MEASUREMENT OF THERMAL AND ELECTRICAL CONDUCTIVITIES OF SMALL CROSS SECTION SAMPLES IN THE 80-400°K RANGE

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A procedure is described for measuring thermal and electrical conductivities of samples of thermoelectric materials having small cross sections and thicknesses of 1-0.01 mm. The thermal conductivity is determined from the change in resistance of the sample as a result of Joule heating within it. The method does not require a direct measurement of temperature of the sample.

The measurement of the electrical and thermal conductivities of samples of thermoelectric materials having small cross sections (<1 mm^2 for a length $l > 3$ mm) is of interest both for physical investigations such as the study of the influence of dimensional effects on the scattering of electrons and phonons, and for the development of thermocouple arms for use in weak-current thermoelectric generators and thermostatic control devices.

The accuracy of measuring the thermal conductivity of small cross section samples is decreased because of the increased heat loss from the lateral surface of the sample, and because of the difficulty in determining the temperature of the sample, since connecting thermocouples significantly distorts the temperature distribution.

In view of this we have used the Kohlrausch (Callendar) method [1, 6] which consists in passing an electric current through a sample whose ends are maintained at a constant temperature. This leads to a change in the resistance of the sample ΔR as a result of Joule heating. By measuring ΔR under stationary conditions we find the related value of the thermal conductivity of the material. In this method the effect of heat loss from the lateral surface of the specimen is much less than in methods of measuring the thermal conductivity in which the heat flow through the sample is produced by external sources [4, 5, 7, 8]. In addition there is no need to connect thermocouples to the sample.

It should be noted, however, that the Kohlrausch method is limited to materials having a large enough temperature coefficient of resistance β so that ΔR for a small temperature rise can be measured to the necessary accuracy. Semiconducting thermoelectric materials generally satisfy this requirement.

In order to establish a relation between ΔR and $\varkappa$ we calculate the temperature distribution in the sample $T(x)$, where x is the coordinate measured from one end, under the following simplifying assumptions: the cross sectional area of the sample ω is small enough so that the heat flow can be considered linear; heat exchange with the surrounding medium is described by Newton's law, with the temperature of the medium the same as the temperature of the ends of the sample, assumed equal to zero; the temperature drop across the sample is small enough so that the effect of the temperature dependence of the parameters of the sample on the temperature distribution within it can be neglected.

By solving the heat conduction equation and satisfying the boundary conditions under these assumptions we obtain

$$T(x) = \frac{I^2}{\omega\sigma Hp}\left[1 - \frac{\operatorname{sh}\eta x + \operatorname{sh}\eta(l-x)}{\operatorname{sh}\eta l}\right], \tag{1}$$

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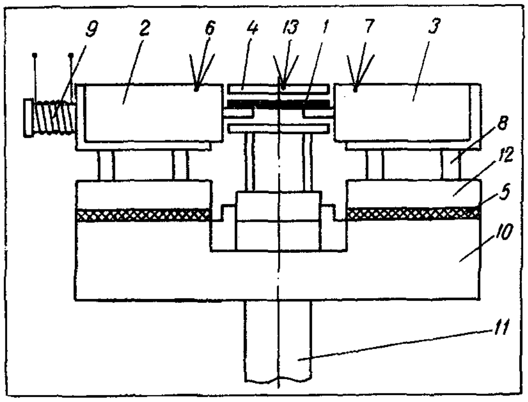

Fig. 1

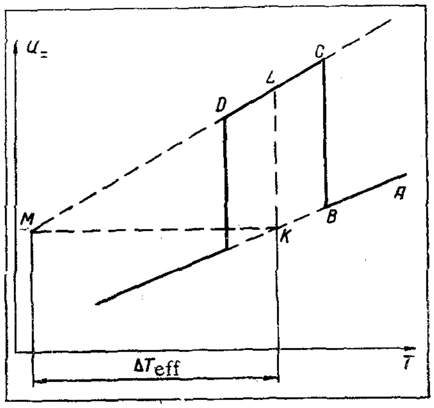

Fig. 2

Fig. 1. Schematic diagram of apparatus. 1) Sample; 2 and 3) electrodes; 4) screen; 5) spacers; 6, 7, 13) thermocouples; 8) supports; 9) heater; 10) slab; 11) rod; 12) plates.

Fig. 2. Schematic portion of the curve showing the potential $u_=$ as a function of temperature. AB) The sample is carrying a direct current which does not produce significant heating of the sample; CD) in addition to the direct current the sample is carrying an alternating current which raises its temperature 10-15°.

