firm good prospects for using average elements for determining contact conductivity in heterogeneous systems.

NOTATION

λ, effective conductivity of heterogeneous system; m_m, volume concentration of discrete component; λ_c, thermal conductivity for cluster; λ, effective thermal conductivity; n_c, coordinate number; λ_M, thermal conductivity of discrete component; λ_d, thermal conductivity of continuous component (polymer); Δl, layer thickness in the contact zone.

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DETERMINATION OF THE THERMOPHYSICAL PROPERTIES OF SEMICONDUCTORS BY MEASURING THE SUPERPOSED GALVANO- AND THERMOMAGNETIC EFFECTS BY THE METHOD OF VARIATION OF ACTION FACTORS

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An analysis is made of the transients of superposed galvano- and thermomagnetic effects (GTME) in semiconductors. Formulas are obtained which permit determination of the thermophysical properties.

A method for the experimental investigation of kinetic effects in solids was proposed in [1], which is based on programmed variations of the action factors (AF) prescribed in the experiment. The possibility of a complete separation and recording of both the fundamental and superposed effects in the specimens under investigation is shown by using an example of determining the effects due to the action of temperature, electric, and magnetic fields. Only the steady-state values of the electrical quantities being recorded are here subjected to separation and subsequent processing. This circumstance narrowed the possibility of realizing one of the fundamental statements of the AF variational principle — obtaining the maximum quantity of information in one experiment for a given quantity of force fields therein.

In this connection, we examined the possibility of obtaining additional information about the thermophysical properties of the substances being studied by recording time measurements of the curves of the effects being superposed. For this an analysis was performed in [2] of the transient due to one of the effects being superposed (Ettingshausen), and it was shown that recording it actually permits the determination of the thermophysical characteristics of semiconductors.

Since superimposed effects, different in absolute value, can be observed in an experiment by the method of T, E, H field variation, as a function of the properties of the materials being studied, then performing a similar analysis for other effects as well is of essential interest.

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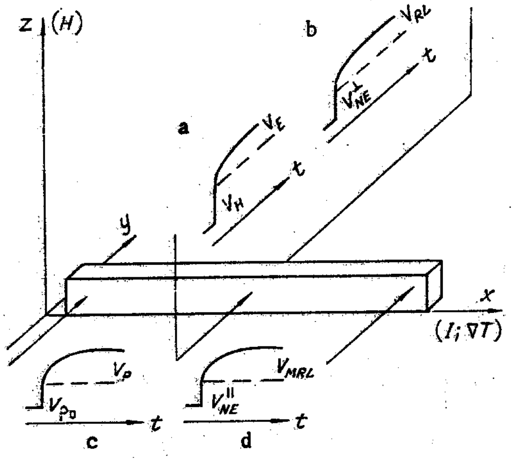

Fig. 1. Diagram of specimen location and of measuring probes relative to the H, E, and T fields and patterns of the emf of the recorded GTM effects: a) AF: E ≠ 0, H ≠ 0, transverse GM of the Hall and Ettinghausen effects; b) AF: T ≠ 0, H ≠ 0, transverse TM effects of Nernst–Ettingshausen and Riggi–Leduc; c) AF: E ≠ 0, longitudinal electrical resistivity and Peltier effects; d) AF: T ≠ 0, H ≠ 0, longitudinal Nernst–Ettingshausen and Magi–Riggi–Leduc TM effects (only the fundamental GTM effects are presented in patterns a–d. The complete diagram of the emf occurring at the probes is examined in [4]).

Each of the thermoelectric (TE), galvano- (GM), and thermomagnetic (TM) effects (Peltier, Ettingshausen, Riggi–Leduc, Nernst, Magi–Riggi–Leduc) are considered separately below, and it is shown that they are all described in the nonstationary mode by analogous formulas, and therefore, any of them can be used to determine the thermophysical properties of the specimens under investigation.

The Peltier effect is superposable relative to the main effect — electrical conductivity. The AF being varied is the electric field in the specimen. Analysis of the nonstationary mode of the Peltier effect was performed in [3], where the Joulean heat, the heat exchange between the specimen and the surrounding medium, and the heat loss in the conducting leads were taken into account.

