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Methods and Apparatus for Measuring Thermopower and Electrical Conductivity of Thermoelectric Materials at High Temperatures

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Abstract

The principles and methods of thermopower and electrical conductivity measurements at high temperatures (100–1000 K) are reviewed. These two properties define the so-called power factor of thermoelectric materials. Moreover, in combination with thermal conductivity, they determine efficiency of thermoelectric conversion. In spite of the principal simplicity of measurement methods of these properties, their practical realization is rather complicated, especially at high temperatures. This leads to large uncertainties in determination of the properties, complicates comparison of the results, obtained by different groups, and hinders realistic estimate of potential thermoelectric efficiency of new materials. The lack of commonly accepted reference material for thermopower measurements exaggerates the problem. Therefore, it is very important to have a clear understanding of capabilities and limitations of the measuring methods and set-ups. The chapter deals with definitions of thermoelectric parameters and principles of their experimental determination. Metrological characteristics of state-of-the-art experimental set-ups for high temperature measurements are analyzed.

Keywords: thermopower, electrical conductivity, high temperature, thermoelectric material, measurement

1. Introduction

Thermoelectric energy conversion is based on two effects discovered in the nineteenth century: Seebeck effect and Peltier effect [1]. Historically, Seebeck effect was the first discovered thermoelectric effect, which consists in appearance of electrical current in the circuit of two different conductors at the presence of temperature difference. In year 1821, Thomas Johann Seebeck discovered, that magnetic field is generated in closed circuit consisting of bismuth (or antimony) and copper in

the presence of temperature difference between two contacts. He first announced this discover in year 1825 in the writings of Berlin Academy of Sciences. Seebeck called this phenomenon thermomagnetism. The term “thermoelectricity” was proposed by Hans Christian Oersted approximately at the same time. There are indications, that this effect was observed and correctly interpreted in years 1794–1795 by Alessandro Volta [2]. Peltier effect was discovered in 1834 by Jean-Charles Peltier. When electrical current is forced to flow through circuit of two conductors, one contact gives out heat, while another absorbs heat. These two physical effects have become the basis for thermoelectric converters. For a long time, their practical application was limited by the use of simple thermoelectric sources for research and metal thermocouples for temperature measurement. The situation changed, when Abram F. Ioffe suggested to use semiconductors instead of metals. Based on PbS and ZnSb compounds, generator for vacuum tube radios was developed.

In the early 1950s, projects on creation of thermoelectric coolers started, and new effective materials based on compounds $(\text{Bi,Sb})_2\text{Te}_3$ were discovered. Alloys, based on these compounds, are still the basic materials for thermoelectric refrigeration units. In the 1950–1960s, the complete elementary theory of thermoelectric conversion was created [3–5]. It was shown, that efficiency is determined by parameter $ZT = T \frac{\alpha^2 \sigma}{\kappa}$, where T , α , σ and κ are absolute temperature, Seebeck coefficient (or thermopower), electrical and thermal conductivity, respectively. Almost all thermoelectric materials currently used in the industry were discovered, technology for their production was developed: synthesis, crystal growth, metal-ceramic technology (Figure 1) [6].

Design and production technology of multi-element assembly of thermocouples, which are called thermoelectric (TE) cells or modules, have been developed. These modules may consist of one or more stages (cascade module); they are used to create different variants of thermoelectric coolers (TEC) and thermoelectric generators (TEG).

After relatively rapid development in years 1950–1960s, further improving of thermoelectric parameters and TE devices progressed more slowly.

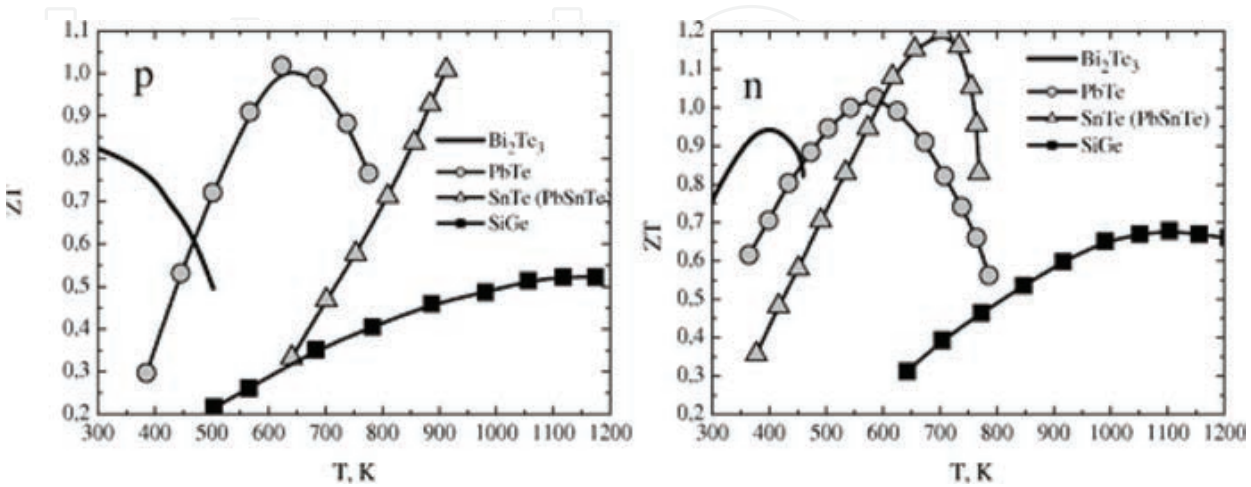


Figure 1. ZT dependence on temperature for the main thermoelectric semiconductor materials according to data of the 1960s: left side is p-type materials; right side is n-type materials.

For a long time, the maximum value of dimensionless parameter ZT does not exceed the value of 1. Areas of application of thermoelectric energy conversion techniques have been largely limited to special applications, such as power sources for spacecraft and military applications, where cost is not a major limiting factor.

In the 1980s, mass application of TE cooling for variety of purposes had started, and the market for thermoelectric cooling continues to expand today. In general, we can say, that method of thermoelectric conversion definitively established itself as one of the high-end technologies, especially for cooling purposes. This is due to its technical advantages. However, its wider application is constrained by insufficiently high efficiency of thermoelectric conversion of modern thermoelectric materials, that make the method economically ineffective. Therefore, the ultimate goal of basic research in physics and chemistry of thermoelectric materials is the development of more efficient thermoelectric materials for TEC and TEG. In view of this problem, precise and reliable measurement of thermoelectric properties (thermoelectric power, electrical and thermal conductivity) of new TE materials plays important role. These measurements must satisfy a number of requirements. Naturally, measurement results must be reliable and sufficiently accurate, measurements must be performed over a wide range of temperatures comparable with a typical range of applications. Despite the relative simplicity of fundamental measuring methods of thermoelectric properties, their practical implementation, accounting of above requirements, is a difficult task. For example, requirements for measurement accuracy are determined by the minimum of practically meaningful change of ZT parameter, which is about 10%. In order to reliably detect such small change of this parameter, measurement accuracy of thermoelectric coefficients α , σ , and κ must be not worse than 3%.

2. Thermoelectric coefficients and principles of experimental determination

2.1. Electrical conductivity

Electrical resistivity ρ , or conductivity $\sigma = \frac{1}{\rho}$, which is inverse value, determines electrical current density \mathbf{j} in conductor, when external electric field \mathbf{E} is applied: $\mathbf{j} = \sigma \mathbf{E}$ (Ohm's law). Coefficient σ does not depend on current value. In general, σ is a second rank tensor, the number of independent components of this tensor depends on the sample material crystallographic symmetry. For crystals with cubic symmetry, tensor σ has only diagonal components, and they are all identical. Thus, it degenerates into scalar in this case. Detailed information on tensor structure for crystal lattice of different symmetry can be found in [7].

Figure 2 shows electrical scheme for measuring electrical conductivity. When electrical current I is forced through the uniform conductor under isothermal conditions, an electric field arises. The sample electrical resistance R can be found from potential difference ΔV between two points on the sample surface and electrical current magnitude: $R = \frac{\Delta V}{I}$. Resistance R depends on parameters of the sample material and its geometrical dimensions: $R = \frac{1}{\sigma} \times \frac{l}{a \times b}$, where l , a , b is distance between potential probes, the sample's width and thickness, respectively. Thus,

electrical conductivity σ of the sample material can be determined from measured values: its resistance R and geometrical parameters l , a , and b :

$$\sigma = \frac{1}{R} \times \frac{l}{a \times b}. \tag{1}$$

It should be noted, that geometric parameters do not necessarily coincide with dimensions of the sample. Electrical conductivity value is always positive, in linear approximation it does not depend on electric field (or magnitude of electric current), but depends on temperature. Depending on type of material, electrical conductivity value changes over very wide range. For metals at room temperature, σ is in the range of 10^6 – 10^4 S cm⁻¹, and for good insulators, it falls to 10^{-20} S cm⁻¹. Electrical conductivity of typical conductor at room temperature or above is inversely proportional to temperature and has finite value as temperature approaches absolute zero 0 K (**Figure 3a**). Electrical conductivity of insulators increases exponentially with increasing temperature and vanishes at low temperatures (**Figure 3b**).

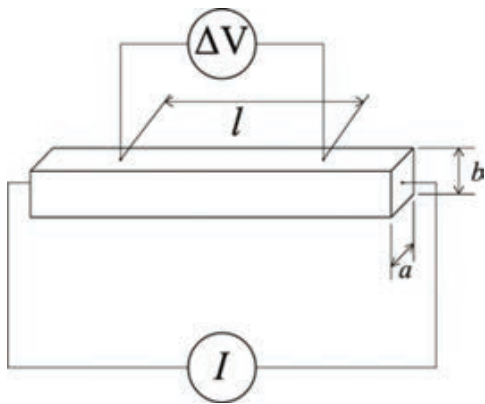


Figure 2. Scheme of electric circuit for measuring electrical conductivity value.

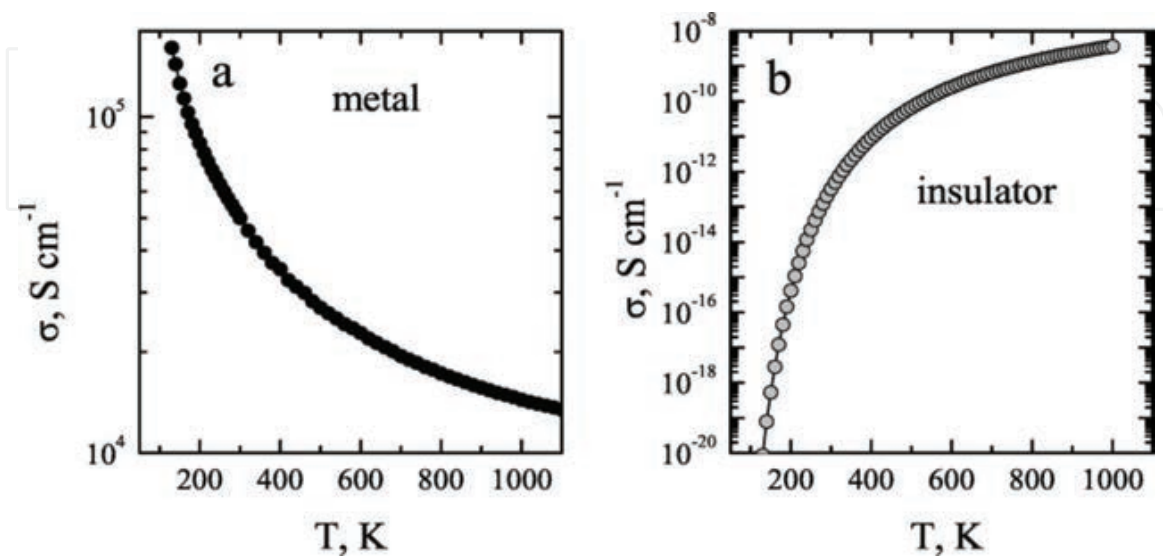


Figure 3. Temperature dependence of electrical conductivity σ of metal (a) and insulator (b).

2.2. Thermoelectric effects

Seebeck effect is occurrence of electromotive force in conductor, which has temperature gradient inside. It can be observed in a simple circuit consisting of two different conductors (x and l), when contacts of these conductors have different temperatures (**Figure 4**). Under these conditions, there will be a potential difference in a circuit: $\Delta V \propto \alpha_{xl}(T_2 - T_1)$, where $T_2 - T_1$ is a temperature difference between contacts and coefficient α is known as Seebeck coefficient or thermoelectric power. Seebeck coefficient is formally defined as follows: $E = \alpha \nabla T$, here E – electric field induced in conductor in the presence of temperature gradient ∇T . Seebeck coefficient α is a second rank tensor. In contrast to electrical conductivity, Seebeck coefficient can be either positive or negative. Potential difference measured by voltmeter in the circuit shown in **Figure 4**, $\Delta V = \varphi_2 - \varphi_1$, where φ_2 and φ_1 are input voltmeter potentials "1" and "2" at the same

temperature T_0 , equals to $\Delta V = \varphi_2 - \varphi_1 = \int_1^2 \nabla \varphi dl$.

