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EFFECTIVE THERMAL AND ELECTRICAL CONDUCTIVITIES OF ANISOTROPIC DISPERSED MEDIA

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We obtain formulas for determining the principal values of the thermal-conductivity and electrical-conductivity tensors of materials obtained by the pressing of a powder consisting of anisotropic grains.

Present-day industry makes extensive use of a number of materials obtained by pressing of a powder consisting of anisotropic particles. Thus, for example, the branches of thermoelements used in refrigerators and generators are obtained by pressing pulverized ternary alloys with a Bi_2Te_3 base [1] which have strong anisotropy in the original (single-crystal) state.

Even though the powder is isotropic before pressing, after the pressing it displays anisotropic properties, although to a lesser degree than in a single crystal. These phenomena were mentioned in [2-4]. The authors of those studies attributed the phenomenon to the presence of microcracks.

However, an explanation of the anisotropy phenomenon on the basis of microcracks alone is unjustified. In [5] it was shown that the anisotropy in thermal conductivity and electrical conductivity that may arise as a result of porosity in the pressing process is much lower than the observed value, and, consequently, cracks alone cannot explain the anisotropy. It should also be noted that in [2], although the anisotropy was attributed to the presence of microcracks, it was stated outright that no microcracks were observed. In [4] it is noted that specimens made of pressed material have a "visible texture," indicating the presence of a certain degree of disorder in the dispersed particles which results from pressing.

We shall show below that the anisotropy of pressed specimens can be completely explained by the appearance of a degree of disorder in the orientation of the dispersed particles with respect to the direction of pressing.

For this purpose, we shall derive relations for the effective thermal conductivity $\varkappa_{eff}$ and the effective electrical conductivity σ_{eff} of a dispersed material consisting of anisotropic particles.

We shall solve the problem for the following assumptions.

1. In deriving the relation, we shall start from the fundamental assumption that a dispersed medium is a system of chaotically arranged anisotropic particles whose orientation is characterized by a differential distribution function with respect to some direction.

2. At distances much greater than the dimensions of the individual grains the dispersed medium is spatially homogeneous.

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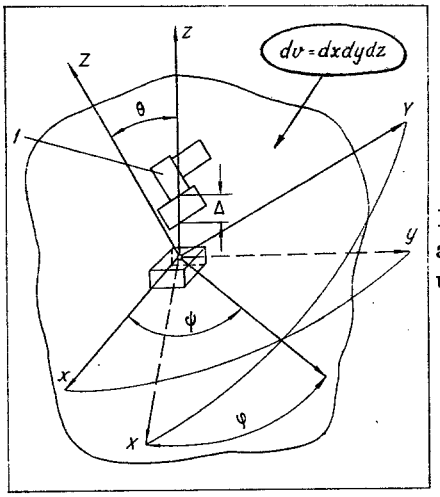

Fig. 1. Element of a dispersed anisotropic medium [1) individual grains].

3. We shall assume that we know the components of the thermal-conductivity and electrical-conductivity tensors for a single crystal along the principal axes: $\varkappa_{xx}, \varkappa_{yy}, \varkappa_{zz}$ and $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}$.

4. The effects of the grain boundaries are negligible.

5. A dispersed particle has the average dimensions l_x, l_y, l_z, respectively, in the directions of the principal axes X, Y, Z.

Such a problem was solved in [6,7]. However, the results of [6] are confined to the case of axial symmetry in the individual crystals making up a polycrystal and also to the case of a low degree of inhomogeneity (i.e., the cases of weakly anisotropic crystals and small dispersion in the orientation of the crystallites).

Odelevskii's study [7] is restricted by the assumption that the crystalline particles are "not elongated" and can be simulated by spheres (whereas the grains of ternary alloys with a Bi_2Te_3 base, owing to their high cleavability, have a lenticular shape, with a thickness-to-diameter ratio of about 1/4) and also by the assumption of equal probability of distribution of the grains along various directions, which is valid only when there is no anisotropy in the pressed specimen. We shall not adopt such restrictions.

Since the relations for the electrical-conductivity tensor are completely analogous to the relations for the thermal-conductivity tensor, all the derivations below will be carried out for the case of thermal conductivity.

Consider an element of volume of the dispersed medium dv = dxdydz, where we assume that the quantities dx, dy, dz are much larger than the dimensions of individual grains. We select the z axis of the Cartesian coordinate system to lie along the pressing axis. Since the directions perpendicular to the pressing axis are equivalent, the orientation of the x and y axes may be arbitrary.

With each grain of the pressed system we associate a Cartesian coordinate system X, Y, Z whose axes will be directed along the principal axes of the thermal-conductivity and electrical-conductivity tensors of the individual grain; the components of these tensors in the directions of the X, Y, Z axes will be $\varkappa_{xx}$, σ_{xx}; $\varkappa_{yy}$, σ_{yy}; $\varkappa_{zz}$, σ_{zz}, respectively.