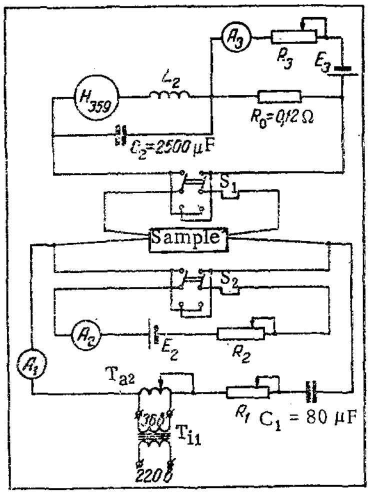

Fig. 3. Circuit diagram of apparatus.

where $\eta = \sqrt{Hp/\varkappa\omega}$. The resistance of the sample R_I when it is carrying a current is

$$R_I = \frac{1}{\omega\sigma}\int_0^l \left[1+\beta T(x)\right] dx. \qquad (2)$$

After substituting (1) into (2), integrating, and expanding in powers of $\eta l/2$ we obtain an expression for the thermal conductivity of the material

$$\varkappa = \frac{I^2 l \beta R_0^2}{12\omega\Delta R}\left[1-\frac{1}{10}\cdot\frac{Hp}{\omega\varkappa}l^2+\frac{1}{100}\left(\frac{Hp}{\omega\varkappa}l^2\right)^2-\ldots\right]. \qquad (3)$$

The heat-transfer coefficient appears in the correction terms. It should be noted that Eq. (3) can also be written in the form

$$\varkappa = \frac{I^2 l^2}{12\omega^2\sigma\Delta T}\left[1-\frac{1}{10}\cdot\frac{Hp}{\omega\varkappa}l^2+\frac{1}{100}\left(\frac{Hp}{\omega\varkappa}l^2\right)^2-\ldots\right],$$

where ΔT is the effective temperature rise of the sample due to the liberation of Joule heat in it.

Figure 1 shows a schematic diagram of the apparatus. Electrodes 2 and 3, to which the sample is soldered, are connected to plates 12 by steel supports. The plates are electrically insulated by beryllium oxide spacers 5 fastened to the copper slab 10, the extension of which forms rod 11, cooled by liquid nitrogen. The sample is surrounded by a copper heater screen 4 used to determine the emissivity of the sample (cf. below).

Heater 9 produces a temperature drop across the sample for the determination of the thermoelectric power. The temperatures of electrodes 2 and 3 and screen 4 are recorded by thermocouples 6, 7, and 13. The system was pumped down to 10^{-5} torr to eliminate convective losses.

Equation (3a) shows that the determination of the thermal conductivity requires, in addition to the linear dimensions, the electrical conductivity σ, the effective heating of the sample ΔT, and the current I producing this heating. The measurements are made with an N-359 two coordinate recording instrument which plots on one axis the potential $u_=$ of the sample when carrying a direct current, and on the second axis the temperature (Fig. 2).

The measurements are performed by lowering the temperature so slowly (~100°/h) that the sample is at all times in thermal equilibrium. To increase the accuracy of the measurements the high sensitivity scales of the N-359 instrument are used, and the emf of thermocouple 6 (Fig. 1) measuring the temperature, and the potential of the sample are partially compensated by preset constant potentials.

The measuring process consists in the following. A relatively small direct current is passed through the sample producing no appreciable heating. Using the N-359 instrument the potential $u_=$ is plotted as the temperature of the sample changes (portion AB of Fig. 2). Then a 50 GHz alternating current is turned on for about a minute, producing effective heating of the specimen by 5-10° and causing a stepwise change in $u_=$ (portion CD of Fig. 2). The alternating current is then turned off.

It is easy to see that the straight line MK drawn parallel to the T axis until it intersects the prolongation of the straight line CD gives the value of ΔT_{eff}. The vertical KL on Fig. 2 corresponds to the average time the alternating current flows.

Figure 3 shows the circuit diagram of the apparatus. The dc circuit consists of the battery E_2, the resistance box R_2, and the ammeter A_2. The ac circuit consists of the isolation transformer T_{i1}, the adjustable autotransformer T_{a2}, the ammeter A_1, the ballast resistor R_1, and the capacitor C_1 eliminating the dc component of the current.

The circuit for measuring the potential of the sample contains, in addition to the N-359 instrument: a filter L_2C_2 to eliminate the alternating voltage component, and a compensating circuit consisting of a voltage divider, the ammeter A_3, and the battery E_3. The emf of the thermocouple is compensated in a similar circuit.