Since $\nabla \varphi = -E$, then: $\Delta V = \int_1^2 -E dl = - \int_1^2 \alpha \nabla T dl$.

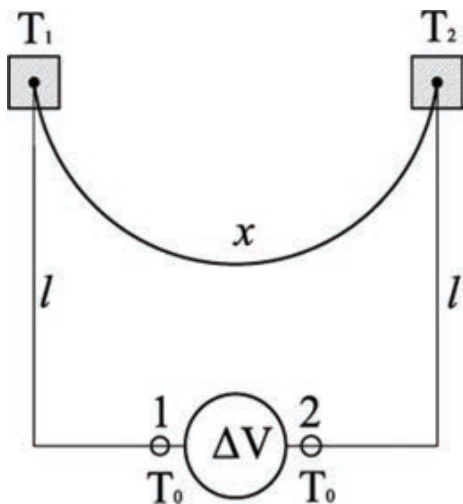


Figure 4. Thermoelectric circuit consisting of two conductors connected in series. Contacts of conductors are maintained at temperatures T_1 and T_2 .

The circuit shown in **Figure 4** consists of two different conductors, x ("sample") and l (wires connecting the sample with voltmeter). We assume, that both conductors are uniform. Seebeck coefficient of the sample and wires are denoted as α_x and α_l , respectively. For homogeneous and isotropic conductors, coefficient α is independent on position along the wire and direction of temperature gradient, but usually it depends on temperature. Therefore:

$$\Delta V = - \int_1^{T_1} \alpha_l \nabla T dl - \int_{T_1}^{T_2} \alpha_x \nabla T dl - \int_{T_2}^2 \alpha_l \nabla T dl \tag{2}$$

or

$$\Delta V = -\int_{T_0}^{T_1} \alpha_l dT + \int_{T_0}^{T_1} \alpha_l dT - \int_{T_1}^{T_2} \alpha_x dT + \int_{T_1}^{T_2} \alpha_l dT = -\int_{T_1}^{T_2} (\alpha_x - \alpha_l) dT. \quad (3)$$

When temperature difference $T_2 - T_1$ is small compared to average temperature $(T_2 + T_1)/2$, then:

$$\Delta V = -(T_2 - T_1) \times (\alpha_x - \alpha_l). \quad (4)$$

Hence, experimentally measured potential difference is proportional to temperature difference between the sample and probe contacts and Seebeck coefficient difference of the sample material and probes. It means, that in this kind of experiment only difference $\alpha_x - \alpha_l$ can be measured, and it is called relative thermoelectric power of "x" and "l" conductors α_{xl} . In order to determine absolute thermopower of the sample α_x , it is necessary to know thermopower of probe α_l (usually called as reference electrode probe). The magnitude of thermopower of metals ranges from $\pm 10^{-6}$ to $\pm 5 \times 10^{-5}$ V/K (at room temperature), while thermopower of thermoelectric semiconductors can reach $\pm 10^{-3}$ V/K.

Peltier effect can be observed in a similar circuit by replacing voltmeter to current source. When electrical current flows through the circuit, then at one contact, heat is emitted and at another heat is absorbed. Quantity of heat (Q) emitted or absorbed per unit time at contact of two materials is given by formula: $Q = \Pi_{lx} \times I$, here Π_{lx} – Peltier coefficient of materials l and x , I – current flowing through the contacts. Similar to thermopower, Peltier coefficient of each material can be determined: $\Pi_{lx} = \Pi_l - \Pi_x$. Thermopower and Peltier coefficient are interrelated by Thompson relation [8, 9]:

$$\Pi = T \times \alpha. \quad (5)$$

Another important thermoelectric effect is Thompson effect. When electrical current passes through homogeneous conductor in the presence of temperature gradient, then some heat energy is released or absorbed depending on mutual orientation of current and temperature gradient. In contrast to Joule heat, in this effect, heat can be emitted, leading to additional heating of conductor or absorbed, leading to cooling. When electrical current with density j flows through conductor, then quantity of heat (q), emitted in unit volume of conductor per unit time, equals to [8, 9]: $q = -\tau_T \times j \times \nabla T$. In contrast to Seebeck and Peltier coefficients, Thompson coefficient τ_T can be measured for individual conductor. Thompson coefficient is interrelated to two other thermoelectric coefficients by second Thompson relation [8, 9]:

$$\tau_T = T \frac{d\alpha}{dT}. \quad (6)$$

This important relation allows to determine thermopower:

$$\alpha(T) = \int_0^T \frac{\tau_T}{T} dT \quad (7)$$

and to build the *absolute thermoelectric scale*, which we will discuss further.

3. Measurement principles

3.1. Electrical conductivity

If the sample is homogeneous (electrical conductivity is the same everywhere inside the sample), then under uniform electrical current distribution inside the sample, electrical conductivity of the material can be determined by formula (1) on the base of experimentally determined values R , l , a and b . In conductivity measurements, some heat energy is always generated in the sample volume due to Joule heating. Amount of heat generated in unit volume of the sample is determined by Joule-Lenz's law: $q_j = j \times E = j^2 \times \rho$. This heat energy can affect the accuracy of conductivity measurement, changing sample temperature, and inducing thermoelectric contribution to measured potential difference (ΔV). In order to reduce influence of Joule heat on conductivity measurement, one has to use lower current density and provide good thermal contact of the sample with environment.

Eq. (1) is applicable, if the sample is in isothermal conditions. In actual practice, this condition is almost never fulfilled. Moreover, electrical conductivity is often measured simultaneously with thermoelectric coefficient, which requires temperature gradient. Under these conditions, potential difference, measured in the circuit shown in **Figure 2**, will include two components: $\Delta V = R \times I + \alpha_{lx} \Delta T = \frac{1}{\sigma} \times \frac{l}{a \times b} I + \alpha_{lx} \Delta T$, where α_{lx} and ΔT – thermopower of the sample and temperature difference between potential probes, respectively. For thermoelectric materials, both contributions can be of the same order of magnitude. To eliminate the influence of thermal gradient in the sample on electrical conductivity, two methods are used:

1. DC measurements: two measurements of ΔV must be performed. One is carried out with electrical current flow, and another is carried out either without current flow or with current flow in opposite direction: $\Delta V^- = -R \times I + \alpha_{lx} \Delta T$, subtracting the results of these measurements, we get: $\Delta V_R = \Delta V - \Delta V^- = 2R \times I$, σ now can be found from measured R . It was assumed here, that thermoelectric contribution to ΔV does not depend on electrical current. In fact, this is not true, and in measurement of σ with direct current, dependence of thermoelectric contribution on electrical current should be considered. We will discuss this issue in the analysis of electrical conductivity measurement errors.
2. AC measurements: typically, AC current with frequency from several tens to thousands of hertz is used. Thus, due to thermal inertia, thermopower contribution does not contain frequency-dependent components, and signal, proportional to electrical resistance, can be measured at AC current frequency. However, it should be remembered, that for materials with high magnetic permeability, such as ferromagnets, thickness of skin layer, even at low current frequencies, may be equal to unit or even fractions of millimeter. If thickness of skin layer is comparable to or less than thickness of the sample, then determination of σ may contain significant errors.

In the following sections, different methods of measurement σ are described. To exclude the contribution of thermoelectric effects in all of them, AC or DC measurements may be used.

3.1.1. Classic measurement scheme

Classic measurement scheme of electrical conductivity is presented in **Figure 5**. In this method, the sample should be prepared in the form of long thin and uniform wire with diameter d . Potential difference ΔV_{12} , is measured between points "1" and "2" separated by distance " l ", when current I passes through the wire. Electrical conductivity is determined by formula:

$$\sigma = \frac{I}{\Delta V_{12}} \times \frac{4l}{\pi d^2}.$$

The wire must be placed into electrically non-conductive medium having sufficiently high thermal conductivity, which absorbs heat generated in the sample, and minimizes temperature gradient in it. When the sample is prepared in the form of long thin wire, then low measuring current density j can be used. In this case, along with reducing quantity of Joule heat, it is possible to maintain large enough potential difference ΔV_{12} by increasing distance l between potential probes, which improves measurements accuracy. However, this method is rarely used in practice.

First, long wire samples are inconvenient, when measurements are performed in chambers with limited volume, such as cryostat for measurements at low temperatures or vacuum chamber at high temperature measurements. Second, majority of materials is difficult or impossible to prepare in the form of thin homogeneous wire. Therefore, usually, short samples are used in the form of cylinder or parallelepiped, thin plate or film. The accuracy of resistance measurement of such samples is lower than in classic configuration.

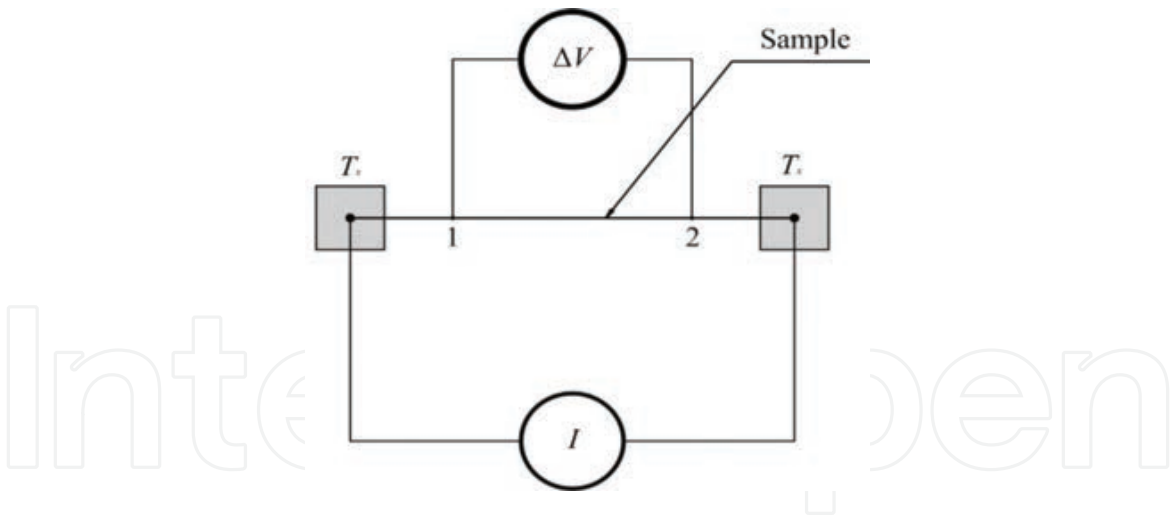


Figure 5. Classic method of electrical resistance measurement. The sample is prepared as a homogeneous wire, contacts with current leads are maintained at temperature T_x .

3.1.2. Samples of regular geometric shape

Figure 6 shows the scheme for measuring electrical conductivity of short samples with a regular geometric shape. The sample for such measurements must have simple geometric shape allowing accurate determination of electrical current density and potential gradient in the sample, which have to be uniform. Current contacts should provide uniform current distribution in the sample.

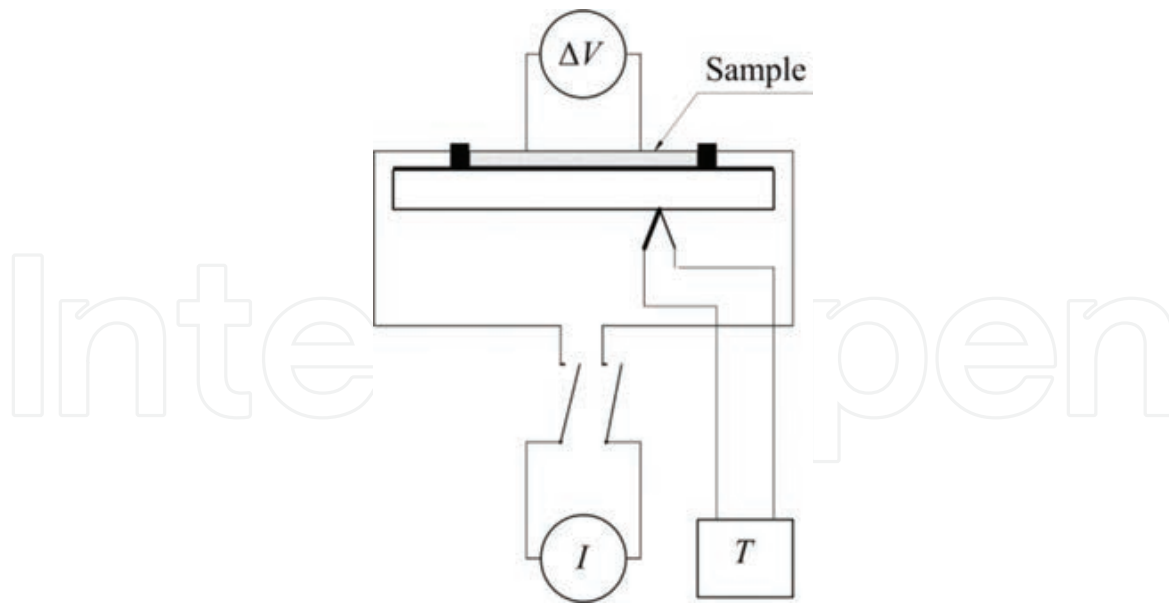


Figure 6. Resistance measuring scheme of short samples.

