# CONDUCTIVITY DETERMINATION FOR A FILLED HETEROGENEOUS SYSTEM

G. N. Dul'nev and V. V. Novikov                                    UDC 536.2.02

A method is given for determining the conductivity of a heterogeneous system
of matrix-filler type.

We consider the thermal and electrical conductivities of a heterogeneous system in which one component (the filler) is randomly distributed in the other (the matrix).

If the components differ greatly in conductivity (by two or three orders of magnitude), then the contacts between the particles play a considerable part in the transport. For clarity we consider heat transport in a compound consisting of a resin (insulator) filled with conducting metal particles. We use a combination of the average-element method with percolation theory.

The following is a qualitative description of the structure change as the volume concentration $m_m$ of the metal increases: initially there is the continuous bonding agent (e.g., polymer), and there are isolated groups oc metal particles, namely isolated clusters, but subsequently these clusters join up and form an infinite cluster, as shown in Fig. 1c.* Any further increase in $m_m$ results in an increase in the volume of the infinite cluster, and at some concentration $m_m = (m_m)_{max}$ the entire volume of the compound V is occupied by the infinite cluster. Data on the structure and properties of such compounds show that $(m_m)_{max} = 0.6$, i.e., the entire volume V is uniformly filled with particles for $m_m = 0.6$. Any further increase in the volume proportion of the particles only alters the particle packing and itself is possible only when a certain external pressure is applied [1].

On this basis, the determination of the effective conductivity splits up into two stages: initially we consider the conductivity of $\lambda_c$ of the clusters consisting of contacting particles, and then the effective conductivity $\lambda$ of the compound.

The metal particles are in contact in the compounds via thin layers of polymer, because the viscosity of the polymer is high and large pressures are needed to displace it from the contact areas, but high pressures are not used in preparing such compounds [2]. This feature of the contact between particles (the thin polymer layers) influences the heat transport and causes the effective thermal conductivity $\lambda$ to be almost independent of that of the filler particles [3-5].

We incorporate the effects on $\lambda$ from the transport through the contact areas by describing around a filler particle a polyhedron such that the faces are tangential to the points of contact (Fig. 1d). Then a cluster of metallic particles consists of polyhedra circumscribed around the particles, and the thermal conductivity of a cluster will be equal to that of the average polyhedron. The number of faces in such a polyhedron is dependent on the average corodination number of the particles in a cluster. Normalization with respect to the volume concentration of the mixture is required, and this can be determined in the form

$$m_{1p} = g m_m \tag{1}$$

where $g = v_p/v_0$ is a normalization factor; $v_p$, volume of a polyhedron; and $v_0$, volume of a particle.

In the case of a cube circumstribed around a spherical particle we have $g = 1.91$, while a hexagonal prism (coordination number $n_c = 12$) around a spherical particle gives $g = 1.56$.

The average-element concept [1] is used in determining the conductivity of a polyhedron drawn around a particle, in which that conductivity is derived from the conductivity of an

---

*This is evident from direct observations, and also from computer simulation of such structures [7-9].
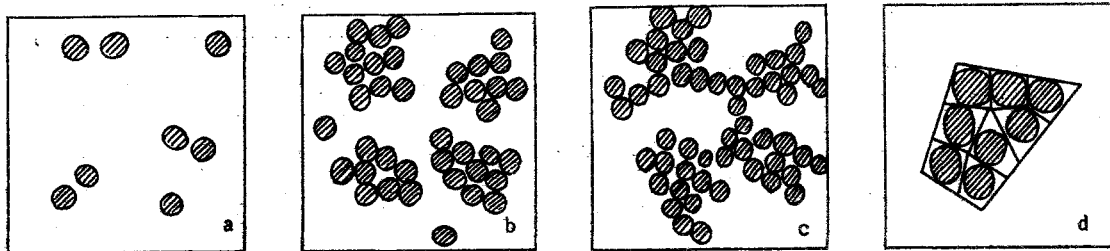
Fig. 1. Structure of a compound in relation to filler concentration: a) $m_m <$ 0.1; b) $0.1 < m_m < m_c$; c) $m_m > m_c$; d) part of a cluster of contacting particles.

average element as shown in Fig. 2a. The geometrical parameters of this element are dependent on the mean coordination number $n_c$ and are [1]

$$y_3 = \sqrt{n_c - 1}/n_c, \quad y_4 = y_3/\sqrt{1 - m_{2c}} \quad h = 1 - \Delta \bar{l} - \sqrt{1 - y_3^2}. \tag{2}$$

In turn, the coordination number is uniquely related to the concentration $m_{2c}$:

$$n_c = (m_{2c} + 3 + \sqrt{m_{2c}^2 - 10 m_{2c} + 9})/(2 m_{2c}),$$

where $y_3 = r_3/r$; $y_4 = r_4/r$; $\bar{h} = h/r$; $\Delta \bar{l} = \Delta l/r$; $\Delta l$ is the height of the thin layer in the contact zone between particles and $m_{2c}$ is the volume of polymer in a cluster of metallic particles as referred to the entire volume of the cluster ($m_{2c} = 0.4$).

