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PECULIARITIES OF THERMOPHYSICAL MEASUREMENTS OF THERMOELECTRIC MATERIALS

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This paper examines a method for direct measurement of the heat losses in determining the thermal conductivity of thermoelectric materials.

In [1] Harman proposed to determine the thermal conductivity of thermoelectric materials by measuring the temperature difference $T_2 - T_1$ between the ends of a thermoelement, through which a current I was flowing, from the formula

$$\varkappa = \frac{d}{s}\,\frac{eI(T_1+T_2)}{2(T_2-T_1)}(1-\gamma). \tag{1}$$

In order to reduce the error γ due to thermal losses from the surface of the specimen, one uses quite long and fine thermocouples and current leads, and the measurements are conducted in vacuum on specimens of dimensions such that the condition $\omega \ll 1$ holds [2, 3]. Below we examine the method of direct measurement of the correction term γ in Eq. (1). The method is based on the phenomenon that if the Peltier effect is used to create a heat flux through the thermoelement, the flux magnitude and direction can be controlled by varying the magnitude and direction of the electric current I.

We consider a thermoelement with current leads whose length satisfies the condition at infinity $d_l \gg (r_l \varkappa_l/\alpha_l)^{-1/2}$. We assume also that the following conditions hold. 1) There is no temperature drop over the cross section of the thermoelement. This condition holds if $(\alpha\delta/\varkappa) \ll 1$. 2) The thermoelectric parameters and the heat-transfer coefficient are independent of temperature. Then the heat-conduction equations for the thermoelement and the current leads in dimensionless form take the form

$$\frac{d^2\theta}{d\chi^2} - \omega^2(\theta-\theta_0) + \nu^2 = 0, \tag{2}$$

$$\frac{d^2\theta_{l_1}}{d\chi^2} - \omega_{l_1}^2(\theta_{l_1}-\theta_0) + C_{l_1}\nu^2 = 0, \tag{3}$$

$$\frac{d^2\theta_{l_2}}{d\chi^2} - \omega_{l_2}^2(\theta_{l_2}-\theta_0) + C_{l_2}\nu^2 = 0. \tag{4}$$

Here and below the subscripts 1 and 2 refer to the first (on the left in Fig. 1) and second faces, respectively, of the thermoelement. This means that the thermal conditions are different at the ends; and θ_0 is the dimensionless temperature of the surrounding medium.

We assume that for a single direction of current through the thermoelement the temperatures $\theta_1' < \theta_2'$ are established at its ends. If the current direction is changed, then $\theta_1'' > \theta_2''$. Thus, Eqs. (2)-(4) can be solved by well-known methods with the following boundary conditions: for the first current direction

$$\theta(0) = \theta_{l_1}(0) = \theta_1',\ \theta(1) = \theta_{l_2}(1) = \theta_2',$$

and for the second direction

$$\theta(0) = \theta_{l_2}(0) = \theta_2'',\ \theta(1) = \theta_{l_1}(1) = \theta_1''.$$

An additional condition for θ_{l_1} and θ_{l_2} is that the heat flux at infinity is zero.

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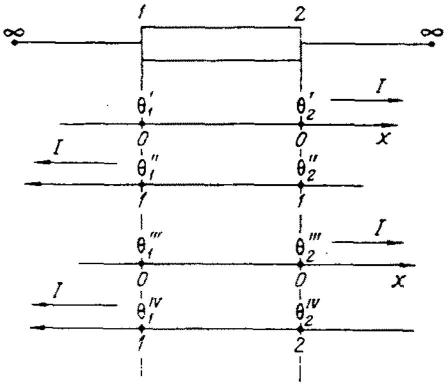

Fig. 1. Schematic representation of the boundary conditions for the thermoelement with the two current directions and various heat-transfer conditions (θ_1', θ_1'', θ_2', θ_2'' are quantities before the change and θ_1''', θ_1^{IV}, θ_2''', θ_2^{IV} after the change in thermal conditions).