Since electrical conductivity depends on temperature, then, during measuring it, temperature of the sample must be set and determine precisely. Electrical conductivity is determined by formula: $\sigma = \frac{I}{\Delta V} \times \frac{l}{A}$, here, A is cross-section area of the sample in plane, perpendicular to electric current direction.

3.1.3. Four-probe method of electrical resistivity measurement

In both schemes of measuring electrical conductivity σ , described above, geometric parameters coincide with cross-section of the sample $A = a \times b$ and distance between potential probes (l). There are modifications of these schemes, in which geometric parameters do not match sizes of the sample. They include four-probe method [10–12] and van der Pauw method [12, 13]. Note that all methods of measuring electrical conductivity described here are essentially four-probe methods in the sense, that potential probes are separated from electrical current leads. However, this term is also used as the name of specific embodiment of methods for measuring electrical conductivity. In the most common variant of this method, all four electrodes are arranged along straight line on flat surface of the sample (**Figure 7**). If electrodes are arranged symmetrically, and thickness (d) and minimum distance from electrodes to the edge of the sample is much greater than distance between electrodes (l) (semi-infinite space approximation), then electrical conductivity is determined by simple expression [10–12]: $\sigma = \frac{2I}{\pi \times \Delta V} \times \left[\frac{1}{S-l} - \frac{1}{S+l} \right]$, here I – electrical current flowing through the sample, S – distance between outermost electrodes (current contacts), l – distance between potential probes. Practical criterion of applicability of this approximation is $S/d < 5$. If electrodes are arranged at the same distance from each other, that is, $S = 3l$, we get $\sigma = \frac{I}{2\pi \times l \times \Delta V}$. In another limit case $d \ll l$, expression for determining electrical conductivity takes the form [10–12]: $\sigma = \frac{I}{\pi \cdot d \cdot \Delta V} \ln\left(\frac{S+l}{S-l}\right)$.

If $S = 3l$, we obtain: $\sigma = \frac{I}{\pi \times d \times \Delta V} \ln 2$. This formula is applicable for $S/d > 5$.

For arbitrary thickness of the sample, expression for σ is as follows [10–12]:

$$\sigma = \frac{2I}{\pi \times \Delta V} \left\{ \frac{1}{S-l} - \frac{1}{S+l} + 2 \times \sum_{n=1}^{\infty} \left[\frac{1}{\sqrt{(S-l)^2 + (4nd)^2}} - \frac{1}{\sqrt{(S+l)^2 + (4nd)^2}} \right] \right\}. \tag{8}$$

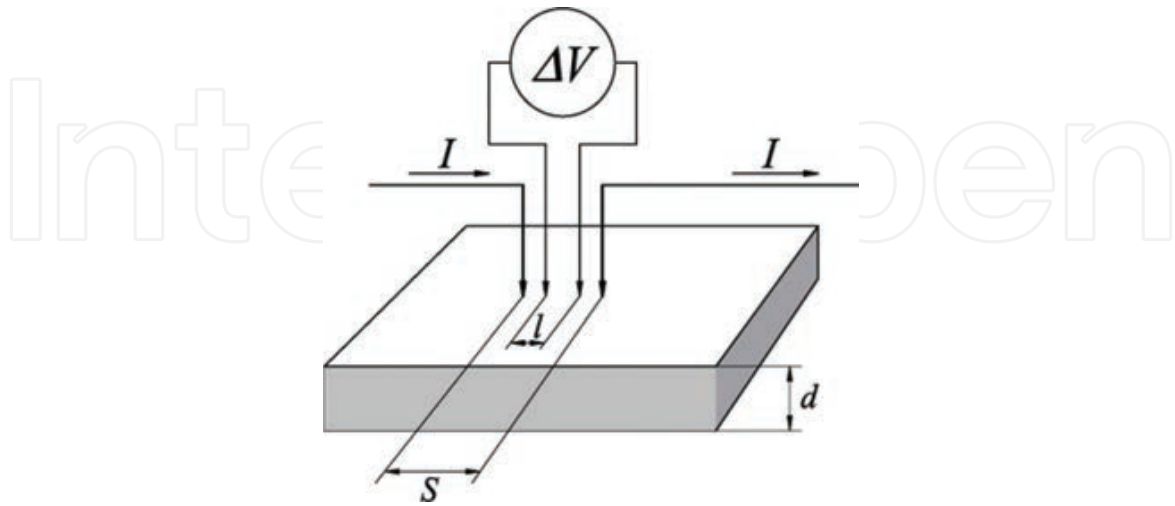


Figure 7. Four-probe method to measure electrical conductivity.

Four-probe method is a convenient way to determine quickly and accurately electrical conductivity and does not require preparation of samples with regular geometric shape. It requires one flat surface only. However, the sample surface area needs to be large enough to satisfy condition $L_{min} > 10S$ for any distance (L) from measuring probes to the edge of the sample. Otherwise, measured potential difference ΔV will depend on type and shape of the sample boundaries.

3.1.4. Van der Pauw method

Van der Pauw method is applied for measuring electrical conductivity of the samples with irregular shape [12–15]. To measure electrical conductivity by van der Pauw method, it is necessary to form four contacts at arbitrary points A, B, C and D on the edge of flat sample (Figure 8).

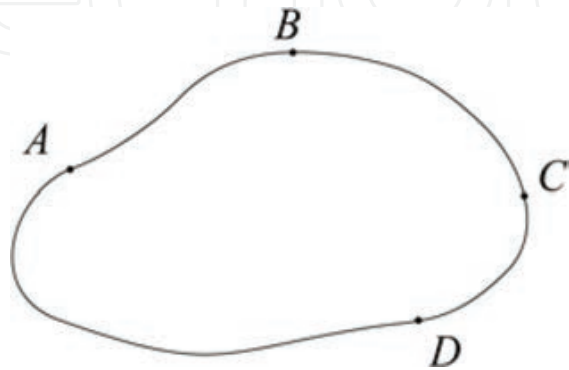


Figure 8. Schematic view of arbitrary shape flat plate (sample) with four contacts A, B, C, D for measuring electrical conductivity by van der Pauw method.

By passing electrical current I_{AB} between contacts A and B, one can determine resistance $R_{AB,CD}$ as follows: $R_{AB,CD} = \frac{\Delta V_{CD}}{I_{AB}}$, where ΔV_{CD} is potential difference between contacts C and D. Similarly: $R_{BC,DA} = \frac{\Delta V_{DA}}{I_{BC}}$.

If the following conditions are fulfilled:

- sample is parallel-sided free form plate,
- sample does not have isolated holes,
- sample is homogeneous (σ is the same everywhere) and isotropic,
- all four contacts are located on the edge of the sample and contact area is negligible compared to dimensions of the sample,

then $R_{AB,CD}$ and $R_{BC,DA}$ satisfy to equation [13, 14]:

$$\exp(-\pi d \sigma R_{AB,CD}) + \exp(-\pi d \sigma R_{BC,DA}) = 1, \quad (9)$$

where d is thickness of the sample plate. Since resistances $R_{AB,CD}$, $R_{BC,DA}$ and d are known, σ is the only one unknown quantity in Eq. (9), and it can be found by solving this equation.

Solution of Eq. (9) can be written in the form [13]:

$$\sigma = \frac{2 \ln 2}{\pi d (R_{AB,CD} + R_{BC,DA})} \frac{1}{f\left(\frac{R_{AB,CD}}{R_{BC,DA}}\right)}, \quad (10)$$

where f is function depending only on the ratio $\frac{R_{AB,CD}}{R_{BC,DA}}$. Graph of this function is shown in **Figure 9**.

When $\frac{R_{AB,CD}}{R_{BC,DA}} \approx 1$, then f can be approximated by expression:

$$f \approx 1 - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^2 \frac{\ln 2}{2} - \left(\frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right)^4 \left[\frac{(\ln 2)^2}{4} - \frac{(\ln 2)^3}{12} \right]. \quad (11)$$

Situation is considerably simplified, if the sample has symmetry axis [14]. Assume that contacts A and C are located on the symmetry axis and contacts B and D are placed symmetrically relative to this axis (**Figure 10**). Then $R_{AB,CD} = R_{AD,CB}$. According to the theorem of reciprocity for passive four poles [16], we have $R_{AD,CB} = R_{CB,AD} = R_{BC,DA}$, and it follows from Eq. (9):

$$\sigma = \frac{\ln 2}{\pi d R_{AB,CD}}.$$

3.2. Thermopower

Figure 11 shows principle of measuring thermoelectric power. There are two direct methods of thermopower measurement: the integral method is historically the first and is conceptually simpler (Eq. (3)); and the differential method, which is practically the most used (Eq. (4)).

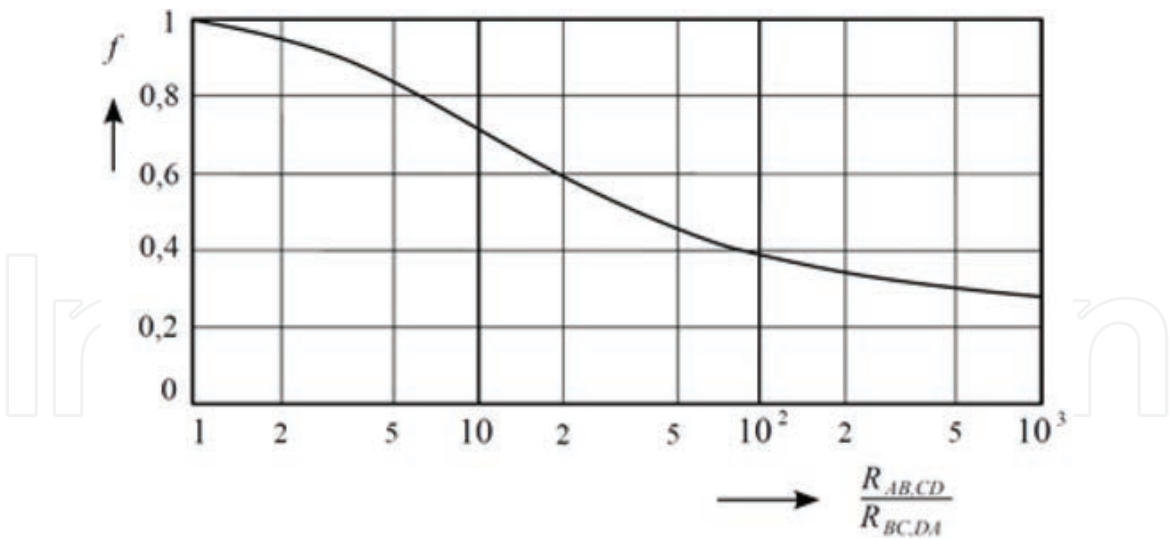


Figure 9. Dependence of function f on ratio $\frac{R_{AB,CD}}{R_{BC,DA}}$ [14].

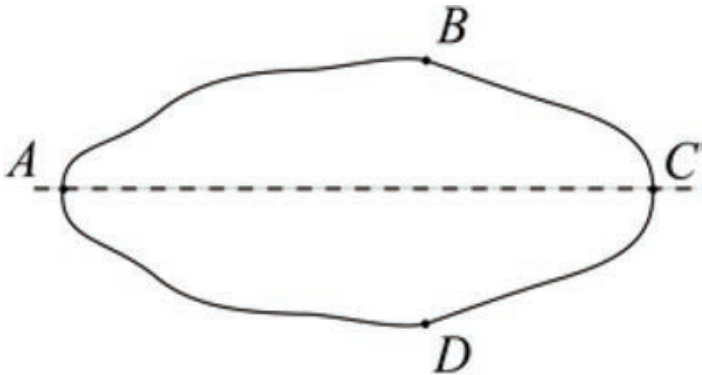


Figure 10. Contacts configuration for the sample having axis of symmetry.