We draw an auxiliary isothermal plane I — I in order to determine the conductivity of the average element; then Fig. 2b shows the equivalent circuit for averaging their resistances, where

$$R_1 = \frac{1}{\sigma_{1c}}; \quad R_2 = \frac{(r - h)}{\lambda_M \pi r_3^2}; \quad R_3 = \frac{r}{\lambda_d \pi (r_4^2 - r_3^2)}. \tag{3}$$

The expression for $\sigma_{1c}$ incorporates the conductivity of the spherical part of the gap and the adjacent part of the particle up to the auxiliary isotherm I–I (Fig. 2a):

$$\sigma_{1c} = \int_0^{2\pi} \int_0^r \left( \frac{r - \sqrt{r^2 - x^2}}{\lambda_d} - \frac{\sqrt{r^2 - x^2} - \sqrt{r^2 - r_3^2}}{\lambda_M} \right)^{-1} x \, dx \, d\vartheta. \tag{4}$$

Integration of (4) gives

$$\sigma_{1c} = \pi r \lambda_d B, \tag{5}$$

where

$$B = \frac{2}{(1 - v_M)^2} \left\{ (1 + \overline{\Delta l} - v_M \sqrt{1 - y_3^2}) \left[ \ln \frac{(1 + \overline{\Delta l} - \sqrt{1 - y_3^2})}{\overline{\Delta l} + v_M (1 - \sqrt{1 - y_3^2})} - (1 - v_M)(1 - \sqrt{1 - y_3^2}) \right] \right\}. \tag{6}$$

The equivalent circuit (Fig. 2b) indicates that the overall resistance $R_c$, on the one hand, is given by

$$R_c^{-1} = R_3^{-1} + (R_1 + R_2)^{-1}, \tag{7}$$

and on the other by

$$R_c = \frac{r}{\pi r_4^2 \bar{\lambda}_c}, \tag{8}$$

where $\lambda_c$ is the effective thermal conductivity of the average element.

We equate (7) and (8) to get

$$\lambda_c = \lambda_d \left[ y_4^2 - y_3^2 + \frac{B y_3^2}{y_3^2 + (1 - \bar{h}) B v_M} \right]. \tag{9}$$

A model has been suggested [6] for an inhomogeneous system based on percolation theory; the following expression was derived for the effective thermal conductivity:

$$\lambda = \lambda_c \left\{ \bar{s}_{1c} + v_{1c} \left[ \frac{\Delta \bar{s}_c}{1 - (1 - v_c) \bar{l}_{2c}} + 2 \frac{\bar{s}_{3c}}{1 - (1 - v_c) \bar{l}_{1c}} + \bar{s}_4 \right] \right\}, \tag{10}$$
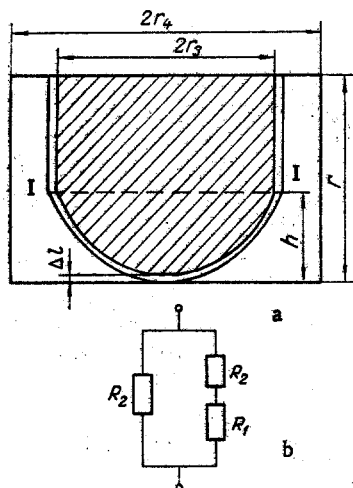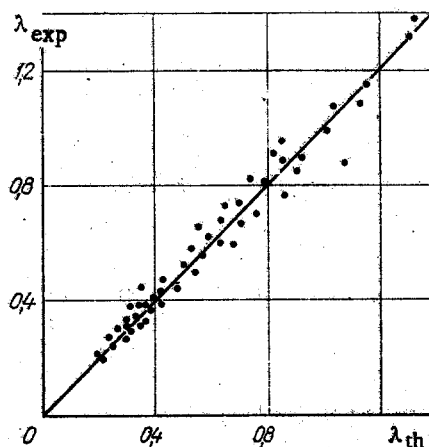
where

Fig. 2                                    Fig. 3

Fig. 2. Determination of the thermal conductivity of contacting particles: a) average element; b) the equivalent circuit for connection of the resistances in an average element.