For simplicity, the heat removal by the leads is not taken into account in this paper. It is also assumed that the temperature of the medium T_m is invariant, the specimen material is isotropic, and there are no components of the temperature gradient in the y and z directions (Fig. 1). The assumptions made are conserved also in examining other kinetic effects. Then the one-dimensional heat-conduction problem is formulated on the basis of [3] as follows:

$$\frac{\partial^2 T'(x, t)}{\partial x^2} - \beta^2 T'(x, t) + \frac{j^2}{\sigma\lambda} = \frac{1}{k}\frac{\partial T'(x, t)}{\partial t}, \tag{1}$$

$$\lambda \frac{\partial T'(0, t)}{\partial x} = aT'(0, t) - w_p(0, t), \tag{2}$$

$$-\lambda \frac{\partial T'(l, t)}{\partial x} = aT'(l, t) + w_p(l, t), \tag{3}$$

$$T'(x, 0) = 0, \tag{4}$$

where

$$w_p = \alpha j T(x, t); \quad \beta^2 = \frac{2a}{\lambda d}; \quad T'(x, t) = T(x, t) - T_m. \tag{5}$$

The Peltier effect is taken into account here in the boundary conditions (2) and (3) by the additional heat flux wp along the x axis, expressed in terms of the thermal emf coefficient α, the current density j, and the temperature T. The problem is solved by the Laplace transform method.

The solution for a longitudinal temperature drop $\Delta T_p(t) = T(0, t) - T(l, t)$ being formed in the initial time period has the form

$$\Delta T_p(t) = \frac{4}{\sqrt{\pi}} \frac{\alpha j T_m}{\lambda} \sqrt{kt}(1 - \xi_p), \tag{6}$$

where

$$\xi_p = \frac{\sqrt{\pi}a}{2\lambda}\sqrt{kt} + \frac{2}{3}\left(\frac{a}{\lambda d} + \frac{j^2}{\alpha\lambda T_m} - \frac{a^2 + \alpha^2 j^2}{\lambda^2}\right)kt + \dots. \tag{7}$$

The initial time period is determined by using the inequality

$$(kt)^{1/2} \ll \min\left\{b,\ \beta^{-1},\ \frac{\lambda}{|a|+|\alpha j|}\right\}. \tag{8}$$

The solution obtained below for the rest of the effects superposed are also subjected to analogous small time criteria.

In the opposite limit case $t \to \infty$ we obtain an expression for the stationary effect $T_{st,P} \equiv \Delta\varphi_P$, which becomes under the condition $\beta l \ll 1$

$$\Delta\varphi_P = \frac{\alpha j T_m l}{\lambda}\left(1 + \frac{j^2 d^2}{2a\sigma T_m (l+d)}\right). \tag{9}$$

For the following values of the quantities $a \simeq 4\ \mathrm{W \cdot m^{-2} \cdot K^{-1}}$, $\lambda \approx 8\ \mathrm{W \cdot m^{-1} \cdot K^{-1}}$, $l \approx d \approx 10^{-2}$ m, $j \simeq 10^4\ \mathrm{A \cdot m^{-2}}$, $\sigma \approx 10^2\ \Omega^{-1} \cdot \mathrm{cm}^{-1}$, $T = 300°$K, which are actually encountered, not only the condition $\beta l \simeq 10^{-1} \ll 1$ is satisfied, but also the condition for which the second component in (9) can be neglected: $j^2 d^2 (2a\sigma T_m)^{-1} (l+d)^{-1} \approx 0.02 \ll 1$.

We therefore obtain a linear dependence of $\Delta\varphi_P$ on l:

$$\Delta\varphi_P = \frac{\alpha j T_m l}{\lambda}. \tag{10}$$

Substituting $\Delta\varphi$ from (10) into (6), we arrive at the main formula

$$\frac{\Delta T_P(t)}{\Delta\varphi_P} = \frac{4}{\sqrt{\pi} l} \sqrt{kt}\,(1 - \xi_P). \tag{11}$$

The Nernst effect is superposable relative to the main effect of magnetoresistivity. The variable AF are the electric and magnetic fields. The galvanomagnetic Nernst effect (the change in the Peltier effect in a magnetic field) can be described by the additional quantity of heat w_N "being evolved and absorbed" at the specimen endfaces in the magnetic field.