The orientation of the X, Y, Z axes with respect to the system of coordinates x, y, z will be characterized by the Eulerian angles φ, ψ, θ (Fig. 1). In view of the chaotic orientation of the grains, the angles φ, ψ, θ will be random quantities.

Let the temperature gradient lie along the z axis (the pressing axis). We define the effective thermal conductivity in this pressing direction as $\varkappa_{eff\ z}$.

Any straight line drawn in the volume element dv parallel to the z axis will intersect some number of grains of the dispersed system (see Fig. 1). We denote the segment of this line which lies inside an individual particle by Δ. Obviously, Δ is a function of the angles φ, ψ, θ and of the coordinates of the center of inertia of the grains, x, y, z:

$$\Delta = F_0(x, y, z, \varphi, \psi, \theta). \tag{1}$$

TABLE 1. Effective Values of Thermal Conductivity and Electrical Conductivity

Conductivity	Calculated values: top	Calculated values: middle (side)	Calculated values: end face	Experimental values	Conductivity	Calculated values: top	Calculated values: middle (side)	Calculated values: end face	Experimental values
n-type alloy: 80% Bi_2Te_3—20% Bi_2Se_3)					p-type alloy: 74% Sb_2Te_3—26% Bi_2Te_3)				
$\varkappa_{eff\,z}$, $W \cdot m^{-1} \cdot deg^{-1}$	0,61	0,65	0,62	0,635	$\varkappa_{eff\,z}$, $W \cdot m^{-1} \cdot deg^{-1}$	0,73	0,783	0,74	0,836
$\varkappa_{eff\,x}$, $W \cdot m^{-1} \cdot deg^{-1}$	0,93	0,945	0,94	0,925	$\varkappa_{eff\,x}$, $W \cdot m^{-1} \cdot deg^{-1}$	0,90	0,935	0,90	0,925
$\sigma_{eff\,z} \cdot 10^{4}$, $\Omega^{-1} \cdot m^{-1}$	3,0	3,5	3,0	2,75	$\sigma_{eff\,x} \cdot 10^{-4}$, $\Omega^{-1} \cdot m^{-1}$	3,75	4,20	3,85	4,00
$\sigma_{eff\,x} \cdot 10^{-4}$, $\Omega^{-1} \cdot m^{-1}$	9,6	9,75	9,6	8,0	$\sigma_{eff\,x} \cdot 10^{-4}$, $\Omega^{-1} \cdot m^{-1}$	8,25	7,90	8,00	8,00
$\sigma_{eff\,x}/\sigma_{eff\,z}$	3,2	2,8	3,2	2,9	$\sigma_{eff\,x}/\sigma_{eff\,z}$	2,20	1,90	2,08	2
$\varkappa_{eff\,x}/\varkappa_{eff\,z}$	1,52	1,45	1,51	1,46	$\varkappa_{eff\,x}/\varkappa_{eff\,z}$	1,23	1,14	1,22	1,1

In view of assumption 1, the coordinates x, y, z and the angles φ, ψ, θ are independent random quantities, and, consequently, we can average the quantity Δ with respect to x, y, z. The averaging process yields $\Delta_{av} = F_1(\varphi, \psi, \theta)$.

The thermal conductivity $\varkappa_z$ of the material of the grain in the direction of the z axis will be [8]

$$\varkappa_z = \varkappa_{zz} \cos^2\theta + \varkappa_{yy} \sin^2\varphi \sin^2\theta + \varkappa_{xx} \sin^2\theta \cos^2\varphi. \tag{2}$$

For heat flux in the direction of the z coordinate we then have

$$q = \varkappa_z \cdot \Delta T/\Delta_{av}, \tag{3}$$

where ΔT is the temperature drop across an individual particle of the dispersed system.

In order to determine the temperature difference dT over a length dz, we must sum the temperature drops over all the particles intersected by the z axis along a length dz. To do this, we must know the probability that the Eulerian angles will have values equal to φ, ψ, and θ. This probability will be characterized by the differential distribution function for the Eulerian angles, $f(\varphi, \psi, \theta)$.