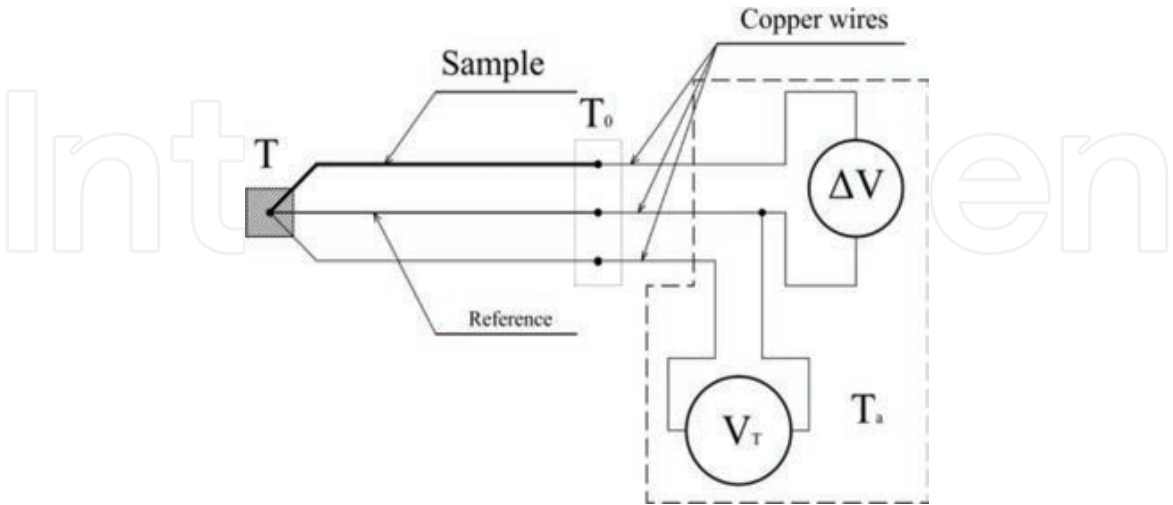


Figure 11. Scheme of integral method for thermopower measurements: voltage of thermocouple, consisting of sample and reference wires, is measured as function of thermocouple junction temperature T by voltmeter ΔV . Temperature is measured with help of another thermocouple by voltmeter V_T . Junctions of the sample, reference and thermocouple wires with copper wires, connected to voltmeters are kept at fixed temperature T_0 . T_a is ambient temperature.

3.2.1. Integral method

Figure 11 shows electrical circuit for measuring thermopower by integral method. Voltage of thermocouple, consisting of the sample and reference electrode wires, is measured as function

of temperature: $\Delta V = - \int_{T_0}^T (\alpha_x - \alpha_l) dT$. Hence, $\alpha_x(T) - \alpha_l(T) = - \frac{d\Delta V}{dT}$.

In this method, besides ΔV , it is necessary to measure temperature T of contacts of material under study and reference electrode. This can be done by using additional electrode with known thermopower, which forms thermocouple with reference electrode. Note, that serious disadvantage of this method is that samples must be prepared in the form of homogeneous wires. But, many materials, which are considered as prospective thermoelectrics, are very difficult or impossible to prepare in form of wire. Therefore, integral method of thermopower measurement is used very rarely now.

3.2.2. Differential method

In contrast to integral method, differential one is designed for measuring thermopower of short samples of any shape, including thin films. Therefore, the vast majority of thermopower measurements have been performed by this method. **Figure 12** shows a scheme of differential method. Temperature difference between two points on the sample is measured with two thermocouples (or other temperature sensors), and thermopower signal ΔV can be measured by the same branches of thermocouples. Using Eq. (4), expression for determining absolute thermopower of the sample can be written as follows:

$$\alpha_x = - \frac{\Delta V}{\Delta T} + \alpha_l. \quad (12)$$

3.3. Absolute thermoelectric scale

In order to determine absolute thermopower of the material α_x , it is necessary to know absolute thermopower of reference electrode α_l . This is a key point in thermopower measurements. There is no direct method for measuring absolute thermoelectric power. Determination of absolute thermopower is based on two physical phenomena:

Thomson's relationship between Seebeck (α) and Thomson coefficients (τ_T) [9].

Property of superconductors: electric field $E = 0$ inside superconductor. Hence, it follows, that thermopower of superconductor is zero.

Based on these two phenomena, absolute thermopower of some materials was determined. Currently, lead, copper, and platinum are the main materials of reference electrodes. Dataset of absolute thermoelectric power of these metals establish *absolute thermoelectric scale*. This scale is based on experimental data of Thomson coefficient τ_T . Absolute thermoelectric power can be calculated according to second Thompson relation (Eqs. (6) and (7)).

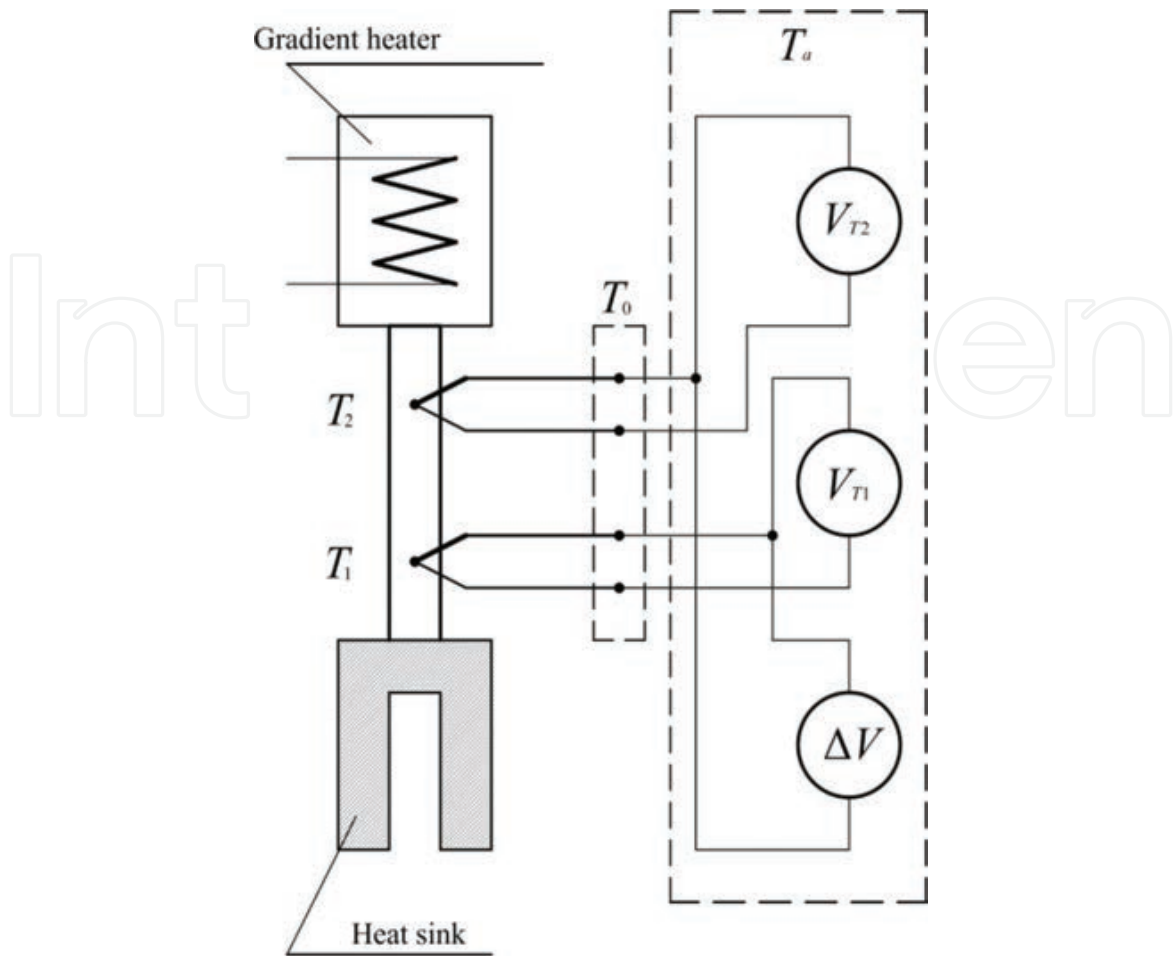


Figure 12. Scheme of differential method for thermopower measurements. Heat flow generated by gradient heater passes through the sample and creates temperature gradient in it. Temperature difference between two points on surface of the sample is measured using thermocouples. The same thermocouple branches are used to measure potential difference between points on the sample.

However, in practice, we cannot determine by Eq. (7) absolute thermopower of studied material, since it requires information about Thomson coefficient in temperature range from absolute zero to T , which is fundamentally impossible. This problem can be solved with superconducting materials. In superconducting state, that is, at $T < T_c$, thermopower $\alpha = 0$. Hence, for such materials, it is sufficient to know Thomson coefficient value at temperature $T > T_c$ only.

Nyström [17] created first absolute thermoelectric scale, which was based on his measurements of Thomson coefficient of copper in temperature range from 723 to 1023 K and Borelius's low-temperature data [18, 19]. Using data of absolute thermoelectric power of copper, Nyström determined absolute thermoelectric power of platinum. Later, Rudnitskii [20] has extrapolated Nyström's data for platinum up to 1473 K. Cusack and Kendall [21] have processed Thompson coefficient data and calculated absolute thermoelectric power of number of metals in wide temperature range, including platinum up to 2000 K, and molybdenum and tungsten up to 2400 K (using Thomson coefficient data obtained by Lander [22]). The most accurate thermoelectric scale was created by Roberts, who carried out

measurements of Thomson coefficient of lead, copper, and platinum [23–25]. Thomson coefficient was measured for lead in temperature range from 7 K (i.e., from superconducting transition temperature) to 600 K (up to nearly melting temperature). Thomson coefficient of copper was measured up to 873 K, and for platinum and tungsten up to 1600 K. On the basis of these data, thermoelectric scale overlapping temperature range between 0 and 1600 K was created. According to Roberts estimations, his thermoelectric scale has error not more than $\pm 0.01 \text{ }\mu\text{V/K}$ at room temperature, $\pm 0.02 \text{ }\mu\text{V/K}$ at 600 K, $\pm 0.05 \text{ }\mu\text{V/K}$ at 900 K, and $\pm 0.2 \text{ }\mu\text{V/K}$ at 1600 K. At higher temperatures, absolute thermopower data is much less precise. Accuracy of the data at 2000 K is about $\pm 2 \text{ }\mu\text{V/K}$. The results of these studies are summarized in **Table 1**.

T (K)	α_{Pb} ($\mu\text{V/K}$) Roberts [23, 24]	α_{Cu} ($\mu\text{V/K}$) Roberts [24]	α_{Pt} ($\mu\text{V/K}$) Roberts [25]	α_{Pt} ($\mu\text{V/K}$) Rudnitskii [20]
80	−0.544			
120	−0.631			
160	−0.734			
200	−0.834			
250	−0.948			
300	−1.05	1.94	−4.92	−4.2
350	−1.16	2.22	−6.33	−2.87
400	−1.28	2.5	−7.53	−7.33
450	−1.41	2.78	−8.59	−8.61
500	−1.56	3.07	−9.53	−9.68
550	−1.73	3.35	−10.41	−10.54
600		3.62	−11.22	−11.33
650		3.89	−11.98	−12.05
700		4.16	−12.71	−12.78
750		4.43	−13.42	−13.50
800		4.7	−14.14	−14.23
900		5.23	−15.66	−15.68
1000			−17.21	−17.13
1100			−18.77	−18.58
1200			−20.29	−20.03
1300			−21.78	−21.45
1400			−23.18	−22.93
1500			−24.49	
1600			−25.67	

Table 1. Thermopower of lead (α_{Pb}), copper (α_{Cu}), and platinum (α_{Pt}).

In practice, for measuring thermopower at high temperature (above 100 K) are used thermocouples copper-constantan and platinum-platinum/rhodium and reference electrode of platinum or copper, respectively. For both, platinum and copper, the absolute thermopower was accurately determined by Roberts only above room temperature. Therefore, it was necessary to expand temperature range of accurate determination of absolute thermopower of these metals to lower temperature region. Absolute thermoelectric power of platinum in temperature range from 25 to 1600 K was determined in [26] using Roberts's data and Moore's and Grave's low temperature data [27], which were adjusted using Roberts's data for lead [23], so that, corrected data are consistent with Roberts' high temperature data. These data and experimental results for platinum are shown in **Figure 13** and summarized in **Table 1** [26].

By using combined experimental data obtained in temperature range 70–1500 K, thermopower of platinum can be described by empirical interpolation formula $\alpha_{Pt}(T)$:

$$\alpha_{Pt}(T) = 0.186T \left[\exp \left(-\frac{T}{88} \right) - 0.0786 + \frac{0.43}{1 + \left(\frac{T}{84.3} \right)^4} \right] - 2.57. \tag{13}$$

This function and its deviation from experimental points are shown in **Figure 13**.

