CONSTANT-POWER RESISTIVE-PROBE METHOD AND MEASUREMENT OF LIQUID-SEMICONDUCTOR THERMAL CONDUCTIVITY

B. M. Mogilevskii, V. N. Sokolov,
and A. F. Chudnovskii

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An experimental device for measurement of thermal conductivity of liquid semiconductors is described. Results are presented from thermal-conductivity measurements of a number of semiconductor alloys.

Of all known methods, the most convenient mode of measuring thermal conductivity is the constant-power probe [1]. This method features relatively simple construction of the measurement cell, allows protection of measurement and heating elements from aggressive media, reduces thermal losses to a minimum, and makes possible simultaneous study of thermal conductivity, electrical conductivity, and thermo-emf.

The constant-power probe method is based on solution of the problem of heating of a conductor (the probe) through which a current is passed, located in the medium whose thermal parameters are to be determined [2].

If the limitations arising from probe thermophysical parameters and finite dimensions of the specimen studied may be neglected, the probe surface temperature then proves to be linearly dependent on the logarithm of time, with the slope of this line being the quantity used in calculation of the coefficient of thermal conductivity [1, 2]:

$$\lambda_m = \frac{Q}{4\pi\gamma_0}, \text{ where } \gamma_0 = \frac{d\theta}{d\ln t}. \tag{1}$$

In practical applications of the method, it is necessary to precisely determine the conditions under which the logarithmic temperature-increase law, Eq. (1), is valid. Therefore, the effect of the shield isolating the probe from the medium and the radial and axial measurement-cell dimensions must be evaluated. The location of the probe within the measurement cell is shown in Fig. 1.

The probe used in the present study is a heater element made of thin, 50-μ-diameter platinum wire, encased in an Alundum shield 0.8-1 mm in diameter. The probe is located in a ceramic cell, formed on Minalundum or porcelain, which is filled with the substance to be studied. The measurement cell, in turn, is located in a cylindrical furnace. The temperature range of the experiments extended from room temperature to 1100°C. Since the platinum wire has a relatively high temperature coefficient, the heating probe may also be used as a resistance thermometer for measurement of transient probe temperature characteristics in the medium studied. In other variants of the method [1] probe temperature is determined by an adjacent thermocouple. The drawbacks of that method are obvious, since then the true probe temperature is unknown; moreover, temperature is determined at a single point, and not averaged over the length of the probe. The variant used in the present study will be termed the constant-power resistive-probe method. In order to eliminate the effects of contact resistance and resistance in the supply leads and to attain high enough heater currents in media with a high thermal conductivity, a Thompson-bridge measurement circuit is employed (Fig. 2). Under the influence of heating of the probe with resistance r_x by a current I_p, the initially balanced bridge unbalances, and a voltage U appears across the bridge arms and is recorded by a chart recorder:

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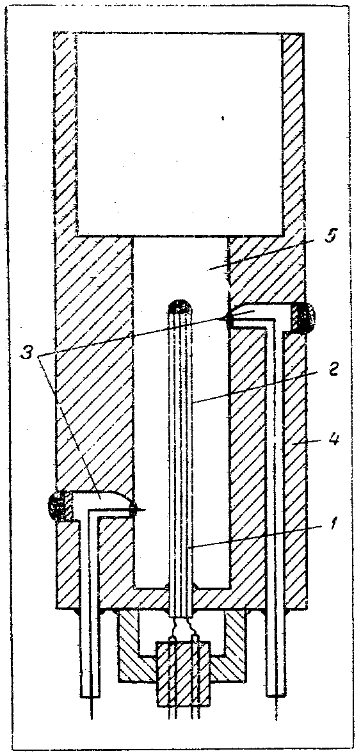

Fig. 1. Schematic diagram of measurement cell: 1) heater wire; 2) ceramic probe shield; 3) current leads, used for electrical-conductivity measurements; 4) measurement cell; 5) internal volume of measurement cell, filled with substance studied.

$$U = I\frac{R_3}{R_3+R_4}\cdot\frac{1}{\nu}\left[r_x - r_r\frac{R_4}{R_3} - \frac{r_A}{1+\beta}\left(\frac{S_1}{S_2}-1\right)\right], \tag{2}$$

where

$$\beta = \frac{r_A}{R_1+R_2};\quad S_1 = \frac{R_2}{R_1+R_2};\quad S_2 = \frac{R_3}{R_3+R_4};$$

and I is the current flowing in the bridge circuit. The quantity ν, close to unity, allows for the difference between the current heating the probe and the current in the bridge supply circuit

$$\nu = 1 + \frac{r_x + r_r}{R_3+R_4} + \frac{r_A}{R_3+R_4}\cdot\frac{R_1+R_2}{R_1+R_2+r_A}. \tag{3}$$