If a magnetic field has already been imposed on the specimen up to the time of connecting the electric field E, then the formulation and solution of the problem agree completely with the problem about the Peltier effect examined above if $\alpha j T_m$ is replaced by $(\alpha j T_m + w_N)$ in this case, and then

$$\Delta T_N(t) = \frac{4}{\sqrt{\pi}} \frac{(\alpha j T_m + w_N)}{\lambda} \sqrt{kt}\,(1 - \xi_N) \tag{12}$$

or

$$\frac{\Delta T_N(t)}{\Delta\varphi_N} = \frac{4}{\sqrt{\pi} l} \sqrt{kt}\,(1 - \xi_N),$$

where

$$\xi_N = \frac{\sqrt{\pi} a}{2\lambda} \sqrt{kt} + \frac{2}{3}\left(\frac{a}{\lambda d} - \frac{a^2 + (\alpha j + w_N T_m^{-1})^2}{\lambda^2} + \frac{j^2}{\sigma\lambda T_m}\right) kt + \ldots \tag{13}$$

The Ettingshausen effect is a galvanomagnetic transverse thermal effect superposed on the main Hall effect. The variable AF are the electric and magnetic fields. The problem of the Ettingshausen temperature drop along the y axis after connecting the magnetic field differs from the problem of the Peltier effect only in that the x axis is replaced by the y axis and the flux $w_P = \alpha j T$ by $w_E = AT$ [2]. Hence, the solution has the form [2]

$$\Delta T_E(t) = \frac{4}{\sqrt{\pi}} \frac{A T_m}{\lambda} \sqrt{kt}\,(1 - \xi_E), \tag{14}$$

where

$$\xi_E = \frac{\sqrt{\pi} a}{2\lambda} \sqrt{kt} + \frac{2}{3}\left(\frac{a}{\lambda d} - \frac{a^2 + A^2}{\lambda^2} + \frac{j^2}{\sigma\lambda T_m}\right) kt + \ldots. \tag{15}$$

We again obtain (11) in the form presented, where $\Delta\varphi_E = A T_m b \lambda^{-1}$, and the transverse dimension b replaces l.

The Riggi–Leduc effect is a thermomagnetic transverse effect superimposed on the emf of the transverse Nernst–Ettingshausen effect. The variable AF are the longitudinal temperature gradient and the magnetic field. Making analogous assumptions about the appearance of w_{RL} along the y axis after the connection of the magnetic field, and taking into account that there is no Joulean heat evolution in this problem, we obtain

$$\Delta T_{RL}(t)=\frac{4}{\sqrt{\pi}}\,\frac{w_{RL}}{\lambda}\sqrt{kt}\,(1-\xi_{RL}), \tag{16}$$

where

$$\xi_{RL}=\frac{\sqrt{\pi}a}{2\lambda}\sqrt{kt}+\frac{2}{3}\left(\frac{a}{\lambda d}-\frac{a^2+(w_{RL}T_m^{-1})^2}{\lambda^2}\right)kt+\ldots, \tag{17}$$

and we obtain (11) in the form presented.

The Magi–Riggi–Leduc effect is a longitudinal thermomagnetic effect superimposed on the effect of a change in the thermal emf in a magnetic field. As in the previous effects, we consider that a thermal flux w_{MRL}, additional to the flux W already existing, occurs upon connection of the magnetic field, and we seek the change in the temperature drop with time:

$$\frac{\partial^2 T'(x,\ t)}{\partial x^2}-\beta^2 T'(x,\ t)=\frac{1}{k}\,\frac{\partial T(x,\ t)}{\partial t}, \tag{18}$$

$$\lambda\frac{\partial T'(0,\ t)}{\partial x}=aT'(0,\ t)-w_{MRL}, \tag{19}$$

$$-\lambda\frac{\partial T'(l,\ t)}{\partial x}=aT'(l,\ t)+w_{MRL}, \tag{20}$$

$$T'(x,\ 0)=\varphi(x). \tag{21}$$

The zero initial value (21) is the essential difference between this and the previous problems.

We find the initial temperature distribution $\varphi(x)$ by solving the stationary heat-conduction problem for the case H = 0. Assuming the temperature distribution $\varphi(x)$ to be determined by the creation of a heat flux W on the boundary x = 0 by an external source, and by the removal of the same quantity of heat per unit time –W at x = l, we obtain

$$\varphi(x)=T'(x,\ 0)=H_-\exp(\beta x)+H_+\exp(-\beta x), \tag{22}$$

where

$$H_\pm=\frac{W(\lambda\beta\pm a)\exp(\pm\beta l)-(\lambda\beta\mp a)}{(\lambda\beta+a)^2\exp(\beta l)-(\lambda\beta-a)^2\exp(-\beta l)}. \tag{23}$$

Problem (18)-(21) can be solved exactly as in the previous cases by using the Laplace transform. We consequently obtain

$$\Delta T_{MRL}(t)\equiv\Delta T(t)-\Delta T=\frac{2}{\sqrt{\pi}}L\sqrt{kt}-Mkt-\ldots \tag{24}$$

(the expressions for the coefficients L and M are not presented because of their awkwardness).