For the samples of bismuth telluride (l = 1 cm, $\omega = 10^{-2}$ cm^2, σ = 800 $\Omega^{-1}\cdot$cm^{-1}, α = 230 μV/deg) the values of the direct and alternating currents are I_1 = 10 mA and I_2 = 500 mA respectively. The heat-transfer coefficient is determined in the following way. The copper screen 4 is heated to a certain temperature T_s and the resulting change $\Delta R'$ in the resistance of the sample is measured.

Solving the problem of the change in resistance of the sample we obtain

$$\Delta R^1 = \frac{R_0\beta l^2 HpT_s}{12\varkappa\omega}\left[1-\frac{1}{10}\cdot\frac{Hp}{\omega\varkappa}l^2+\frac{1}{100}\left(\frac{Hp}{\omega\varkappa}l^2\right)^2-\dots\right). \quad (4)$$

Discarding the correction terms in (4), which is permissible since the required quantity H enters (3) as a correction, we find

$$H\approx\frac{12\varkappa\omega\Delta R^1}{R_0\beta l^2 pT_s}. \quad (5)$$

Substituting (5) into (3) we obtain for $\varkappa$

$$\varkappa=\frac{I^2 l\beta R_0^2}{12\omega\Delta R}\left[1-\frac{12}{10}\cdot\frac{\Delta R^1}{\beta T_s R_0}+\frac{144\cdot 17}{16\cdot 105}\left(\frac{\Delta R^1}{\beta T_s R_0}\right)^2-\dots\right]. \quad (6)$$

We compare the magnitude of the first correction term in (3) with the correction for heat transfer from the lateral surface of the sample in measuring the thermal conductivity with an external heat source (e.g., heat is liberated at one end of the sample at a definite rate and the resulting temperature drop across the sample is measured [4]). Neglecting all correction terms except the first we write (3) in the form

$$\varkappa\approx\varkappa_0\left(1-\frac{1}{10}\cdot\frac{Hp}{\omega\varkappa}l^2\right). \quad (7)$$

It is easy to show that the thermal conductivity measured by heat release at one end of the sample is approximately

$$\varkappa\approx\varkappa_0\left(1-\frac{1}{2}\cdot\frac{Hp}{\omega\varkappa}l^2\right). \quad (7a)$$

It follows from the above that the correction term is a fifth as large. This is accounted for by the fact that the fraction of the heat dissipated by the lateral surface when heat flows the whole length of the sample from a source at one end is appreciably larger than for a heat source distributed through the volume of the sample.

TABLE 1. Measured Values of the Thermal Conductivity

Material	T, °K	$\varkappa$ (cal/cm·sec·deg)10^3, large samples	$\varkappa$ (cal/cm·sec·deg)10^3, thin samples
Bi_2Te_3	300	4,5	4,3
	80	14,5	14,0
$Bi_2Te_{2,7}Se_{0,3}$	300	4,0	4,1
	80	6,7	6,4
$Bi_{0,5}Sb_{1,5}Te_3$	300	3,9	4,1
	80	6,7	6,5

Note. The large samples were measured on the apparatus and by the method described in [7]. The thin specimens 1 × 1 mm^2 in cross section and 1 cm long were cut from the large samples and measured on our apparatus.

Indeed, for identical source strengths the effective temperature drop between the lateral surface and the surrounding medium, and consequently the heat loss, is less in the case of internal sources. The average distance heat propagated from internal sources is less than from a source at one end.

The magnitudes of the first correction term in Eq. (3) (in % of $\varkappa_0$) for radiative heat loss (ε = 0.5) from the lateral surface of the samples of bismuth telluride are the following:

T, °K	$s=1\times1$ mm^2 $l=10$ mm	$s=1\times0,1$ mm^2 $l=6$ mm	$s=1\times0,01$ mm^2 $l=3$ mm
300	8	15	30
80	0,03	0,06	0,2

The magnitude of the corrections in this method, even for rather thin samples, is insignificant.

Table 1 compares thermal conductivities of large samples measured on the apparatus and by the method described in [7], and thin specimens 1 × 1 mm^2 in cross section and 1 cm long cut from the large samples. It is clear that the results are in satisfactory agreement.

Because of the relatively small effect of the heat loss from the lateral surface of the sample the Kohlrausch method is of interest also for high-temperature measurements of the thermal conductivity of samples of thermoelectric materials with "ordinary" sized cross sections (~0.5 cm^2). In this case it may be necessary to take account of the radial variation of temperature in the sample arising from the heat loss from its lateral surface.

The problem reduces to calculating the steady-state temperature distribution in a finite cylinder of radius a and length l with internal heat sources, constant temperature of the ends, and heat transfer by Newton's law from the lateral surface. We introduce cylindrical coordinates x and r.