With the bridge initially balanced, the expression in square brackets on the right side of Eq. (2) is equal to zero. Therefore, the change $\Delta r_x = r_x - r_{x_0}$ (r_{x_0} being the value of r_x at balance) is expressed by

$$\Delta r_x = \frac{U}{I}\nu\frac{R_4+R_3}{R_3}. \tag{4}$$

If the change Δr_x is produced by heating of the probe to a temperature θ, then $\Delta r_x = \alpha\theta$, where $\alpha = dr_x/dT$ is the temperature (uncorrected) coefficient of resistance. Then from Eqs. (1), (4) we obtain

$$\theta = \frac{U\nu}{I\alpha}\cdot\frac{R_3+R_4}{R_3}, \tag{5}$$

$$\lambda_m = B\frac{R_4}{R_4+R_3}\cdot\frac{I^3}{\gamma}. \tag{6}$$

Here $B = 0.185\,\alpha r_r/l_3\nu^3$, $\gamma = dU/d\log t$, and at the balance point $\nu = 1 + r_r/R_3$, since the third term of Eq. (3) is very small (the shunt resistance r_A is low). It then follows from Eq. (6) that B is a constant quantity, independent of temperature, if α, r_r, and R_3 are constant and independent of temperature under experimental conditions. Constancy of r_r and R_3 can be achieved by use of highly stable resistors. As for α, a weak temperature dependence is possible. Consideration of this change in α may be achieved by calibration of the platinum probe at various temperatures. If we introduce the ratio of the coefficients α at different temperatures T and T_c in the form

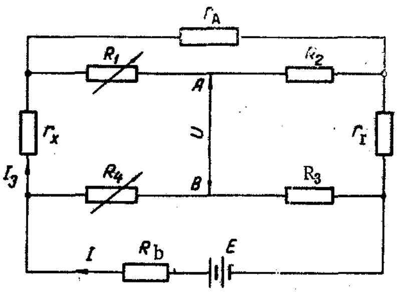

Fig. 2

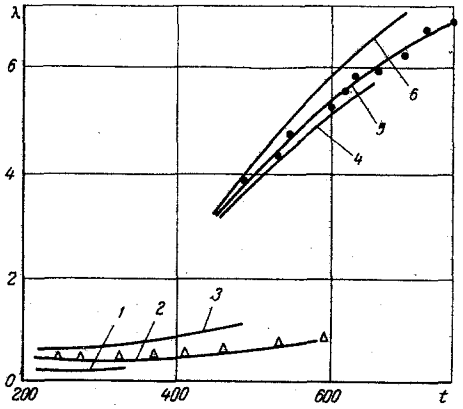

Fig. 3

Fig. 2. Bridge circuit for thermal-conductivity measurement: r_x) probe resistance; r_r) reference resistance; R_1, R_4) variable bridge resistors; r_A) current shunt resistance; R_b) ballast resistor in power-supply circuit.

Fig. 3. Coefficient of thermal conductivity of tellurium and selenium in the liquid state versus temperature: 1-3) Se; 1) [8]; 2) experimental points; 3) [7]; 4-6) Te; 4) [4]; 5) experimental points; 6) [3], t, °C.

$$N = \frac{\alpha(T)}{\alpha(T_c)} = f(T),$$

we obtain the formula

$$\lambda_m = B_c N \frac{R_4}{R_4 + R_3} \cdot \frac{I^3}{\gamma}, \tag{7}$$

where B_c is the calibration constant, referred to a calibration temperature T_c.

To calculate λ we measure the resistances R_3, R_4, the current I, and the value of γ, i.e., we construct the function U(log t), with the time zero point set at the moment of switch-on of the measurement current I. Then γ is the slope of the function U = f(log t). The coefficient B_c can be calculated from probe length, and the values α, r_r are known. However, it is possible to use an experimental value for B_c, determined with calibration liquids, for which water, glycerine, and mercury were used. Calibration was performed at room temperature. The computed and experimental values of B_c were close to each other.

At high heater currents in highly conductive media even a small temperature change in resistance r_r can introduce significant error in the measurement results. If it is impossible to achieve good temperature stability in reference resistor r_r, it is convenient to replace the latter by a probe immersed in a reference substance. Then the slope of the unbalanced voltage as a function of the logarithm of time is determined by the difference in the reciprocals of the thermal-conductivity coefficients of the specimen and reference substances. The right side of Eq. (6) remains the same, while in the left side the quantity λ is replaced by the expression

$$[\lambda_x^{-1} - D\lambda_r^{-1}]^{-1}, \tag{8}$$

where the indices x and r refer to the studied and reference media. The parameter D is equal to

