agilent U3606A multimeter according to the operational documentation on these devices.

3. Start computer and the AMS-v.4.0software.

4. Select the appropriate interface for measuring devices on the computer monitor in the «interface selection» window (Fig. 10).
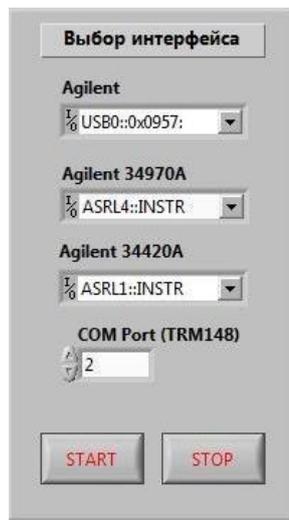
Рис. 10 – Window of interface selection

5. Enter the measured dimensions of the test specimen (length, width, height, distance between the potential contacts) on the computer monitor in the "sample sizes" window.

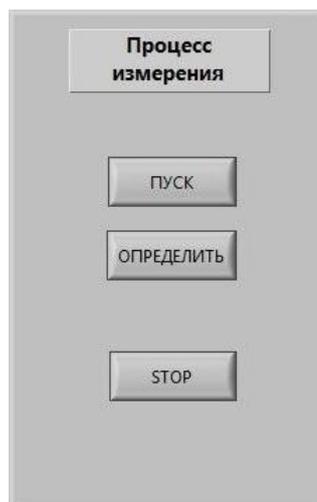6. Press the «ПУСК» key in the main window (Fig. 11).

Fig. 11 – Window for the start of measurement process

7. Set the desired value of the current through the sample using the panel of the Agilent U3606A device. To do this, press sequentially the keys "Local", "Current", select the desired current value, and again press the "Current" key.

8. Press the "START" key in the main window of the program. The program will determine the "parasitic" voltages between current (U_{00} field in Fig. 9, in microvolts) and potential (U_{00z} field in Fig. 9, in microvolts) contacts, as well as the "parasitic" temperature difference ($T_1 - T_{2\_00}$ field in Fig. 9, in Celsius degrees), and then direct current will flow through the sample that will be accompanied by an increase of the temperature difference between its faces.

9. Press the "Определить" key upon reaching the stationary temperature difference. The program will measure automatically the voltages between current (U_0 field in Fig. 9, in microvolts) and potential (U_z field in Fig. 9, in microvolts) contacts under current flow, as well as the temperature difference ($T_1–T_{2\_}$ field in Fig. 9, in Celsius degrees), then switch off the current and measure the voltages between the current and potential contacts again (U_a and U_{za} field in Fig. 9, in microvolts).

16

10. Using the determined values of voltages and temperatures, as well as the magnitude of the current through the sample and its geometrical dimensions, calculate the parameters that define its thermoelectric figure-of-merit (quality factor, Seebeck coefficient, thermal conductivity, electrical conductivity).

11. Repeat steps 8 - 10 at the opposite direction of the current through the sample. To do this, interchange the wires connected to the Agilent U3606A power supply.

WARNING! It is strictly forbidden to perform this operation when the «OUT» inscription is displayed on the panel!

To determine the above parameters at high temperature, it is necessary to perform the following operations on the control panel of the AMS-v.4.0 software:

1. On the computer monitor in the «Уставка температуры образца» window (Fig. 12) enter the desired temperature, at which the thermoelectric characteristics of the tested sample should be determined.

2. Start the automatic process of the chamber heating, pressing the «УСТАНОВИТЬ» key (Fig. 12). The program will select the value of the heater power required to reach a desired temperature.

3. After reaching the set temperature, the program automatically starts the measurement of the temperature difference between the ends of the sample and displays the results on the monitor.
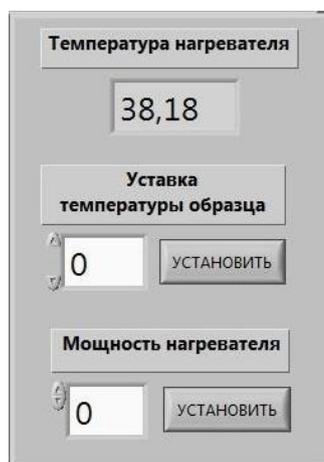

Fig. 12 –Program window for input of the sample temperature

Completion of work with AMS

After completion of the measurement process with AMS it is necessary to perform the following steps:

1. Close the vacuum valve.
2. Turn off the evacuation unit.
3. Close computer program АИК-v.4.0.
4. Turn off the computer.
5. Turn off the measuring devices: Agilent 34420A nanovoltmeter, Agilent 34970A and Agilent U3606A multimeters, TPM 148 thermoregulator.
6. Turn off the main switch.