With the given initial conditions we obtain the temperature distribution along the thermoelement and the current leads: $\theta'(\chi)$, $\theta_{l1}'(\chi)$, $\theta_{l2}'(\chi)$ for the first current direction and $\theta''(\chi)$, $\theta_{l1}''(\chi)$, $\theta_{l2}''(\chi)$ for the second current direction. We write down the thermal balance equations at the ends. For the first current direction: $\chi = 0$ (the cold junction)

$$\nu\theta_1' = \frac{d\theta'(\chi)}{d\chi}\bigg|_{\chi=0} - \frac{\varkappa_{l1}s_{l1}}{\varkappa s}\,\frac{d\theta_{l1}'(\chi)}{d\chi}\bigg|_{\chi=0} + \mathrm{Bi}_1(\theta_0 - \theta_1'), \tag{5}$$

$\chi = 1$ (the hot junction)

$$\nu\theta_2' = \frac{d\theta'(\chi)}{d\chi}\bigg|_{\chi=1} - \frac{\varkappa_{l2}s_{l2}}{\varkappa s}\,\frac{d\theta_{l2}'(\chi)}{d\chi}\bigg|_{\chi=1} + \mathrm{Bi}_2(\theta_2' - \theta_0). \tag{6}$$

For the second current direction: $\chi = 0$ (the cold junction)

$$\nu\theta_2'' = \frac{d\theta''(\chi)}{d\chi}\bigg|_{\chi=0} - \frac{\varkappa_{l2}s_{l2}}{\varkappa s}\,\frac{d\theta_{l2}''(\chi)}{d\chi}\bigg|_{\chi=0} + \mathrm{Bi}_2(\theta_0 - \theta_2''), \tag{7}$$

$\chi = 1$ (the hot junction)

$$\nu\theta_1'' = \frac{d\theta''(\chi)}{d\chi}\bigg|_{\chi=1} - \frac{\varkappa_{l1}s_{l1}}{\varkappa s}\,\frac{d\theta_{l1}''(\chi)}{d\chi}\bigg|_{\chi=1} + \mathrm{Bi}_1(\theta_1'' - \theta_0). \tag{8}$$

Combining Eq. (5) with (8) and Eq. (6) with (7), and evaluating the derivatives, we obtain

$$2\nu\bar{\theta}_1 K_0 = \Delta\theta_1' K_1 K_0 + \Delta\theta_2', \tag{9}$$

$$2\nu\bar{\theta}_2 K_0 = \Delta\theta_1' + \Delta\theta_2' K_2 K_0, \tag{10}$$

where

$$\Delta\theta_1' = \theta_1'' - \theta_1', \quad \Delta\theta_2' = \theta_2' - \theta_2'',$$

$$\bar{\theta}_1 = (\theta_1' + \theta_1'')/2, \quad \bar{\theta}_2 = (\theta_2' + \theta_2'')/2,$$

$$K_1 = \omega\,\mathrm{cth}\,\omega + \frac{\varkappa_{l1}s_{l1}}{\varkappa s}\,\omega_{l1} + \mathrm{Bi}_1, \quad K_0 = \frac{\mathrm{sh}\,\omega}{\omega},$$

$$K_2 = \omega\,\mathrm{cth}\,\omega + \frac{\varkappa_{l2}s_{l2}}{\varkappa s}\,\omega_{l2} + \mathrm{Bi}_2.$$