$$D = \frac{\alpha_r l_x}{\alpha_x l_r}.$$

The use of two similar bridges, shown in Fig. 2, in one of which the probe is immersed in the medium to be studied, in the other, in the reference liquid, avoids the necessity of constructing the log time dependence. Switching each of the unbalanced voltages (from one Thompson bridge to the other) to the corresponding inputs of a two-coordinate chart recorder, a readout may be obtained in the form of a straight line whose slope is the ratio between the unknown and known thermal conductivities. A further modification of this method consists of eliminating the time recording of the unbalanced voltage. To do this the bridges are connected at points A. At the points B a galvanometer null indicator is connected. By adjusting the current in one of the bridges a balance point is reached, in which the rates of change of the unbalanced voltages of the two bridges coincide, and the indicator pointer does not deviate despite the increases in probe temperature. The ratio between the unknown and reference thermal conductivities is determined from the condition $d(U_1 - U_2)/dt = 0$, where U_1 and U_2 are the unbalanced voltages [Eq. (2)] across the first and second bridges, respectively. Finally, in the balance position we have

$$\frac{\lambda_x}{\lambda_r} = \left(\frac{I_x}{I_r}\right)^3 \left[\frac{r_x\alpha_x}{l_x} \cdot \frac{R_3}{R_3+R_4}\right]_x \left[\frac{r_r\alpha_r}{l_r} \cdot \frac{R_3}{R_3+R_4}\right]_r^{-1}. \qquad (9)$$

The advantage of this variant is that it eliminates the need of graphically recording transient processes. In the present study all of the above modifications were utilized. Data from the different variants were compared and found to be in satisfactory agreement.

In estimating the error in the method, it is especially important to consider that with the construction used Eq. (1) is approximately valid only over a certain time interval $t_{min} < t < t_{max}$, where the value t_{min} is connected with the effect of thermophysical parameters of probe and shield and t_{max}, with heat losses through the specimen faces and walls of the measurement cell. In order to determine t_{min}, we solve the problem of the temperature field of two coaxially arranged cylinders [1], using an expansion in large Fourier criteria $Fo_{ps} = t/\tau_{ps} \gg 1$ ($\tau_{ps} \geq \tau_{pm}$). From the complete solution, which has the form of a rapidly converging series, we retain only the first terms, which describe the departure from a logarithmic rule of temperature increase. Analogous treatment of small values $Fo_{sm} = t/\tau_{sm} \ll 1$ gives the value of t_{max}, i.e., the criterion for selection of maximum measurement time, beyond which the departure of the function $\theta = f(\ln t)$ from linearity becomes significant [1].

The time range over which, with the given approximation, Eqs. (1), (7) are applicable is defined by the condition [1]

$$t_{min} = L_1\tau_{pm} \leqslant t \leqslant L_2\tau_{sm} = t_{max}. \qquad (10)$$

The parameter L_1 must lie within the limits $10(a_s/a_m)(r_h/r_0)^2 \leq L_1 \leq 10$ (depending on the ratio λ_s/λ_m), if it is required that the function $\theta = f(\ln t)$ or the corresponding Eq. (1) approximate linearity within 5%.

More severe restrictions on experimental conditions with reference to end effects (the effects of finite length and radius of the specimen) develop with large differences between the thermal diffusivities of cell-wall material and specimen ($a_s \ll a_m$). Under such conditions the computational error of Eqs. (1), (7) does not exceed 5% if $L_2 = 0.3$ (at $l_3/R \geq 8$-10).

The total error in the thermal-conductivity determination, together with the methodical error, includes error produced by drift in the furnace temperature, instability in the probe-heating current, and errors in the bridge method of probe-temperature measurement; moreover, it is dependent on the accuracy of establishing calibration constant B_c [Eq. (7)]. For Minalundum vessels the total error does not exceed ±10%. For porcelain vessels error in λ measurement of highly conductive media ($\lambda > 2$ W/m · deg) increases to ±20% due to limitations on t_{max} (inner vessel radius did not exceed 8-10 mm).

To make a comparison with data from the literature, measurements were first made on substances whose thermal conductivity had been studied by various authors: Bi_2Te_3 [3,4], Te [5, 6], Se [1, 8]. Agreement with the more reliable results of [3, 4] was good (Fig. 3). In the metallized liquids Bi_2Te_3 and Te electron heat transfer predominates, its value being represented satisfactorily by the Wiedemann – Franz law: $\lambda_{el} = L_0\sigma T$ (with a small decrease in Bi_2Te_3; $L \sim 0.8\ L_0$). The increase in thermal conductivity (of quasilattice origin) with temperature in selenium is anomalous for dielectric liquids and is produced by strong associative bonds in the melt. The high temperature value $\lambda = \lambda_l = 0.4$ W/m · deg corresponds to theoretical evaluations by the Osida – Rao formula [10] and is characteristic of a dissociated liquid.