As follows from (6), (11), (12), (14), (16), (24), the growth processes for the superposed GTM effects considered at the initial times are subject to the law $\Delta T(t)\sim\sqrt{kt}$.

<u>Disconnect Mode.</u> The heat-conduction boundary-value problems in the AF disconnect mode differ from the AF-connect problems by nonzero initial conditions and the absence of additional heat fluxes w in the boundary conditions. For all the cases considered they turn out to be similar and only differ by the Joulean term in the heat-conduction equation, being present in problems for the GM and TE effects, and absent in the problems for the TM effects. The solution of the problem obtained for the galvanomagnetic Ettingshausen effect in the disconnect mode [2] shows that the terms dependent on the current j in the final formulas vanish since homogeneous evolution of Joulean heat only raises the mean temperature of the specimen and does not alter the temperature distribution therein. The drop of all the considered temperature drops relative to the stationary values of $\Delta\varphi$ at the initial times after disconnecting the AF is described [2] in the first approximation by the formula

$$\frac{\Delta\varphi-\Delta T(t)}{\Delta\varphi}=C\left(\frac{2}{\sqrt{\pi}}\sqrt{kt}-\frac{a}{\lambda}kt-\ldots\right), \tag{25}$$

where C = $(a/\lambda)+\beta\coth(\beta b/2)$. Under adiabatic conditions (a = 0) expression (25) simplifies:

$$\frac{\Delta\varphi - \Delta T(t)}{\Delta\varphi} = \frac{4}{\sqrt{\pi} b} \sqrt{kt} + O((kt)^{3/2}). \qquad (26)$$

Therefore, measurement of the nonstationary superposed effects considered permits the determination [formulas (11) and (26)] of the coefficient of thermal diffusivity k, and therefore, also of the heat-conduction coefficient λ for known c (specific heat) and ρ (density), as well as the thermal fluxes of the effects w_E, w_{RL}, w_N, w_P, w_{MRL} [formula (6) and its variants (12), (14), (16), (24)].

Under certain conditions several (usually two) of the superposed effects can be registered simultaneously on the measurement probes in the experiment. In these cases (26) and (11) retain their form; just Δφ therein has the meaning of a total (complete) stationary temperature drop. Therefore, the simultaneous measurement of the superposed effects does not hinder the determination of k and λ. Further investigations in this area should concern the explanation of nature and formulas for the additional heat fluxes of the effects w_E, w_{RL}, etc.

The analysis performed on the possibilities of determining the thermophysical properties of semiconductors substantially expands the prospects for using the method of variation of the AF in experimental investigations. The results obtained can turn out to be useful in studying the physical properties of thin films of solid materials and compounds, as well as in rheological investigations of different fluid media.

NOTATION

T_m, temperature of the surrounding medium; j, current density; w, heat flux of the different effects; σ, λ, k, α, a, coefficients of electrical, thermal conductivity, thermal diffusivity, thermal emf, and heat exchange with the surrounding medium; d, perimeter of the specimen cross section, and Δφ, initial temperature difference in the specimen.

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LATTICE THERMAL CONDUCTIVITY AND CHEMICAL BOND IN THE HYPOVALENT TWO-CATION SEMICONDUCTORS $A^1SbC_2^6$ AND $TlB^5C_2^6$

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The relation between the lattice thermal conductivity of $A^1SbC_2^6$ (A^1 = Li, Na, K, Rb, Cs; C^6 = S, Se) and $TlB^5C_2^6$ (B^5 = As, Sb, Bi; C_2^6 = S, Se, Te) and the nature of the chemical bond is investigated. It is shown that the relative radii of the atoms affects the melting point and thermal conductivity of these compounds.

The lattice thermal conductivity of complex semiconductors depends significantly on the chemical composition, structure, and nature of the chemical bond [1, 2]. The two groups of compounds that we selected as objects of investigation are largely analogous. Compounds of both groups are hypovalent chalcogenide semiconductors, since the B^5 elements are trivalent, and Tl in the second group of compounds is monovalent. They are formed in analogous quasi-binary sections A_2^1—$B_2^5C_3^6$ and Tl_2C^6—$B_2^5C_3^6$ with an equimolar ratio of the binary components [4-7].

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