Fig. 3. Comparison of the calculated effective thermal conductivity of a compound with measured values.

$$\bar{s_1} = \left(\frac{m_{1g} - m_{cg}}{1 - m_{cg}}\right)^{1,6}; \quad m_{cg} = gm_c; \quad l_{1c} = (s_{1c})^{-\frac{1}{2}}; \quad \bar{s}_{2c} = (m_{cg})^{-\frac{2}{3}}; \quad \bar{s_4} = 1 - \bar{s_2} - 2\bar{s_3}. \tag{11}$$

Here

$$\Delta\bar{s} = \bar{s}_{2c} - \bar{s}_{1c}, \quad l_{2c} = (m_{cg})^{-\frac{1}{2}}, \quad \text{if} \quad s_{2c} > s_{1c}$$

$$\overline{\Delta s} = 0, \quad l_{2c} = l_{1c}, \quad \text{if} \quad s_{2c} \leqslant s_{1c}. \tag{12}$$

Here $m_{cg}$ is the volume content of the filler at which a continuous group of particles arises.

We note that $\lambda_c$ has been derived on the assumption that the conductivity of a thin layer $\Delta l$ is that of the matrix $\lambda_d$. In fact, the structural orientation of the polymer molecules at the surface may mean that $\Delta l$ has conductivity $\lambda_t$ different from $\lambda_d$. However, the maximum possible difference $\Delta\lambda = \lambda_t - \lambda_d$ is small, i.e., $\delta = |\lambda_t - \lambda_d|/\lambda_d < 1$ is small, and therefore the effects of deviation of $\lambda_t$ from $\lambda_d$ on the effective conductivity will be slight. Therefore, the assumption that $\lambda_t = \lambda_d$ does not appear to result in a substantial error in approximate calculations on the effective thermal conductivity.

It is found that $\Delta l$ varies from a few molecular layers to some tens of such layers [2]; direct measurement of $\Delta l$ is difficult and no exact data on $\Delta l$ have been published. Therefore, for the approximate calculation of $\lambda$ we assume $\overline{\Delta l} = 0.05$, and $\Delta l$ can be refined by comparing the calculated $\lambda$ with experiment.

Therefore, the effective thermal conductivity is calculated in the following sequence:

1) The geometrical parameters of the average element are derived from (2).

2) The conductivity of the average element is derived from (9).

3) The volume concentration is renormalized from (1).

4) The effective conductivity is derived from (10).

These formulas were used in calculating the thermal conductivity of a compound as a function of the volume concentration of the particles for $m_m$ of 0-0.6, and in a comparison with experiment [3-5]. For $\overline{\Delta l} = 0.05$ the standard deviation of 64 results of measurement was $\sigma^* = 0.133$; the confidence range was $\varepsilon = 0.043$ for confidence probability $p = 0.99$ (Fig. 3).

This average element therefore allows one to determine the contact conductivity between particles in a heterogeneous system. Note that the shape of the contact area and the transport processes near the contact may vary, and therefore, the contact of an average element itself can vary. Figures have been given for average elements and the contact conductivity for granular systems [1] poured freely and after pressing and sintering. The results con-

firm good prospects for using average elements for determining contact conductivity in hetero-geneous systems.

## NOTATION

$\lambda$, effective conductivity of heterogeneous system; $m_m$, volume concentration of discrete component; $\lambda_c$, thermal conductivity for cluster; $\lambda$, effective thermal conductivity; $n_c$, coordinate number; $\lambda_M$, thermal conductivity of discrete component; $\lambda_d$, thermal conductivity of continuous component (polymer); $\Delta l$, layer thickness in the contact zone.

## LITERATURE CITED

1. G. N. Dul'nev and Yu. P. Zarichnyak, Thermal Conductivity of Mixtures and Composites [in Russian], Énergiya, Leningrad (1974).
2. Yu. S. Lipatov, Physical Chemistry of Filled Polymers [in Russian], Khimiya, Moscow (1977).
3. V. K. Baranovsky and W. B. Duschtschenko, Plaste Kautsch., No. 2 (1973).
4. K. W. Garrett and H. M. Rosenberg, J. Phys. D, Appl. Phys., 7, 1247 (1974).
5. F. F. T. Arauyo and H. M. Rosenberg, J. Phys. D, Appl. Phys., 9, 665 (1976).
6. G. N. Dul'nev and V. V. Novikov, Inzh.-Fiz. Zh., 36, No. 5 (1979).
7. S. Kirkpatrick, Rev. Mod. Phys., 45, No. 4 (1973).
8. B. I. Shklovskii and A. L. Éfros, Usp. Fiz. Nauk, 117, No. 3 (1975).
9. A. S. Skal and B. I. Shklovskii, Fiz. Tekh. Poluprovodn., 8, No. 8 (1974).

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

I. S. Lisker and M. B. Pevzner

UDC 536.2.083:538.665

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.