Using the solution given in [2, 3] we obtain

$$T(\rho,\ \zeta)=\frac{4q}{\pi}\sum_{\mu}\frac{\mu j}{\mu^2+j^2}\cdot\frac{J_0(\mu\rho)}{J_0(\mu)}\sum_{n=0}^{\infty}\cos\left[\left(n+\frac{1}{2}\right)\zeta\right]\frac{(-1)^n}{\left(n+\frac{1}{2}\right)\left[\mu^2+b^2\left(n+\frac{1}{2}\right)^2\right]}, \tag{8}$$

where

$$\rho=\frac{r}{a};\ \zeta=\frac{\pi x}{l};\ j=\frac{aH}{\varkappa};\ b=\frac{\pi a}{l};\ q=\frac{I^2R_0}{\varkappa l\pi};$$

J_0 is a Bessel function, the μ's are the positive roots of the characteristic equation

$$\mu J_0'(\mu)+jJ_0(\mu)=0.$$

In order to determine the change in resistance of the sample when an electric current flows* Eq. (2) must be integrated over the volume of the cylinder, which leads to cumbersome expressions. It is possible, however, to estimate qualitatively the effect of the deviation of the heat flow from the axial direction by

*We neglect the deviation of the electric current lines from the axial direction.

determining the largest radial temperature drop in the sample $\Delta T'$ (the drop in the middle cross section) and comparing it with the largest axial temperature drop ΔT. Evidently

$$\Delta T' = T\left(l;\ \frac{\pi}{2}\right) - T\left(0;\ \frac{\pi}{2}\right).$$

Using (1) and (8) we obtain

$$\frac{\Delta T'}{\Delta T} = \frac{16\omega\left[2+(\eta l/2)^2\right]}{\pi l^2} \sum_{\mu} \frac{\mu j}{\mu^2 + j^2} \left(\frac{1}{J_0(\mu)} - 1\right) \sum_{n=0}^{\infty} \frac{(-1)^n}{\left(n+\frac{1}{2}\right)\left[\mu^2 + b^2\left(n+\frac{1}{2}\right)^2\right]}. \quad (9)$$

Estimates performed for boron, a prospective high-temperature thermoelectric material, showed that for $b = 1$, $T \approx 1500°K$, $\Delta T'$ is ~2% of ΔT, and in this case Eq. (3) for linear heat flow can be used.

A preliminary estimate must be made in each specific case to determine the possibility of using this method to measure the thermal conductivity of other materials.

The main source of error in measuring the thermal conductivity of small cross section samples is the determination of the dimensions of the samples. The error depends on the specific circumstances. We note that the measurement of $\varkappa/\sigma$ is of interest in a number of physical investigations. In this case the dimensions of the sample enter only in the correction terms.

The total error in measuring $\varkappa$, related to the determination of β, ΔR, R_0, the dimensions of the sample, and the error in determining the correction for heat transfer do not exceed 15%. The total error in measuring σ is 5%.

NOTATION

p	is the perimeter of the cross section of the sample;
I	is the electric current through the sample;
H	is the heat-transfer coefficient;
l	is the length of the sample;
σ	is the electrical conductivity;
$\varkappa$	is the thermal conductivity;
ω	is the cross-sectional area;
β	is the temperature coefficient of resistance;
T_s	is the temperature of the screen;
R_I	is the resistance of the sample when carrying a current;
R_0	is the initial resistance of the sample;
ΔR	is the change in the resistance of the sample when a current flows in it;
$\Delta R'$	is the change in resistance of the sample due to the absorption of thermal radiation from the screen;
α	is the thermoelectric power;
$\varkappa_0$	is the thermal conductivity measured without taking account of heat transfer from the lateral surface of the sample;
ε	is the emissivity of the sample;
ΔT_{eff}	is the effective heating of the sample;
$u_{=}$	is the potential of the sample.

LITERATURE CITED

1. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, Oxford, New York (1947).
2. A. V. Lykov, Theory of Heat Conduction [in Russian], Vysshaya Shkola, Moscow (1967).
3. T. L. Perel'man, Inzh.-Fiz. Zh., 5, 138 (1960).
4. H. J. Goldsmid, Proc. Phys. Soc., London, B 69, 203 (1956).
5. A. V. Ioffe and A. F. Ioffe, Zh. Tekh. Fiz., 28, 2357 (1958).
6. F. Kohlrausch, Ann. der Phys., 1, 132 (1900).
7. A. V. Petrov, in: Thermoelectric Properties of Semiconductors [in Russian], Izd. AN SSSR, Moscow–Leningrad (1963), p. 27.
8. C. H. Lees, Phil. Trans., A208, 381 (1908).