WARNING! When working with AMS it is forbidden:

1. Open the lid of the vacuum chamber during the measurement;
2. Heat the vacuum chamber of the measurement unit above 500 °C;
3. Perform the heating of the vacuum chamber in the case of vacuum violation;
4. Perform the heating of the vacuum chamber in the case of failure of the vacuum gauge;
5. Depressurize the vacuum chamber of the measurement unit at a temperature within the chamber above 200 °C;

6. Disconnect or connect measuring devices to the computer, if the computer or devices are in the ON state.

Determination of thermoelectric figure-of-merit based on the results of measurements of electrical conductivity, Seebeck coefficient and thermal conductivity. To measure the thermoelectric power, the sample is placed on a copper table-electrode (Fig. 13). To the opposite face of the sample a heated copper electrode is applied. The potential difference (the thermoelectric power) between the hot and cold electrodes is measured with an Agilent 34411A multimeter. Temperature of "hot" and "cold" electrodes are determined using platinum resistance thermometers attached to them using a thermal conductive paste. Resistance of thermometers is measured by Agilent 34410A multimeters. Readings of measuring instruments during the experiment are transmitted to the control computer and monitored as time dependencies. It is recommended to adhere the following sequence of measurements. Recording of temperatures of electrodes and the potential difference between them U has to start at zero temperature difference ΔT. Next, the heater of the electrode is turned on and $U = f(\Delta T)$ dependence is registered, from which the Seebeck coefficient can be determined by differentiating.
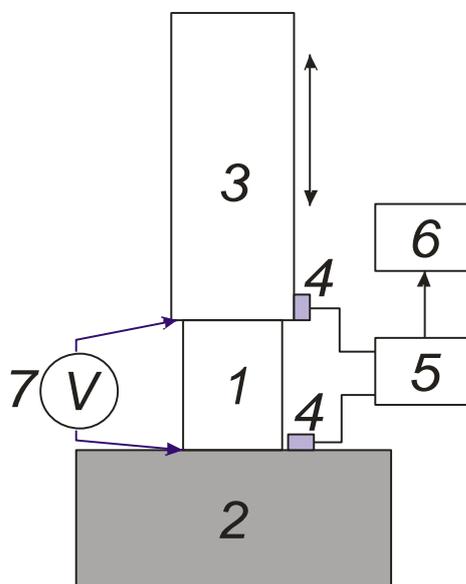
1 – studied sample; 2 – copper holder; 3 – movable copper heater;
4 – resistance thermometers; 5 – ohmmeters
Fig. 13 – Setup for the measurements the thermoelectric power

For determination of the conductivity, the current-voltage characteristics are measured. For this purpose on the opposite faces of the samples of regular shape (in the form of parallelepipeds) the current contacts are formed. Point potential probes are located on the long edge. A ballast resistor is connected in the measuring circuit in series with a test sample and the voltage drop on this ballast resistor is used for determination of the current. Voltage across the sample and the ballast resistor and the resistance of the latter are measured using Agilent 34410A multimeters. Geometric dimensions of the samples are determined by caliper.

Coefficient of thermal conductivity is determined by the comparative method in the stationary regime. For this purpose the sample studied in series with the heat flow meter is located between two thermostated blocks (brass cylinder). Using thermal insulation materials an insulation of the side sample surfaces is provided.

By pumping of hot water through the thermostat and one of the brass cylinder, a temperature difference between the brass cylinder is provided. Temperatures on the surface of the sample and the heat meter are measured by thermocouples attached to the registration system.

Coefficient of thermal conductivity λ_s of the studied sample is calculated by the formula

$$\lambda_o = \lambda_m \frac{d_o}{d_m} \frac{\Delta T_m}{\Delta T_o}, \qquad\qquad (29)$$

where λ_m is the thermal conductivity of the heat meter material,
d_o is the sample thickness,
d_m is the heat flow meter thickness,
ΔT_m is the temperature difference between the faces of the heat meter,
ΔT_o is the temperature difference between the faces of the sample.