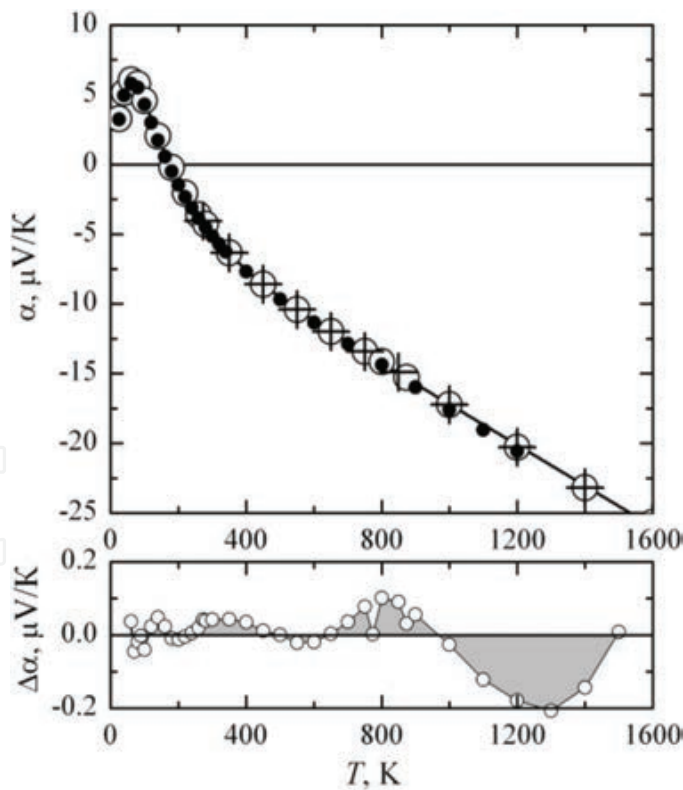


Figure 13. The top panel shows absolute thermoelectric power of platinum: • – Moore's data [27]; + – Roberts's data [24, 25]; ○ – combined data (not all data points are depicted). Solid line shows interpolation function. The bottom panel presents deviation of interpolation function from experimental data $\Delta\alpha = \alpha_{\text{exp}} - \alpha_{Pt}(T)$.

Absolute thermoelectric power of copper was determined in [26] using Roberts' data for temperature range 273–900 K [24], and at temperatures below 273 K using Cusack's and Kendall's results [21]. Small correction was introduced in the data, so that, this low-temperature dependence smoothly joints with Roberts' high-temperature data. Adjusted and original experimental data and empirical interpolation formula α_{Cu} for temperature range 70–1000 K are shown in **Figure 14** and **Table 1** [26]. Interpolation function α_{Cu} is given by:

$$\alpha_{Cu}(T) = 0.041\ T \left[\exp \left(-\frac{T}{93} \right) - 0.123 + \frac{0.442}{1 + \left(\frac{T}{172.4} \right)^3} \right] + 0.804.$$

(14)

The error of this practical thermoelectric scale (considering the interpolation error) is estimated as follows [26]:

In temperature range 70–900 K: $\pm 0.1\ \mu\text{V/K}$ and 1000–1500 K: $\pm 0.5\ \mu\text{V/K}$.

In formulas (13) and (14), thermopower is expressed in $\mu\text{V/K}$, and temperature is expressed in Kelvin degree.

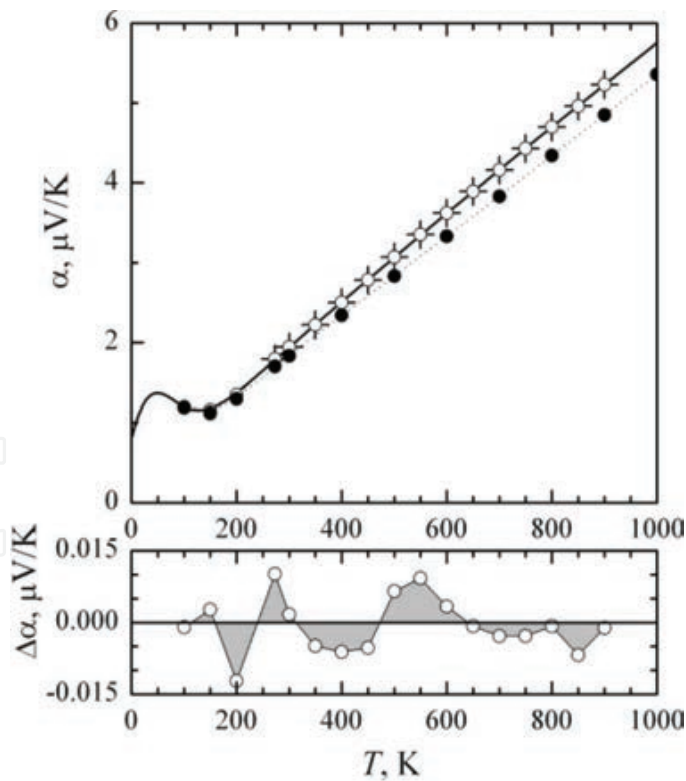


Figure 14. The top panel shows absolute thermoelectric power of copper: • – Cusack's data [21]; + – Roberts's data [24]; ○ – adjusted data. Solid line is interpolation function. The bottom panel shows deviation of interpolation function from experimental data $\Delta\alpha = \alpha_{\text{exp}} - \alpha_{Cu}(T)$.

4. Error analysis

4.1. Electrical conductivity

Errors in measurements of electrical conductivity can be divided into three categories. First, it is electrical signal measurement errors, that is, potential difference and current magnitude. Second, it is errors associated with shape of the sample and of measuring electrodes. And third, there are errors associated with change in temperature of the sample during measurement process.

The first kind of errors is common to all measurements of electrical signals and are not specific for measuring electron transport properties. When modern measuring equipment is used and proper organization of measuring system and procedure are applied, then these errors generally are not a factor limiting the accuracy of measurements. Possible exceptions are measurements of electrical conductivity of high pure metals at very low temperatures. However, these cases are not typical for high-temperature measurements of thermoelectric materials, and not analyzed here.

4.1.1. Errors associated with shape

Errors associated with sample's and electrode's shape are, perhaps, the main problem in most cases. When measuring conductivity, actual measured value is a total resistance of the sample between potential probes $R = \frac{\Delta V}{I}$. In order to obtain electrical conductivity of the sample, it is necessary to know cross-section of the sample (A) and distance between potential probes (l) $\sigma = \frac{1}{R} \times \frac{l}{A}$. There are four sources of errors associated with geometric factor. The easiest is inaccuracy in determining size and shape of the sample. Assume, that the sample has parallelepiped shape with typical dimensions $2 \times 2 \times 10 \text{ mm}^3$. In ordinary methods of sample machining and measurement of lengths, typical error of size determination is of the order 0.01 mm. This error includes distance measurement inaccuracy, and shape and surface imperfections of the sample as well. This error causes error of determining the section $\Delta A/A$ equals to 1%. The error of determining distance l , which includes both error in measurement of length and finite size of potential contact, is of the order 0.1 mm. Thus, total error in determining geometric factor is equal to $\frac{\Delta A}{A} + \frac{\Delta l}{l} = 0.02$, that is, 2%. It is accuracy limit of measuring resistance by four-probe method using bulk samples. Of course, accuracy can be improved by using a special high-precision technology for manufacturing of the sample and measuring its dimensions. However, these methods are not applicable for mass measurements.

A second important factor, determining accuracy of resistivity measurements, is electrical current distribution in the sample. Ideally, electrical current distribution in the sample must be uniform (**Figure 15a**). In this case, electrical current lines are parallel to axis of the sample and potential distribution on sample surface, where it can be measured, is the same as in the bulk. However, in most cases, point current contacts are used for measuring resistance and, in such case, current distribution is not uniform in the sample (**Figure 15b**).

As a result, potential distribution on surface of the sample may differ significantly from distribution in volume. To minimize this error, distance between the nearest current and potential

probes must be (for highly conductive samples) more, than the maximum transverse dimension of the sample. With increasing resistance of the sample material, this distance must be also increased. Potential probes must be arranged along electrical current lines. If potential probes are arranged along line directed at angle ψ with respect to current lines, then effective length is $l^* = l \cos \psi$. For small angles ψ , error can be expressed as follows: $\Delta l = |l - l^*| = l(1 - \cos \psi) \approx l \times \psi^2$ and $\frac{\Delta l}{l} = \psi^2$. The probe position error of 6° results in resistance error of 1%.

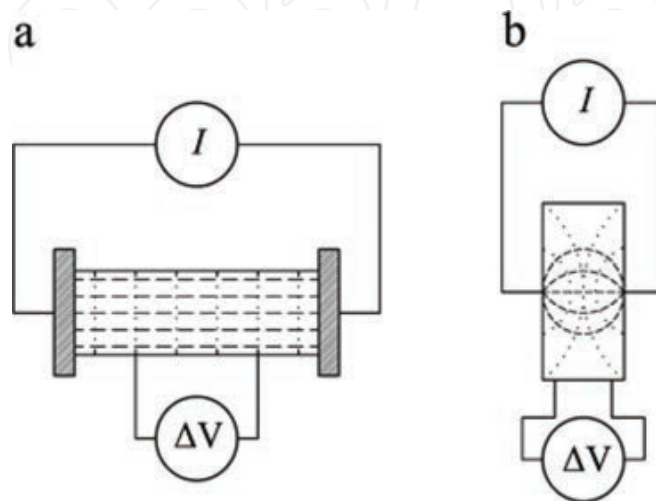


Figure 15. Errors associated with geometry of the sample and current leads. Dashed lines indicate electrical current flow; dotted lines represent equipotential surfaces: a. ideal current lead contacts-homogeneous current distribution; b. point current lead contacts-nonhomogeneous current distribution.

Errors related to mechanical imperfection of samples are the most common and bring the greatest trouble. This may be pores, cracks, non-uniformity in composition, and so on. There is no general recipe to minimize such errors. Errors associated with the presence of pores can be reduced in part by corrections proportional to deviation of actual density of the sample from theoretical, calculated on the basis of structural data. It should be noted, that geometrical factor leads also to errors in determining temperature coefficient of electrical conductivity $\frac{d\sigma}{dT}$.

4.1.2. Errors associated with changes in thermal regime of the sample during measurement

Two types of phenomena leading to such kind of errors can be distinguished: sample temperature changes due to Joule heating and changes of temperature distribution in the sample due to thermoelectric effects.

Since Joule heat released in the sample is equal to $I^2 R$, then measuring at lower current and improving heat transfer from sample to the environment can effectively solve the problem of temperature changes. More difficult task is to eliminate the influence of thermoelectric effects, namely, Peltier and Seebeck effects. This influence arises, when measurement of electrical conductivity is performed with direct current (DC), whereas in measurements of electrical conductivity with alternative current (AC), thermoelectric effects do not affect measurement accuracy.

Since the sample and connected to it electrical current leads represent nonuniform electrical circuit, Peltier heat will be released at one contact of current lead with the sample, while at another contact it will be absorbed. This will produce temperature difference across the sample. **Figure 16** shows time diagram of potential difference across the sample during measurement of resistance with taking into account Peltier effect. We assume, that in the initial state, when electrical current is turned off, there is no temperature gradient in the sample, so the potential difference $\Delta V_0 = 0$. Due to finite sample heat capacity, immediately after electrical current is switch-on, temperature of the contact is not changed and measured voltage is equal to $\Delta V^+ = R \times I^+$. However, due to Peltier effect, heat flow from one contact to another creates in the sample temperature gradient. Therefore, additional potential difference arises, so that the total potential difference between probes is $\Delta V^+ = R \times I^+ + \alpha \times \Delta T(t)$, here α is relative thermoelectric power of the pair “sample-potential probe,” ΔT is temperature difference between potential probes. This difference increases with time at rate depending on heat capacity of the system and rate of release and absorption of heat on the contacts due to Peltier effect.

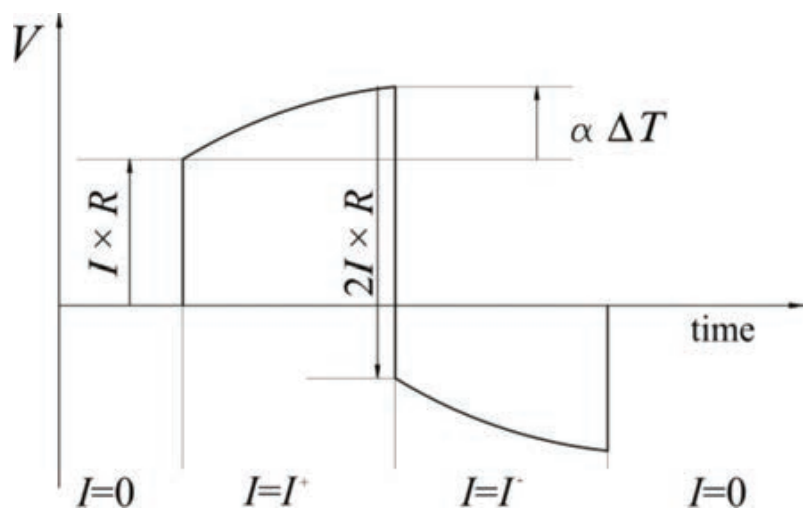


Figure 16. Timing diagram of potential difference across the sample, when measuring electrical conductivity with DC current.