It can be seen from the equations obtained that if we change the thermal conditions in any fashion at the second end of the thermoelement (e.g., we increase the parameter Bi_2 by the quantity Bi_2', supplied to the end of the thermally insulated rod), the unknown quantities remain unchanged in Eq. (9). Using a method analogous to the previous, we obtain

$$2\nu\bar{\theta}_3 K_0 = \Delta\theta_1'' K_1 K_0 + \Delta\theta_2'', \tag{11}$$

$$2\nu\bar{\theta}_4 K_0 = \Delta\theta_1'' + \Delta\theta_2'' K_0 (K_2 + \mathrm{Bi}_2'), \tag{12}$$

where θ_1''', θ_2''' are the temperatures of the ends for the first current direction; and θ_1^{IV}, θ_2^{IV} are the temperatures of the ends for the second current direction;

$$\overline{\theta}_3 = \frac{(\theta_1''' + \theta_1^{IV})}{2}, \quad \overline{\theta}_4 = \frac{(\theta_2''' + \theta_2^{IV})}{2};$$

$$\Delta\theta_1'' = \theta_1^{IV} - \theta_1''', \quad \Delta\theta_2'' = \theta_2''' - \theta_2^{IV}.$$

In Eqs. (9)-(12) we may assume that $\overline{\theta}_1 = \overline{\theta}_2 = \overline{\theta}_3 = \overline{\theta}_4$. This condition holds with an error which is much less than γ. Then from Eqs. (9) and (10) we obtain an expression for the measurement of the thermal conductivity of the thermoelement:

$$\varkappa = \frac{e\overline{T}_1 Id}{s\Delta\overline{T}'}[1 - (\gamma' - \gamma'')] = \varkappa_0(1 - \gamma), \tag{13}$$

$$\gamma' = 1 \Big/ \left[1 + \frac{K_0(K_1 + K_2) - 2}{(K_1K_0 - 1)(K_2K_0 - 1)}\right], \tag{14}$$

$$\Delta\overline{T}' = \frac{\Delta T_1' + \Delta T_2'}{2}, \quad \gamma'' = K_0 - 1. \tag{15}$$

We obtain an expression for the direct measurement γ' from Eqs. (9) and (11)

$$\gamma' = \left(1 - \frac{\Delta\overline{T}''}{\Delta\overline{T}'}\right) \Big/ \left(\frac{\Delta T_1''}{\Delta T_1'} - \frac{\Delta\overline{T}''}{\Delta\overline{T}'}\right), \tag{16}$$

where

$$\Delta\overline{T}'' = \frac{\Delta T_1'' + \Delta T_2''}{2}.$$

The experiment may be set up in such a way that the condition $K_1 = K_2$ holds. We note that this case is considered in all the references as the Harman method. If here the heat-transfer coefficient from the lateral surface and the ends of the thermoelement are equal, then from Eqs. (14) and (15) for $\omega \ll 1$ we obtain

$$\gamma' = \frac{3 + 6\beta}{2}\gamma'' + \frac{1}{2}\gamma''', \tag{17}$$

where

$$\beta = \frac{s}{pd}, \quad \gamma''' = \frac{\varkappa_n s_n}{\varkappa s}\omega_n.$$

Allowing for Eq. (17), we obtain an expression to determine the correction term γ in Eq. (13)

$$\gamma = \frac{1 + 6\beta}{3 + 6\beta}\gamma' + \frac{1}{3 + 6\beta}\gamma'''. \tag{18}$$

In Eq. (18) the correction term γ' is experimentally measured according to Eq. (16). The terms γ'' and γ''' cannot be determined by a similar method because the value of Bi_2' in Eq. (12) is not known. This means that for different heat-transfer conditions at the ends, the correction term γ will be determined with a method error of γ''. For the same thermal conditions this error will be equal to the second term in Eq. (18). Calculated values of these errors are given in Table 1 for a cylindrical thermoelement at room temperature, of radius $r = d/4$ and made of material based on Bi_2Te_3. From the calculation it can be seen that this method should be used for conditions when $K_1 = K_2$. An experimental check of the validity of these conditions will be the equality $\Delta T_1' = \Delta T_2'$. Then, from Eq. (18) the error in determining the thermal conductivity is

$$\frac{\Delta\varkappa}{\varkappa} = \frac{\Delta\varkappa_0}{\varkappa_0} + \frac{\Delta\gamma'}{\gamma''}\gamma' + \frac{1}{3 + 6\beta}\gamma''', \tag{19}$$

where $\Delta\gamma'/\gamma'$ is the relative error in measurement γ' from Eq. (16). It can be shown that for $\gamma < 1$ the second term in Eq. (19) does not exceed the error in measuring the temperature difference $\Delta T_1'$, which, according to the data of [4], is 0.3% for the method which measures the timewise differences in copper–Constantan thermocouples. If we have $\Delta\varkappa_0/\varkappa_0 = 1\%$, then, $\Delta\varkappa/\varkappa = 1.6\%$.