Since φ, ψ, θ are independent random variables, it follows that $f(\varphi, \psi, \theta)$ can be represented in the form of a product [9]

$$f(\varphi, \psi, \theta) = f_1(\varphi)\, f_2(\psi)\, f_3(\theta). \tag{4}$$

Thus, the number of particles dN intersected by a straight line over the length dz for which the z axis has direction cosines corresponding to the angles φ, ψ, θ will be

$$dN = \frac{1}{\Delta_{av}} f(\varphi, \psi, \theta)\, dz d\varphi d\psi d\theta. \tag{5}$$

Making use of (3)-(5), we find

$$q \int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \frac{\Delta_{av}}{\varkappa_z} \cdot \frac{1}{\Delta_{av}} f_1(\varphi)\, f_2(\psi)\, f_3(\theta)\, d\varphi d\psi d\theta dz = dT. \tag{6}$$

Since

$$q = \varkappa_{eff} \frac{dT}{dz}, \tag{7}$$

it follows that for $\varkappa_{eff\,z}$ we obtain from (3), (6), (7) the expression

$$\varkappa_{eff\,z} = \frac{1}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \frac{f_1(\varphi)\, f_2(\psi)\, f_3(\theta)\, d\varphi d\psi d\theta}{\varkappa_{zz}\cos^2\theta + \varkappa_{yy}\sin^2\varphi\sin^2\theta + \varkappa_{xx}\cos^2\varphi\sin^2\theta}}. \tag{8}$$

Similarly, for the direction of the y and x axes we obtain

$$\varkappa_{\text{eff}\,y} = \frac{1}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \frac{f_1(\varphi)\, f_2(\psi)\, f_3(\theta)\, d\varphi d\psi d\theta}{\Phi(\varphi,\ \psi,\ \theta)}}, \tag{9}$$

where

$$\Phi(\varphi,\ \psi,\ \theta) = \varkappa_{zz}\cos^2\psi\sin^2\theta + \varkappa_{yy}(\cos\psi\cos\varphi\cos\theta - \sin\psi\sin\varphi) + \varkappa_{xx}(\cos\varphi\sin\psi + \sin\varphi\cos\psi\cos\theta)^2,$$

and

$$\varkappa_{\text{eff}\,x} = \frac{1}{\int_0^{2\pi}\int_0^{2\pi}\int_0^{\pi} \frac{f_1(\varphi)\, f_2(\psi)\, f_3(\theta)\, d\varphi d\psi d\theta}{F(\varphi,\ \psi,\ \theta)}}. \tag{10}$$

where

$$F(\varphi,\ \psi,\ \theta) = \varkappa_{zz}\sin^2\psi\sin^2\theta + \varkappa_{yy}(\cos\psi\sin\varphi + \sin\psi\cos\varphi\cos\theta)^2 + \varkappa_{xx}(\cos\psi\cos\varphi - \sin\varphi\sin\psi\cos\theta)^2.$$

Formulas (8)-(10) are the desired relations for determining the effective thermal conductivity. The formulas for σ_{eff} are obviously obtained by a simple substitution of σ for $\varkappa$.

In order to determine $\varkappa_{\text{eff}}$ and σ_{eff}, we must know the distribution functions $f_1(\varphi)$, $f_2(\psi)$, and $f_3(\theta)$, which can be obtained by x-ray structural analysis.

We conducted investigations of the anisotropy of the branches of thermoelements obtained by powder metallurgy from the ternary alloy $Bi_2Te_3 + Bi_2Se_3$ and $Sb_2Te_3 + Bi_2Te_3$.

The original powder had isotropic properties. Because of the high cleavability of the material along planes perpendicular to the Z direction, the particles had the shape of a lamella, with a much smaller dimension in the Z direction than in the X and Y directions. The dimensions along X and Y varied between 0.2 and 2 mm for powders of various degrees of granularity.

Since the single crystal is axially symmetric with respect to the Z axis,

$$\varkappa_{xx} = \varkappa_{yy} \text{ and } \sigma_{xx} = \sigma_{yy}. \tag{11}$$

Despite the isotropic properties of the original powder, during the pressing process, because of the characteristic form of the grains, the individual lamellae slip with respect to one another along cleavage planes, and as a result the pressed material displays anisotropic properties. Since axial symmetry is ensured by the pressing conditions, it follows that if we choose the z axis in the direction of pressing, there will be no anisotropy in the angles φ and ψ, i.e.,

$$f_1(\varphi) = \text{const} \text{ and } f_2(\psi) = \text{const}. \tag{12}$$

Taking account of (11) and (12), we can write Eqs. (8)-(10) in the following form:

$$\varkappa_{\text{eff}\,z} = \frac{1}{\int_0^{\pi} \frac{f_3(\theta)\, d\theta}{\varkappa_{zz}\cos^2\theta + \varkappa_{xx}\sin^2\theta}}, \tag{13}$$

$$\varkappa_{\text{eff}\,y} = \frac{1}{\int_0^{2\pi}\int_0^{\pi} \frac{f_3(\theta)\, d\psi d\theta}{\varkappa_{zz}\cos^2\psi\sin^2\theta + \varkappa_{yy}(1 - \cos^2\psi\sin^2\theta)}}, \tag{14}$$

$$\varkappa_{\text{eff}\,x} = \frac{1}{\int_0^{2\pi}\int_0^{\pi} \frac{f_3(\theta)\, d\psi d\theta}{\varkappa_{zz}\sin^2\psi\sin^2\theta + \varkappa_{yy}(1 - \sin^2\psi\sin^2\theta)}}. \tag{15}$$