ΔT is stabilized at level, which is determined by balance between rate of heat generation at the contacts, thermal conductivity of the sample and conditions of heat exchange between sample and the environment. To estimate the maximum value of the effect, we assume, that there is no heat exchange between sample and the environment. When electrical current with density j flows, then the amount of Peltier heat q_p , generated at contact between current lead and the sample, is equal to: $q_p = \Pi \times j$, where Π is Peltier coefficient of the pair “sample-current lead”. At stationary conditions and in the absence of heat exchange with the environment, whole heat flow passes through the sample due to thermal conductivity: $q = -\kappa \nabla T$, here κ is a thermal conductivity of the sample. The flow balance $q_p = -q$ determines temperature gradient: $\nabla T = \frac{\Pi \times I}{\kappa}$. The effect of this temperature gradient on conductivity measurement precision depends on ratio of voltage drop across the sample $\Delta V_\rho = I \times R = j \times A \times \rho \times \frac{l}{A} = j \times l \times \rho$, which occurs when electrical current passes, to potential difference related to temperature gradient $\Delta V_{thermo} = \alpha \times l \times \nabla T$:

$$\frac{\Delta V_{thermo}}{\Delta V_{\rho}} = \frac{\Pi \times j \times \alpha \times l}{\rho \times j \times \kappa \times l} = T \frac{\alpha^2 \sigma}{\kappa}. \quad (15)$$

In deriving the latter expression, Thompson relation (5) was used. As we can see, $\frac{\Delta V_{thermo}}{\Delta V_{\rho}}$ is determined by dimensionless figure of merit $ZT = T \frac{\alpha^2 \sigma}{\kappa}$. For good thermoelectric materials, this value can be of the order of unity. It is important, that error related to Peltier effect does not depend on direction or magnitude of electrical current or sample geometry. Therefore, it cannot be eliminated by changing these parameters of experiment. The error can be significantly reduced in two ways:

1. Proper design of the sample holder should provide good thermal contact between sample and environment, that assures absorption of heat released in the sample and provides uniform temperature distribution in the sample. Very effective is gas environment with high thermal conductivity. Taking into account all the properties, helium is the best environment.
2. The signals measurement must be properly organized. From **Figure 16**, it is clear, that measurement of voltage drop should be performed as soon as possible, immediately before and immediately after electrical current switch (on, off or change direction).

4.1.3. Measurement errors in four-probe method

When conditions of applicability of four-probe method are fulfilled, then errors of electrical conductivity measurements will be caused by inaccuracy of determining the distance between potential contacts and sample thickness. Distance between potential contacts is limited by conditions of method applicability, and it should be much less than linear dimensions of the sample. For typical sample having flat surface area $10 \times 10 \text{ mm}^2$, the distance between the contacts must be less than 1 mm. Typically, the diameter of contact area of potential probe is of order of 0.01 mm, therefore, the error in determining distance between contacts will be $\Delta l/l \geq 1\%$. The error in determining of average thickness of the sample is of the same order. Thus, accuracy of determining electrical conductivity with four-probe method will usually be at least 2%.

4.1.4. Error estimation: van der Pauw method

Measurement errors in van der Pauw method are associated with non-ideal contacts, that is, with their finite size and offset from the edge of the sample. Estimation of errors has been done for three typical cases of non-ideal contacts and is shown in **Figure 17** [14]. For simplicity, let us consider circle shape sample with diameter D , electrical contacts to which are arranged at equal distance from each other. Assume, that only one contact is imperfect. In practice, there are no ideal contacts. To the first approximation, the total error is the sum of errors on each contact. Advantage of van der Pauw method is applicability to samples of different (including irregular) forms, because in many cases test material is available in the form of small plates. Such samples do not require further processing and can be used for other purposes after van der Pauw measurement. However, in cases, where high measurement accuracy is required, the

samples of special form should be used [12]. They can be divided into two groups. The first group includes the samples having the shape of cloverleaf. Such form allows to increase the length of the border, so that imperfect contacts make negligible error in measurement results. The second group includes samples, having symmetrical shape and extended contacts, which respective correction functions have already been calculated for.

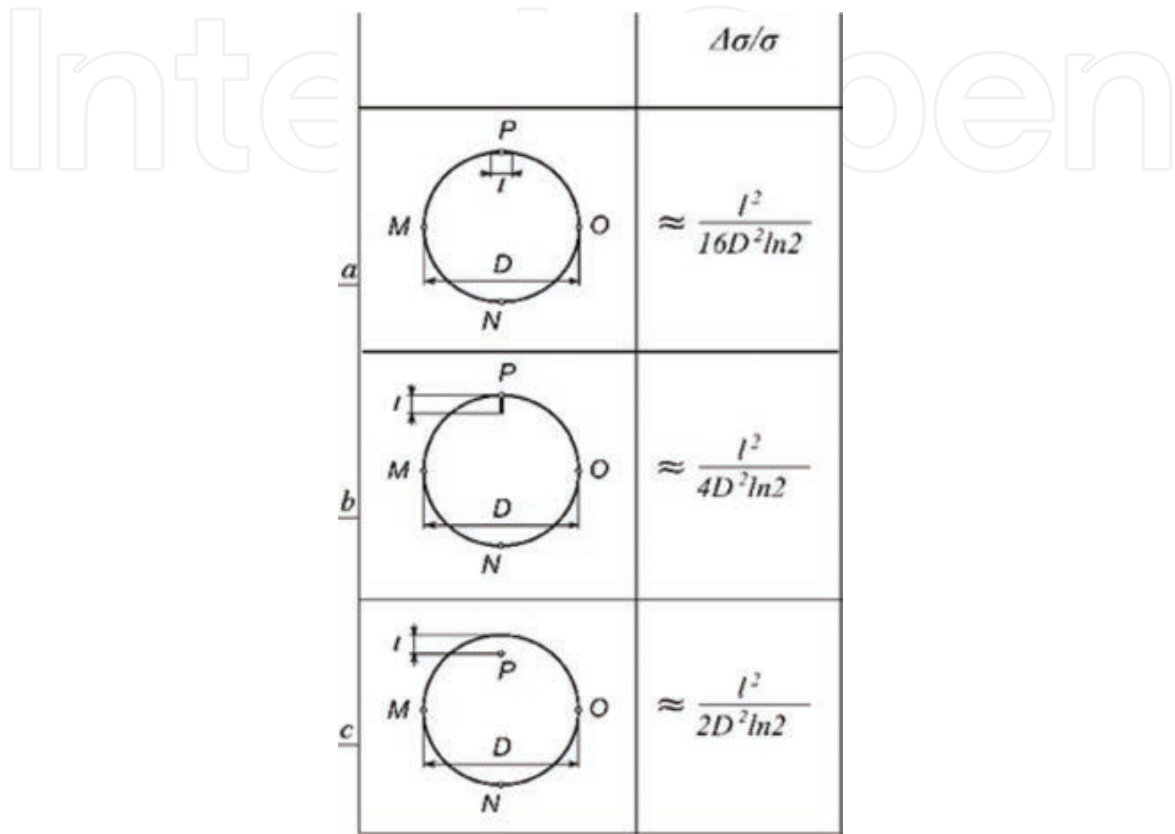


Figure 17. The relative errors $\Delta\sigma/\sigma$ when measuring electrical conductivity of circle shape sample [14]: a. One of contacts has length l along the edge of the sample; b. One of contacts has length l perpendicular to the edge of the sample; c. One of contacts is point contact located at distance l from the sample edge.

4.2. Measurement errors of thermopower

Measurement errors of thermopower by differential method are mainly related to incorrect determination of temperature difference ΔT . We can distinguish two sources of errors in determination of ΔT :

1. Temperature sensors and calibration are non-ideal. Thermocouples are almost exclusively used as temperature sensors at high-temperature thermopower measurements. To ensure precise determination of ΔT , thermocouple must satisfy very rigid requirements, such as the branches homogeneity and stability of their properties. Typical value of ΔT is about 10 K. At sample temperature of about 1000 K, just 0.1% difference in average thermopower of two thermocouples will lead to errors in determining ΔT of 10%. For example, average thermopower of one of the most commonly used thermocouple, consisting of platinum wire and wire of alloy Pt+10% Rh, is about 10 $\mu\text{V/K}$ in temperature range 300–1000 K. Deviation of average thermopower of one thermocouple on another of the order of 0.01 $\mu\text{V/K}$ will result in error in ΔT of 10%. Therefore, for measurements of thermopower, high-

quality thermocouple wires should be used only and their homogeneity should be monitored during operation.

2. The main source of errors in thermopower measurements associated with mismatch between the points, where ΔT and ΔV are measured (see, e.g., [28]). Junction of thermocouple used for measuring temperature at the point of electrical contact of reference electrode (which is usually one of used thermocouple branches) has finite dimensions. In real conditions of high temperature measurements, significant heat flow may occur along thermocouple branches. Combination of these factors leads to the fact, that average temperature of the junction and real temperature of electrical contact of reference electrode with the sample differ, that leads to error in determining of thermopower. For this type of errors, it is difficult to make general numerical estimate, because errors depend on several factors, which are difficult to control: size of thermocouple junction, cross-section and thermal conductivity of thermocouple branches, the value of thermal resistance at contact of thermocouple with the sample, temperature distribution in contact area. Error evaluation can be done by measuring thermopower of well-known materials, which have stable properties. Unfortunately, as we have already noted, so far, there is no standard for thermopower at high temperatures. Some metals can be used as reference samples. Due to the combination of the properties, platinum and nickel are the most suitable for high temperatures. It should be noted, that if platinum is used as a reference electrode for thermopower measurements, platinum sample is not suitable as a reference for evaluation of measurement error. In this case, as follows from Eq. (4) $\Delta V = 0$ (since $\alpha_x = \alpha_l$). Thermopower $\alpha_x = \frac{\Delta V}{\Delta T} + \alpha_l$, determined in such measurements, will have correct value, regardless of the accuracy of determining ΔT .

Specifications analysis of set-ups for thermopower measurements and experience allow to state, that accuracy of determination of thermopower at high temperatures is limited by about $\pm 5\%$. This estimate includes also uncertainty of modern absolute thermoelectric scale, which at high temperatures reaches $\pm 0.5 \mu\text{V/K}$. However, for thermoelectric materials, in which thermopower value is of the order of $100 \mu\text{V/K}$ or more, this uncertainty is not significant. Note also, that errors associated with inhomogeneity of thermocouple wires may be partially removed, when using alternating temperature difference [29–32]. At the same time, the second-type errors cannot be eliminated with alternating temperature difference and/or by use of differential thermocouple for measuring temperature difference, as it is sometimes assumed [30].

5. Devices for measuring thermopower and electrical conductivity

Devices realizing differential thermopower measurement technique can be divided into two classes: with variable (modulated) and static temperature difference. Measurements with variable temperature difference allow to eliminate or significantly reduce errors associated with inhomogeneity of branches of thermocouples, with slow instrumental drift or constant voltages caused by inhomogeneity of electrical circuits due to thermoelectric effects. This method has an advantage comparing to measurements with static temperature difference at low temperatures, when amplitude of ΔT is very small, because condition, which must be

satisfied is $\Delta T \ll T$. Therefore, there have been numerous variants of its implementation, designed for measuring thermopower at low temperatures [31–36]. At high temperatures, gradient modulation does not bring significant increase in accuracy, and implementation of this method is more difficult. Nevertheless, variable gradient method has been used at high temperatures as well [37–39].

Further, we describe in detail two experimental set-ups for measuring thermopower and electrical conductivity in temperature range from 80 to 2000 K [26, 40] and give brief overview of other devices for measurement of these properties.

5.1. Set-up for thermopower and electrical conductivity measurements at 80–1300 K

General view of measuring apparatus shown in photograph (Figure 18). Set-up was built to provide the fast and high quality electrical conductivity and Seebeck coefficient measurements using samples of any shape, including thin films. These objectives were fully achieved [26, 40].



Figure 18. Experimental set-up for thermopower and electrical conductivity measurements at 80–1300 K.

The set-up consists of four main parts:

1. Sample holder.
2. Main heater and temperature control system.
3. Vacuum system.
4. Data collection and processing system.

Sample holder is located inside vacuum chamber, which can be pumped out using turbo molecular pump to residual pressure down to 10^{-4} Pa. Typically, chamber is filled with helium gas to pressure slightly above atmospheric. Measurements can be performed in vacuum, but in this case, accuracy of measurement of thermoelectric power decreases. Moreover, it must be borne in mind, that metallization of isolators may occur at high temperatures due to vaporization of metals.

General view of sample holder is shown in **Figure 19** [26]. The basis of the holder is two coaxial tubes made of high-temperature steel, which are mounted on vacuum flange (19). Inner tube (16) is mounted on top of the flange (19). Gradient heater (11), supporting plate (8) and heat sink (4) mounted on other end of inner tube. Outer tube (15) is centered relative to inner tube with steel disks (14), which are mounted on inner tube at distance of 50 mm from each other. This system of two coaxial tubes is rigid and stable, which is especially important at high temperatures. All current and thermocouple wires are arranged in the space between inner and outer tubes and, therefore, they are well protected from mechanical damage and contamination. Outer tube can be easily removed, allowing access to the wires in case of repair. Sample supporting plate (8) is located between gradient heater (11) and heat sink (4) made of molybdenum. Selection of molybdenum as material for heater and heat sink is motivated by its high thermal conductivity and mechanical stability at high temperatures. The sample (5) is pressed against supporting plate (8) by press arm (10), pressure plate (9) and steel spring (13). These parts are made of special high-temperature steel. Cold junctions of thermocouples are made in the form of copper block (17), inside of which is made connection of thermocouple branches with copper wires, connecting thermocouple with the measuring equipment.