Data for several quasicrystalline semiconductor melts are presented in Fig. 4. These alloys were $0.8\ Sb_2Se_3 - 0.2\ Bi_2Se_3$; $0.6\ Sb_2Se_3 - 0.4\ PbSe$; $0.5\ Sb_2Se_3 - 0.5\ Sb$. Separation of the quasilattice and electron components of thermal conductivity may be done by extrapolation of the function $\lambda = \lambda_l + L\sigma T$ to zero values of the product σT. The initial ordinate of this function (at $\sigma T = 0$) corresponds to the quasilattice thermal conductivity, while the slope L is the Wiedemann – Franz ratio. Another method of evaluating λ_l is by use of the Osida – Rao formula [9].

For all the alloys mentioned λ_l lies within the limits 0.3-0.5 W/m · deg. At the same time the total Lorentz number $L = 1.5$-$2\ L_0$, for the composition $0.8\ Sb_2Se_3 - 0.2\ Bi_2Se_3$ and $L = 3$ for $0.6\ Sb_2Se_3 - 0.4\ PbSe$.

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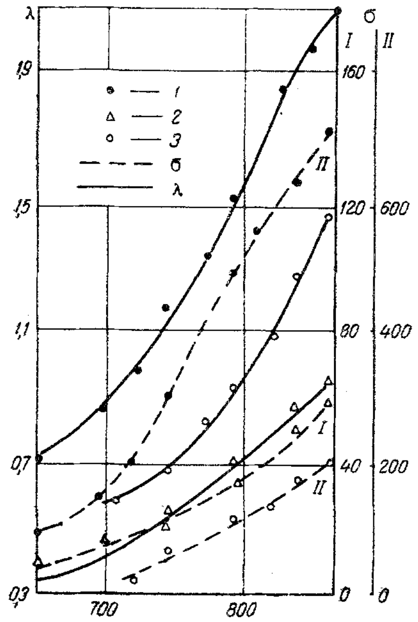

Fig. 4. Coefficient of thermal conductivity versus temperature for alloys in liquid state: 1) 0.5 $Sb_2Se_3 - 0.5$ Sb; 2) 0.6 $Sb_2Se_3 - 0.4$ PbSe; 3) 0.8 $Sb_2Se_3 - 0.2$ Bi_2Se_3. Abscissa, t, °C.

This increase in L values above the standard L_0 value is a consequence of bipolar thermal diffusion, preserved in the semiconductor liquids, and denotes the existence of an energy gap between zones. The high activation dependence of electrical conductivity and its values are additional evidence of the semiconductor character of the melts.

In contrast to previous alloys the mixture 0.5 $Sb_2Se_3 - 0.5$ Sb shows a small bipolar thermal-diffusion contribution only in the precrystallization region ($L \leq 1.25\text{-}1.5\,L_0$), which disappears rapidly with growth in temperature and electrical conductivity; $L = L_0$ even at $\sigma T = 4 \cdot 10^5\ \Omega^{-1} \cdot cm^{-1} \cdot deg$. Such rapid suppression of bipolar heat transfer permits classifying this mixture as a relatively more highly metallized liquid (at the same electrical-conductivity values) than the preceding alloys, and the alloys $Sb_2Te_3 - Sb_2Se_3$ [10]. The cause of this phenomenon should probably be sought in the high structural and composition microinhomogeneities distinguishing the electrical systems from solid-solution melts (such as the Sb_2Se_3 with Sb_2Te_3 and Bi_2Se_3 studied here).

NOTATION

$Q = I^2(r_x / l_r)$	is the power generated per unit probe length at current I;
r_x, r_r	are the probe resistances;
l_x, l_r, l_p	are the probe lengths;
θ	is the probe surface temperature;
t	is the time measured from switch-on of heater current I;
t_{min}, t_{max}	are the minimum and maximum times defining time range over limit of which probe temperature increase is a linear function of ln t to a given accuracy;
λ_m, a_m	are the thermal conductivity and thermal diffusivity of material studied;
λ_s, a_s	are the thermal conductivity and thermal diffusivity of casing material;
a_c	is the thermal diffusivity of measurement-cell material;
R	is the internal radius of measurement cell;
r_0	is the shield radius;
r_h	is the heater radius;
B_c	is the calibration constant in Eq. (7), determined at temperature T_c;
σ	is the electrical conductivity;
$\tau_{pm} = r_0^2 / a_m$;	
$\tau_{ps} = r_0^2 / a_s$;	
$\tau_{sm} = R^2 / a_m$;	
$\lambda = \lambda_r + \lambda_l$;	
λ_l	is the quasilattice thermal conductivity;
λ_r	is the electron thermal conductivity;
$L = \lambda_r / \sigma T$	is the Wiedemann – Franz ratio (Lorentz number);
$L_0 = (\pi^2/3)(k/l)^2$	is the Sommerfeld value of Lorentz number.