TABLE 1. Conditions for the Measurement and Computation of Errors γ'' and γ'''

$\varkappa$, W/m · deg	$\alpha=\alpha_l$, W/m² · deg	$\varkappa_l$, W/m · deg	$d=4r$, m	r_l, m	γ''	γ'''
2	3	400	10^{-2}	$5 \cdot 10^{-5}$	$2 \cdot 10^{-2}$	$3 \cdot 10^{-3}$

Expressions (13)-(18) were obtained by solving the one-dimensional heat-conduction equation with the condition that the thermoelectric parameters are independent of temperature. In regard to the additional errors which can appear when the assumptions adopted are invalid, we can restrict ourselves to the following comments.

1. In [5, 6] γ was calculated for a cylindrical thermoelement, allowing for the temperature distribution over the section. It was shown that the additional terms which would then appear in γ have no practical significance if $(\alpha r/\varkappa) \leqslant 0.5$. From the data of Table 1, this condition is reached for $T \approx 1200°K$.

2. It was shown in [7] that if the thermal conductivity, the electrical conductivity, and the Thomson coefficient depend on temperature, then the heat-conduction process proceeds basically as it does for constant coefficients. The difference is that the Joule and Thomson heats in the general case are not divided strictly equally between the junctions of the thermoelement, through which the electric current flows. Then different terms, proportional to the differences of these heats, must appear in the expressions for K_1 and K_2. From the data of Table 1 and of [8], these additional terms can be neglected for a current through the element of 0.1 A, and a temperature difference between the junctions of 3°K.

3. From Eqs. (9) and (10) we can obtain the result that if the additional terms in K_1 and K_2 are small, then the functions $\Delta T_1'(I)$ and $\Delta T_2'(I)$ must be linear. Measurements conducted on specimens of materials based on Bi_2Te_3 have shown that the linearity of these relations is retained for currents up to $0.05I_0$, where I_0 is the optimal thermoelectric current. To create isothermal conditions at the ends, the latter were covered with a layer of solder of thickness up to $0.5 \cdot 10^{-3}$ m.

The method considered can be also used in determining the thermal diffusivity, the thermoelectric efficiency, and the heat-transfer coefficient of thermoelectric materials.

NOTATION

T, absolute temperature; Z, thermoelectric efficiency; $\varkappa$, ρ, e, thermal conductivity, specific resistance, and thermoelectric coefficient of the thermoelement; I, thermoelectric current; d, s, r, δ, length, cross-sectional area, radius, and thickness of the thermoelement; α, heat-loss coefficient from the lateral surface of the thermoelement; $\varkappa_l$, ρ_l, thermal conductivity and specific resistance of the current leads; α_l, heat-transfer coefficient from the surface of the current leads; p, perimeter of the thermoelectric cross section; r_l, s_l, radius and cross-sectional area of the current leads; $\chi = x/d$, dimensionless coordinate; $Bi = \alpha d/\varkappa$, the Biot number; $ZT = \theta$, dimensionless thermoelectric temperature; $\theta_l = ZT_l$, dimensionless temperature of the current leads; $\nu = (edI/\varkappa s)$; $\omega = d(\alpha p/\varkappa s)^{1/2}$; $\omega_l = d(2\alpha_l/\varkappa_l r_l)^{1/2}$; $C_l = (\varkappa s^2 \rho_l/\varkappa_l s^2_l \rho)$.

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