In this case, two conditions should be fulfilled:

1. All junctions of thermocouple branches with copper wires should be at the same temperature T_0 .
2. All junctions should just be electrically isolated from each other. Quality of isolation must satisfy condition: $R_{ij} > 10^3 \times R_{\max}$, where R_{ij} – resistance between any two junctions of open thermocouple, R_{\max} – maximum resistance of the samples.

Connection of sample holder with measuring equipment is carried out by means of connector made of conductors with low thermopower relative to thermopower of copper. Temperature of reference point (17) is measured by thermistor (18).

Selection of thermocouple is mainly determined by temperature measurement interval. For temperature range from 80 to 600 K, the best choice is thermocouple copper-constantan, it has

good sensitivity, stable enough, thermopower of copper is well-known and it is rather low. For temperatures from 300 K to ≈ 1600 K Pt-Pt/Rh thermocouples are the best choice, where the second branch is alloy of platinum and rhodium. Usually, as the second branch of these thermocouples, alloys of platinum with 10 and 13% rhodium are used. Thermopower of platinum, which is normally used here as reference electrode in measurements of thermopower, is also well known.

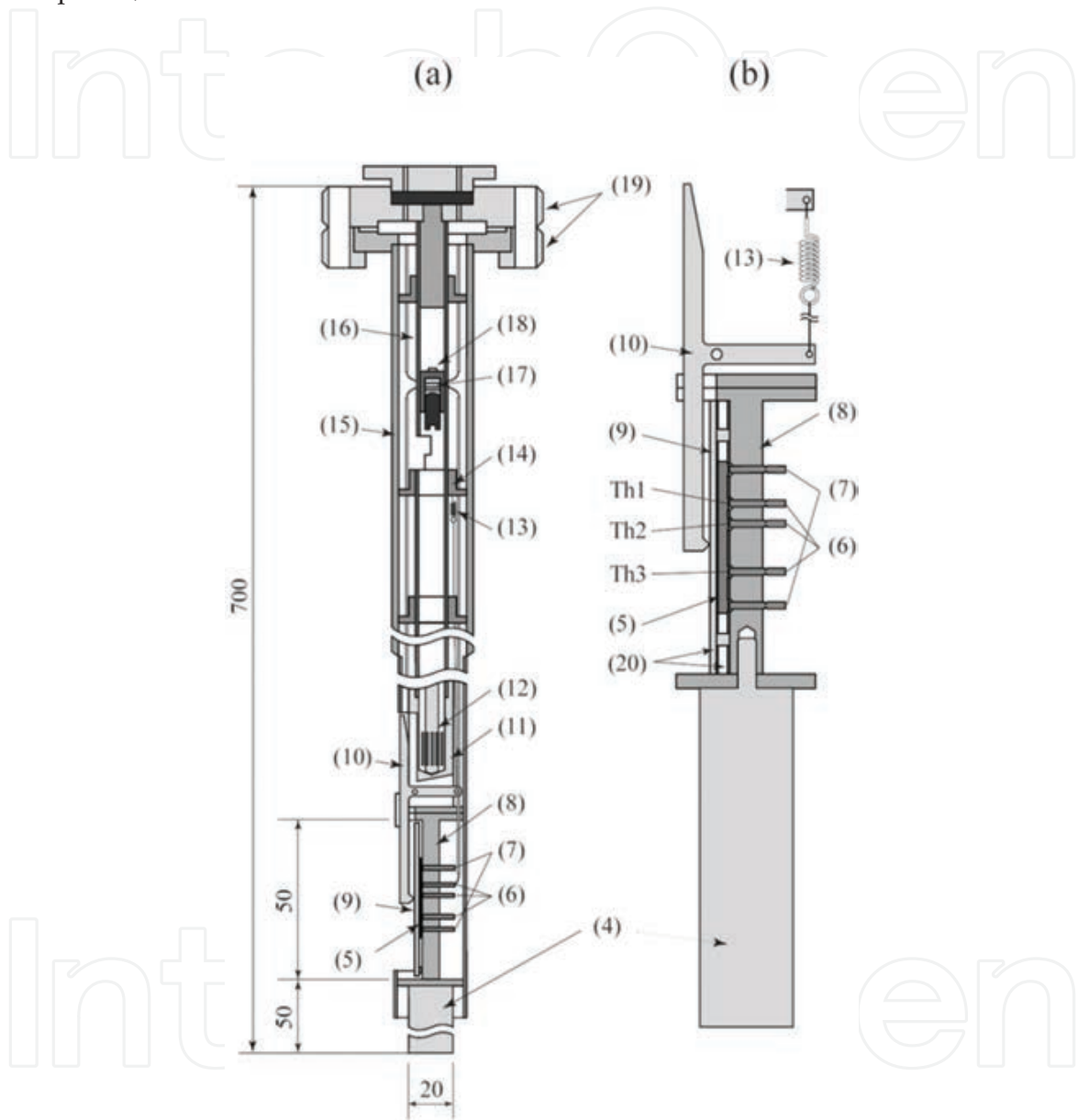


Figure 19. General view of sample holder (a), and sample supporting plate (b). The dimensions are given in millimeter.

Figures 19b and **20** show details of mounting and pressing mechanism of thermocouples on the supporting plate. The basis for mounting thermocouples (6) and current contacts (7) are two-channel tube (21) made of Al_2O_3 of 1 mm diameter. Tubes are pressed against the sample (5) using small springs (22) made of iridium wire. The springs are welded to the supporting plate (8). Such system provides reliable contact of thermocouples and current contacts with the sample within the whole operating temperature range. The choice of

material for the springs (22) is important for providing reliable and stable contacts. The most important condition is to maintain elasticity of the material up to about 1300 K, as well as, mechanical and chemical stability. Iridium satisfies in full these requirements. Other good materials are tungsten-rhenium alloys; however, they cannot be used in oxidizing atmosphere. For electrical isolation of the sample from supporting (8) and pressing (9) plate, thin mica sheets (20) are used. Gradient heater (12) (**Figure 19a**) is used to regulate temperature gradient in the sample. Temperature gradient is mainly formed by slightly asymmetric sample's position relative to the center of the heater (**Figure 18**). Typical value of temperature gradient between measuring thermocouples is in the range from 5 to 20 K (depends on temperature).

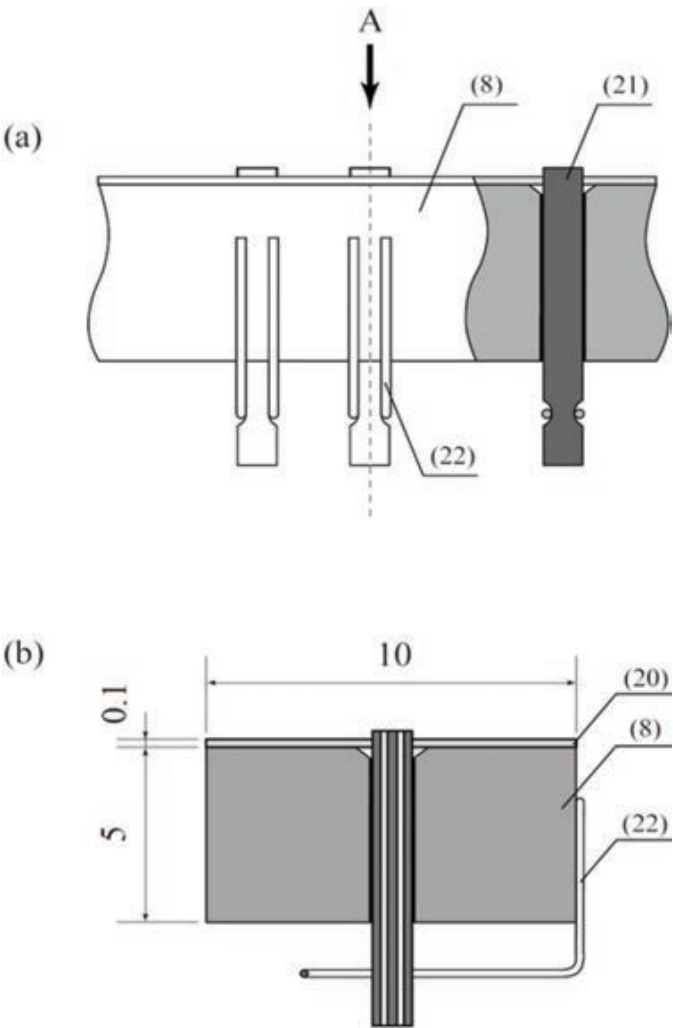


Figure 20. Detailed view of mechanical contact mechanism: (a) side view of the sample supporting plate with ceramic tubes (21) and springs (22); distance between tubes is not in scale with their diameter; (b) cross-sectional view of the sample supporting plate.

Five electrodes are used in the sample holder: 3 – for thermocouple contacts and 2 – for current contacts. The distance between Th1 and Th2 equals to 3 mm, between Th1 and Th3 – 10 mm (**Figure 19**). Such configuration allows measuring properties of the samples of various sizes

with optimal accuracy. The sample holder allows measurements with both bulk samples and thin films as well.

5.1.1. Measurement procedure

Standard four-probe DC current method is used for measurements of electrical conductivity. Differential method with constant temperature gradient is utilized for thermopower measurement. Performing reliable measurements of thermopower requires accurate temperature measuring and availability of precise and detailed information about thermoelectric power of reference electrodes depending on temperature. As shown above, thermopower in differential measurement method is given by Eq. (12). To determine ΔT , precise calibration data for thermocouples must be used: $T = F(V)$. For standard thermocouples, calibration dependences are usually presented in the form of tables or dependencies of $V(T)$. If measurement is automated, it is more convenient to have calibration dependence in the form of analytic functions. In this case, it is important to choose the most natural analytic representation. In rough approximation, metal thermopower is linear function of temperature (generally, this is incorrect statement, but for metals and alloys used in thermocouples it is true), and then thermopower of thermocouple can be

expressed as follows:
$$V(T) = \int_{T_0}^T \alpha_{12}(T) dT \propto \int_{T_0}^T kT dT = \frac{1}{2}k(T^2 - T_0^2) \quad \text{and, hence,}$$

$$T \propto \left(\frac{2}{k}\right)^{1/2} \times \sqrt{V + \frac{k}{2}T_0^2}.$$
 Therefore, we represent thermocouple calibration dependence in the form of:
$$T = \sum_{i=0}^n b_i (\sqrt{V + a})^i.$$

Coefficients b_i of interpolating polynomials for four standard thermocouples are shown in **Table 2**.

	Pt-Pt+13% Rh	Pt-Pt+10% Rh	Chromel-alumel	Copper-constantan
a	0.1676	0.2045	6.4	6.1
b_0	237.54	230.43	28.5	34.4
b_1	0	0	0	0
b_2	273.7	269.884	135.5	116.9675
b_3	-179.79	-162.308	-90.6	-73
b_4	85.454	65.836	33.363	29.5
b_5	-22.35955	-9.851	-6.6509	-7.02
b_6	2.9002	-1.207	0.7315	1.488
b_7	-0.13503	0.524	-0.04125	-0.9712
b_8	-0.0015	-0.04238	-0.00092	0.0347

Table 2. Coefficients of interpolating polynomials for thermocouples [26].

These polynomials can be used in the following temperature ranges:

Pt-Pt+13% Rh from 273 to 1873 K;

Pt-Pt+10% Rh from 233 to 1883 K;

chromel-alumel from 43 to 1543 K;

copper-constantan from 53 to 673 K.

Polynomial coefficients were obtained by fitting polynomials to calibration tables recommended by International Electrotechnical Commission for standard thermocouples. Deviation from calibration tables in specified temperature ranges does not exceed 0.1 K for copper-constantan and Pt-Pt+13% Rh thermocouples; 0.15 K for thermocouple Pt-Pt+10% Rh; and 1.5 K for chromel-alumel thermocouple. Additional error in determining temperature difference across the sample due to these deviations is within $\pm 1\%$ for copper-constantan thermocouple and both platinum thermocouples, and $\pm 3\%$ for chromel-alumel thermocouple.

Measurements of both properties are performed simultaneously. When measuring temperature dependence of the parameters, it is not required to establish steady temperature at each point. Measurements are performed with a continuous change in temperature at rate up to 10 K/min.