Averaging with respect to the angle ψ in (14) and (12), we obtain

$$\varkappa_{\text{eff}\,x} = \varkappa_{\text{eff}\,y} = \frac{1}{\int_0^{\pi} \frac{f_3(\theta)\, d\theta}{\sqrt{\varkappa_{yy}(\varkappa_{zz}\sin^2\theta + \varkappa_{yy}\cos^2\theta)}}}. \tag{16}$$

The distribution function $f_3(\theta)$ was obtained from x-ray structural analysis data [in (16), $f_3(\theta)$ is normalized].

The results of the experimental determination of $f_3(\theta)$ for specimens of various degrees of granularity are given in [4]. According to the data of [4], in pressed specimens there is strong anisotropy in the orientation of the crystals, which must also affect the amount of anisotropy in the coefficients $\varkappa$ and σ. In [4] the absence of any texture in two cases in the middle of the specimen should be attributed not to the absence of anisotropy, but to the fact that in order to take x-ray pictures in the middle of the specimen, the experimenters cut it into two parts, which probably led in some cases to a breakdown of the structure and to a change in the anisotropy in comparison with whole specimens.

In Table 1 we show the experimentally measured effective values of electrical conductivity $\sigma_{\text{eff}\,z}$, $\sigma_{\text{eff}\,x}=\sigma_{\text{eff}\,y}$, the effective values of the lattice component of the thermal conductivity $\varkappa_{\text{eff}\,z}$, $\varkappa_{\text{eff}\,x}=\varkappa_{\text{eff}\,y}$, and the ratios of the coefficients $\sigma_{\text{eff}\,x}/\sigma_{\text{eff}\,z}$ and $\varkappa_{\text{eff}\,x}/\varkappa_{\text{eff}\,z}$ (characterizing the anisotropy in the x and z directions) and the same coefficients obtained by calculation using formulas (13) and (16). The calculations were carried out for specimens of types n and p (see Table 1), with grain sizes ranging from 0.2 to 0.25 mm for the n-type and from 1 to 2 mm for the p-type. The calculations performed for specimens of types n and p with different granularity (from 0.05 to 2 mm) yielded analogous results.

The components of the electrical-conductivity and thermal-conductivity tensors along the principal axes for the material of the grains are the following [4]:

$$\text{n-type: } \sigma_{zz}=2.10\cdot10^4\ \ \Omega^{-1}\cdot\text{m}^{-1};\ \sigma_{xx}=\sigma_{yy}=12\cdot10^4\ \ \Omega^{-1}\cdot\text{m}^{-1};$$
$$\varkappa_{zz}=0.526\ \ \text{W}\cdot\text{m}^{-1}\cdot\text{deg}^{-1};\ \varkappa_{xx}=\varkappa_{yy}=1.02\ \ \text{W}\cdot\text{m}^{-1}\cdot\text{deg}^{-1};$$
$$\alpha=183\cdot10^{-6}\ \text{V}\cdot\text{deg}^{-1};$$

$$\text{p-type: } \sigma_{zz}=2.50\cdot10^4\ \ \Omega^{-1}\cdot\text{m}^{-1};\ \sigma_{xx}=\sigma_{yy}=10.0\cdot10^4\ \ \Omega^{-1}\cdot\text{m}^{-1};$$
$$\varkappa_{zz}=0.647\ \ \text{W}\cdot\text{m}^{-1}\cdot\text{deg}^{-1};\ \varkappa_{xx}=\varkappa_{yy}=0.98\ \ \text{W}\cdot\text{m}^{-1}\cdot\text{deg}^{-1};$$
$$\alpha=210\cdot10^{-6}\ \text{V}\cdot\text{deg}^{-1}.$$

The calculated values in Table 1 are shown for three values of the distribution function $f_3(\theta)$, which characterize the orientation of the grains both near the surface ("top," "end face") and in the middle ("middle," "side"). As can be seen from the table, the calculated values are in satisfactory agreement with the experimental data.

Thus, it must be recognized that the observed anisotropy in the values of $\varkappa$ and σ in pressed specimens can be completely explained by the orientation of the grains during the pressing process, and the conclusions drawn in [4] concerning the absence of grain orientation in pressed specimens are based on an incorrect treatment of the data obtained by x-ray structural analysis.

NOTATION

$\varkappa$, lattice component of thermal conductivity; σ, specific electrical conductivity; q, heat flux; T, absolute temperature; x, y, z, axes of Cartesian coordinate system associated with the pressed specimen (where the z axis coincides with the pressing direction); X, Y, Z, axes of Cartesian coordinate system associated with an individual grain.

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