Tasks and the order of work execution
1. Read the description of laboratory facilities and guidelines for their operation.
To perform measurements by the Harman method:
2. Turn on the devices, allow them to warm up.
3. Under guidance of the teacher to place the sample of thermoelectric material to be studied in the measuring cell, and then do its evacuation.
4. Set the value of the constant current through the sample as high as 100 – 200 mA (too small current will not allow to obtain a sufficient temperature gradient on the sample, and too large one will cause heating of the sample due to the Joule heat).
5. Perform the measurement by the Harman method at room temperature and save the results.
6. Change the direction of the current through the sample, and then repeat step 5.
7. Compare the values of the stationary temperature difference arising due to the Peltier effect for two directions of a current of the same magnitude. A significant divergence of these two values indicates the difference between resistances of two current contacts that leads to a difference in the magnitude of Joule heat. In this case it is necessary to remove the sample from the setup and re-form the current contacts.
8. Repeat the measurements at elevated temperatures.
9. To obtain the temperature dependence of the thermoelectric figure-of-merit, Seebeck coefficient, electrical conductivity, and thermal conductivity.
10. Analyze the sources of error and to estimate the inaccuracy of measurement.
For determination of thermoelectric figure-of-merit based on the results of measurements of electrical conductivity, Seebeck coefficient and thermal conductivity coefficient:
11. Measure the resistance of the ballast resistor and connect it in series with the test sample to the voltage source. By increasing the voltage at the power supply output, measure the current-voltage characteristic. Measure the sample dimensions (width, thickness, distance between the potential probes) with a caliper. Calculate the value of the sample electrical conductivity from the current-voltage characteristics.
12. Place the sample in the apparatus for thermopower measurement (Fig. 13). Turn on the heater of electrode and measure the dependence of the thermopower on the temperature drop across the sample, to calculate the Seebeck coefficient from this dependence by differentiation.
13. Place the sample in series with the heat meter between two thermostated blocks (brass cylinders). With thermal insulation materials provide a thermal insulation of the side surfaces of the sample. By pumping a hot water through the thermostat and one of the brass cylinders to create a temperature difference between the thermostated blocks. Measure the temperature differences arise between the faces of the test sample and the heat meter. Calculate the thermal conductivity coefficient.
14. Compare the results of the determination of the thermoelectric parameters obtained by different methods. Interpret the results.

Test questions

1. What are the basic requirements for a highly-effective thermoelectric material?

2. Why metals having a high electrical conductivity are characterized by a low Seebeck coefficient and a high thermal conductivity?

3. Are there any fundamental limitations for thermoelectrical figure-of-merit? Efficiency of thermoelectrical energy conversion?

4. What are the advantages and disadvantages of the Harman method for determination of thermoelectrical figure-of-merit?

5. Is the Harman method applicable to study the thermoelectric properties of metals?

Instructions for report execution

The report should contain:

1. Title of the work.

2. Name of students who performed the work.

3. Introduction, where the aim of investigation is formulated.

4. Short summary of the theory explaining the physical nature of the investigated effects, meaning of physical quantities and measured dependencies.

5. Methods of investigation: description of the experimental setup and the objects under investigation, as well as estimation of inaccuracies should be given.

6. Experimental results and their discussion. Based on the experimental data, the main regularities should be marked and physical phenomena underlying them should be analyzed.

7. Conclusions. Critical analysis of the results should be contained here.

Recommended literature

1. Голдсмит, Х.Дж. Эксперименты по непосредственному измерению термоэлектрической добротности/ Х.Дж. Голдсмит // Термоэлектричество. – 2006. – № 1. – С. 5–15.

2. Дмитриев, А.В. Современные тенденции развития физики термоэлектрических материалов / А.В. Дмитриев, И.П. Звягин // Успехи физических наук. 2010. – Т. 180, № 8. – С. 821–838.

3. Методы измерения характеристик термоэлектрических материалов и преобразователей / А.С. Охотин [и др.]. М. 1974. – 167 с.

4. Thermoelectrics handbook: macro to nano / edited by D.M. Rowe // Boca Raton. London – New York. 2006. – 954 p.