5.2. Set-up for measuring thermopower and electrical conductivity at 300–2000 K

Thermopower measurements at very high temperatures, particularly above 1500 K, are rather difficult due to several factors:

1. Structural materials lose their strength and stability. Cycling of temperature between room temperature and high temperatures leads to deformation of structures.
2. Almost all electrical insulating materials have significant electrical conductivity at these temperatures.
3. At temperatures approaching to 2000 K, difficulties with heating of the sample and maintaining stable temperature and temperature gradient in the sample arises. Therefore, measurement of transport properties, in particular thermopower, at temperatures above 1000 K is quite rare. Typically, measurements at higher temperatures are less accurate compared with measurements at low temperatures.

Described apparatus allows measurements of thermopower and resistance of bulk samples of conductors at temperatures from 300 K to temperature slightly above 2000 K with good accuracy. This system allows to work with samples of various shapes and sizes. Perhaps, this is the most high-temperature experimental device for direct measurement of thermopower described in the literature. The exception is the device used Lander [22] for measurement of Thompson coefficient of some metals up to 2400 K.

The main original part of this set-up is sample holder [41]; scheme of this holder is shown in **Figure 21**. The basis of holder is molybdenum tube (2), in the lower part of which is fixed

molybdenum massive heat sink (1), where replaceable molybdenum bottom sample support (4) is installed. At the top of the tube (working position of the holder is vertical), molybdenum pusher (8) is located, which is isolated from tube by ceramic (Al_2O_3) rings (7). The lower ring is held by molybdenum stop (6), which also protects ceramic ring from metallization by metal vapors from the hot zone at the bottom. The sample (3) is clamped between the upper (5) and lower (4) supports under weight of gravity transmitted through molybdenum (8) and stainless steel (9) pushers. The holder is mounted in vacuum chamber with heater through ceramic insulating tube (10).

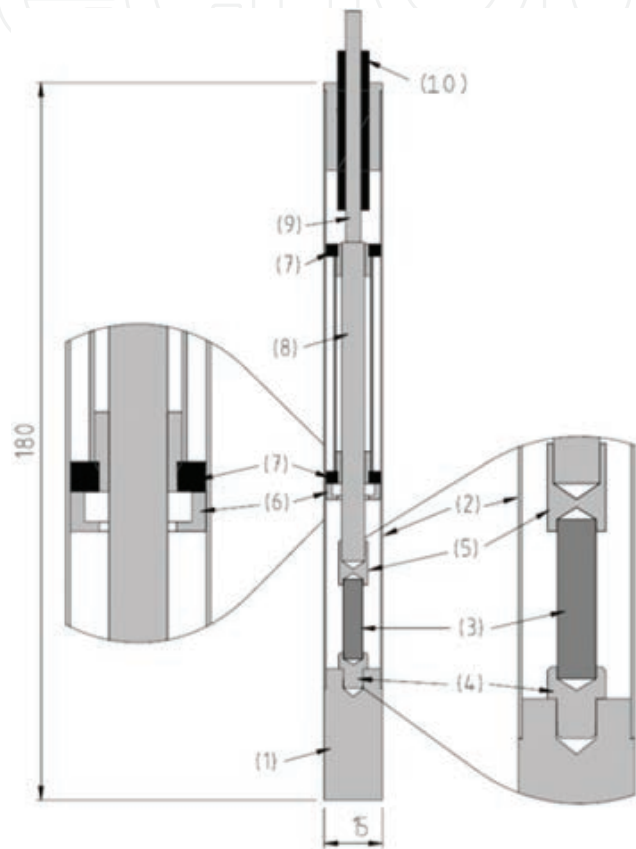


Figure 21. Sample holder for measuring thermopower and resistance at 300–2000 K: (1) – heat sink; (2) – outer molybdenum tube; (3) – sample; (4) – bottom sample support; (5) – upper sample support; (6) – molybdenum support for insulation; (7) – insulating ring made of Al_2O_3 ; (8) – molybdenum pusher; (9) – stainless steel pusher; (10) – ceramic insulation.

To measure temperature and thermopower in this set-up, thermocouples of tungsten-rhenium alloys are used: WR10-WR20. These are alloys of $\text{W} + 10\% \text{Re}$ and $\text{W} + 20\% \text{Re}$, respectively. WR20 alloy is used as the reference electrode in measuring thermopower. For thermocouple WR10-WR20, there is standard calibration, however, the absolute thermopower of the branches is not known. The absolute thermoelectric power of WR20 alloy was determined by measuring thermopower of reference metal samples. As standards were used: platinum in temperature range 300–1700 K, and molybdenum at 1700–2100 K. Thermopower of high-purity molybdenum sample was beforehand accurately measured in temperature range from 80 to 1600 K relative to copper and platinum. Cusack and Kendall data [21] were used at

higher temperatures. However, in order to provide a smooth joining of low-temperature data with Cusack's data, it must be entered temperature-independent correction of 2 $\mu\text{V/K}$ in these data. A possible reason for this difference is insufficient purity of metal, which was used by Lander [22] in measurement of Thomson coefficient of molybdenum. Thermopower of molybdenum and WR20 alloy are shown in **Figure 22**. At temperatures from 100 to 2000 K, thermopower of WR20 can be calculated using interpolation polynomial:

$$\alpha_{WR20} = 1.6337 \times 10^{-12} \times T^4 - 1.2669 \times 10^{-8} \times T^3 + 2.6192 \times 10^{-5} \times T^2 - 1.6889 \times 10^{-2} \times T + 3.111. \tag{16}$$

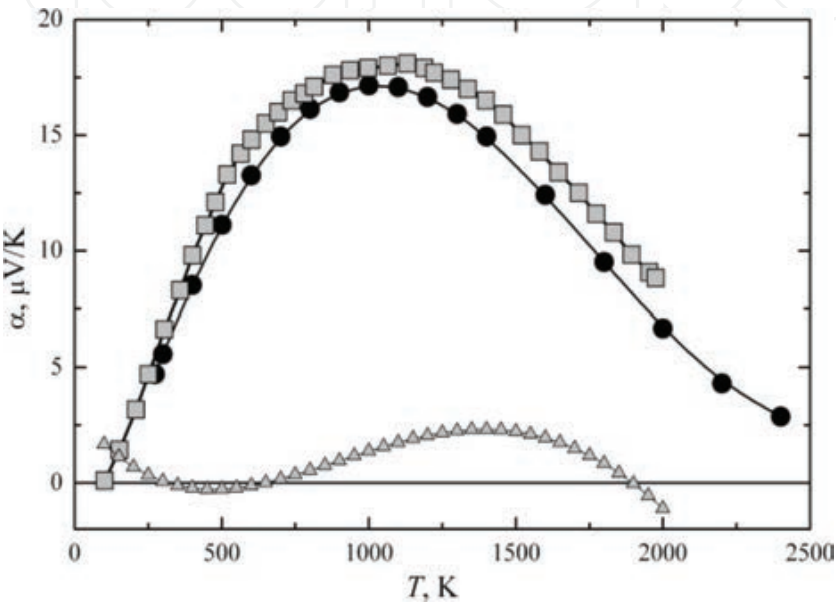


Figure 22. Thermopower of molybdenum and WR20 alloy: ● – molybdenum thermopower according Cusack [21]; ■ – adjusted molybdenum thermopower; ▲ – thermopower of WR20 alloy.

5.3. Other techniques

Petrov [42] built set-up for simultaneous measurement of thermopower, thermal conductivity and electrical conductivity of thermoelectric materials (i.e., materials with very low thermal conductivity), at temperatures from 100 to 1300 K, which operates successfully (in upgraded form) up to nowadays. In this device, method of electrical conductivity measurement with DC current, differential method of thermopower measurement and classic steady-state method of thermal conductivity measurement are used. The measurements at each value of temperature must be carried out in stationary temperature conditions. Since, achievement of thermal equilibrium, especially at low temperatures, is slow, measurements over whole temperature range takes several days. To suppress the heat loss by radiation, active heat shield and special ceramic filling with very low and known thermal conductivity are used. This system allows to determine parameter ZT as a result of simultaneous measurement of α , σ , and κ with accuracy of $\pm 5\%$.

In contrast to electrical conductivity measurements, thermopower measurement is difficult to automate using analog methods. Therefore, before the advent of personal computers, these

measurements were very time-consuming. There are several original analog automated devices for measuring thermoelectric power [30, 33]; however, they were not widely used.

Interesting device for measuring thermopower at high temperatures has been developed by Wood et al. [37]. This device uses a differential method for measuring thermoelectric power with modulation of temperature difference over the sample. Interchangeable heating the ends of the sample by light flash lamps was used for the modulation of temperature difference. Light beam energy was applied to the sample by means of sapphire optical fibers, between which the sample was clamped. The device allowed to measure thermopower up to 1900 K, with amplitude of temperature difference modulation of a few degrees. Author estimates measurement error of thermopower as $\pm 1\%$, but does not specify experimental evidence of stated accuracy.

In apparatus for measuring thermal conductivity and thermoelectric power at temperatures 300–750 K, described in Ref. [43], stationary method of measuring thermal conductivity and differential method of thermopower measurement are used. Measurement of thermal conductivity is based on the comparison between temperature difference of heat source and heat sink in the presence of the sample and without the sample. At each temperature, after thermal stabilization, measurements of ΔT with the sample in contact with heat source and heat sink are performed. Then, heat source is disconnected from the sample and ΔT is measured again. Assumed, that heat losses in the system are the same in both states, and losses due to radiation from the sample are not considered. This put in question the correctness of the measurement. Thermopower is measured by differential method with constant temperature gradient.

In set-up for measuring electrical conductivity and thermoelectric power at 300–1300 K [44], electrical conductivity is measured with AC current at frequency 16 Hz, and for measuring thermopower, differential method with constant temperature difference is used. Thermocouples, which are used for the measurement of temperature gradient and thermopower, are mounted in holes drilled in the sample by using graphite paste. After installation of the sample, paste must be heat treated to ensure proper contact. This, as well as, current leads design, which cannot provide stable electrical contact, is a serious disadvantage of the system. Extremely small thermopower measurement error 0.3%, stated by authors, has not been experimentally confirmed.

AC electrical conductivity measurement procedure and differential method with temperature gradient modulation for measuring thermopower are utilized in set-up for thermopower and electrical conductivity measurements at 300–1273 K [38]. The publication, however, contained only measurement principles, which are not original. No details of measuring device were presented.

Interesting sample holder design for measuring thermoelectric power at temperatures up to 1200 K was suggested in Ref. [45]. This is further development of Wood's system [37], but with significant changes. Distinctive feature of the design is axial location of thermocouples. Thermocouples, supported by four-channel thin tubes, extend along the central axis of gradient heaters, between which is clamped the sample. Working junctions of

thermocouples are pressed against the ends of the sample by springs. Therefore, sample does not require special preparation for measurement. Thermopower is measured by differential method with temperature gradient modulation; amplitude of modulation is up to 20 K. The article provides fairly detailed analysis of measurement errors of thermopower.

A feature of the holder for measuring thermopower and electrical conductivity proposed in Ref. [46] is the material: the main parts of this device are made of ceramics (Al_2O_3). Therefore, this device can be used for high temperature (1200 K) measurements in oxidizing atmosphere in the case of using platinum thermocouples. Thermoelectric power is measured by differential method with variable temperature gradient.

Relatively detailed overview of methods and devices for measurement of thermopower and electrical conductivity was published by Martin et al. [47].

Apart from temperature, pressure and magnetic field are accessible experimental parameters affecting the material properties. Dependences of electrical conductivity and thermoelectric power on magnetic field and pressure provide important information about electronic structure and conductivity mechanisms. Generally, studies of thermoelectric and conductivity dependencies on pressure and magnetic field are carried out at low temperatures. However, for thermoelectric materials, dependence of their properties on pressure and magnetic field at high temperatures is of considerable interest. Therefore, considerable effort has been directed toward the study of these dependences and development of devices for such measurements [48–52].

6. Conclusion

Research and successful development of novel effective materials for thermoelectric energy converters is critically dependent on obtaining accurate and reliable information about properties of these materials. The most important characteristics of thermoelectric materials are thermopower and electrical conductivity. They determine potential effectiveness of thermoelectric material and provide important information on its electronic structure. Measurements of these properties must meet a number of requirements. Measurement results must be reliable and sufficiently accurate. Measurements must be performed over a wide range of temperatures comparable with a typical range of applications. In experimental research for new thermoelectric materials, the versatility of measurement set-ups is especially important. They should make affordable measurements of samples of different shapes and dimensions in a wide range of temperatures. Despite relative simplicity of fundamental methods of measuring thermoelectric properties of materials, their practical implementation is a difficult task. Additional difficulty is the lack of commonly accepted reference materials for measuring thermopower at high temperatures, making it difficult to compare the results obtained by independent groups. In such circumstances, it is crucial to understand clearly possibilities and limitations of different methods for measuring thermoelectric properties and unconditional implementation of some basic requirements by researchers. When measuring

thermopower, the most important points are: (1) thermoelectric signal and temperature difference must be measured between the same points of the sample; (2) potential contacts and temperature sensors must be in good thermal and electrical contact with the sample; (3) when using thermocouples, special attention must be given to thermoelectric homogeneity of their branches.

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