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ON THE ELECTRIC CONDUCTIVITY OF CONTACTING PARTICLES OF THERMOELECTRIC MATERIAL

In the isotropic approximation the electric conductivity was calculated for a physical model – two half-spheres contacting in a circle with regard to electron scattering on the contact boundary as applied to Bi_2Te_3. It is shown that the value of effective electric conductivity of this material in the temperature range of 300 K and higher can be retained if contact radius exceeds 10.4 of mean free path of electron (hole). Calculated data are briefly discussed from the general physics and applied standpoints of thermoelectric material science.

Key words: thermoelectric material, extrusion, figure of merit, conductivity, shape-forming element, contact, boundaries, electrons, phonons, scattering.

Introduction

One of the most efficient conventional thermoelectric materials used today for the manufacture of working members of thermoelectric instruments and devices is bismuth telluride Bi_2Te_3. Its single crystals are traditionally prepared by one of the three methods, namely zone recrystallization, Czochralski pulling and oriented crystallization. The specific feature of Bi_2Te_3 single crystal is the presence of cleavage planes, along which it easily splits, by virtue of which with a reasonable degree of accuracy it can be considered to be layered. Besides, Bi_2Te_3 single crystal possesses a pronounced thermal conductivity and electric conductivity anisotropy. Thermal conductivity χ_{11} of this crystal along cleavage planes is 2 – 3 times larger than its thermal conductivity χ_{33} in the direction normal to these planes. Quite similarly, electric conductivity σ_{11} of Bi_2Te_3 along cleavage planes for *p*-type material is a factor of 2.7, and for *n*-type material – a factor of 4 – 6 larger than electric conductivity σ_{33} in the direction normal to cleavage planes. For this reason, to maximize thermoelectric figure of merit, thermoelectric modules of single crystals are made so that electric current and temperature gradient are parallel to cleavage planes.

Alongside with single-crystal materials, polycrystalline materials are used for the manufacture of thermoelectric modules. They can be divided into two classes: materials with oriented cleavage planes of individual crystallites and materials with a disordered (random) orientation of cleavage planes of individual crystallites. For the latter materials, according to the Odelevsky formula, electric conductivity is $\sigma = \sqrt{\sigma_{11}\sigma_{33}}$ and thermal conductivity is $\chi = \sqrt{\chi_{11}\chi_{33}}$.

Materials prepared by extrusion method in their structure are similar to polycrystalline materials with disordered orientation of cleavage planes of individual crystallites. Therefore, by virtue of the Odelevsky formula, in going from a single crystal to extruded material, the thermoelectric figure of merit must mostly drop. However, in actual practice such a drop is not observed. Hence, a mechanism must exist due to which material thermal conductivity drops, and electric conductivity is retained.

One of possible mechanisms of electric conductivity retention is quantum tunneling mechanism which manifests itself at small, i.e. comparable to electron (hole) de Broglie wavelength dimensions of thermoelectric material particles and contacts between them. The authors of [1] were among the first to pay attention to this fact. In [2] this mechanism was studied in more detail as applied to $Bi_xSb_{2-x}Te_3$. Exactly due to a large role of tunnelling effect in the formation of electric conductivity the researchers' attention is drawn to materials of the type TTF-TCNQ and similar to them with large carrier mobilities and the lowest lattice thermal conductivity [3-5].

At the same time, in the manufacture of thermoelectric products of conventional materials by hot pressing or extrusion, of current concern is a problem of optimal in terms of thermoelectric figure of merit dimensions of thermoelectric material grains and contacts between them. In particular, a question arises whether these dimensions can be selected so as to retain the electric conductivity of thermoelectric material particle aggregates with a simultaneous reduction of their thermal conductivity.

The form-shaping element of extruded material structure can be a system of two half-spheres of macroscopic radius R contacting in a circle of radius r [6]. The purpose of this work is to calculate the electric conductivity of such a system with regard to electrons or holes scattering on the contact boundaries.

Phenomenological consideration of the problem

Let us determine the effective electric conductivity of a system of two half-spheres of radius R of thermoelectric material contacting in a circle of radius r as a ratio of current through the system to potential difference between the large circles of half-spheres. A physical model of this problem is shown in Fig. 1.

In the formulation of the problem it is assumed that the surfaces of half-spheres are electrically isolated, their bases (large circle planes) are maintained at given potentials φ_1 and φ_2, and tunnelling of carriers to a gap between the spherical surfaces is ignored.

For the analytical calculation of potential distribution in such a system we will make direct use of Ohm's law. Let us direct the Z axis of coordinate system along the common axis of half-spheres. Then in the area of half-sphere with a larger potential from Ohm's law follows the equation:

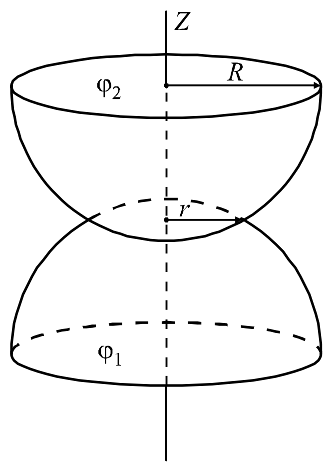


Fig. 1. Physical model of the problem.

$$-\sigma_0\pi\left(R^2 - z^2\right)\frac{\mathrm{d}\varphi}{\mathrm{d}z} = I \;, \tag{1}$$

where σ_0 is known electric conductivity of half-sphere material, φ is potential, I is current through the system to be determined from the boundary conditions. The solution of Eq. (1) is of the form:

$$\varphi = \varphi_1 - \frac{I}{2\sigma_0\pi R}\ln\frac{R+z}{R-z}\,. \tag{2}$$

Hence we find the contact potential:

$$\varphi_s = \varphi_1 - \frac{I}{2\sigma_0 \pi R} \ln \frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}}. \tag{3}$$

If, however, current coordinate varies within a half-sphere with a smaller potential $\sqrt{R^2 - r^2} \le z \le 2\sqrt{R^2 - r^2}$, from Ohm's law follows the equation:

$$-\sigma_0 \pi \left(R^2 - \left(2\sqrt{R^2 - r^2 - z} \right)^2 \right) \frac{d\varphi}{dz} = I. \tag{4}$$

Solution of Eq.(4) is given by:

$$\varphi = \varphi_1 - \frac{I}{\sigma_0 \pi R} \ln \frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}} - \frac{I}{2\sigma_0 \pi R} \ln \frac{R - 2\sqrt{R^2 - r^2} + z}{R + 2\sqrt{R^2 - r^2} - z}. \tag{5}$$

Satisfying condition $\varphi|_{z=2\sqrt{R^2-r^2}} = \varphi_2$, we get the following expression for current through the system:

$$I = \frac{\pi R \sigma_0 (\varphi_1 - \varphi_2)}{\ln\left(\frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}} \right)}. \tag{6}$$

Therefore, the effective electric conductivity of a system of two half-spheres in S (Ω^{-1}) is equal to:

$$\sigma_{ef} = \frac{\pi R \sigma_0}{\ln\left(\frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}} \right)}. \tag{7}$$

At $r/R << 1$ this formula goes over into:

$$\sigma_{ef} = \frac{\pi R \sigma_0}{\ln\left(4R^2/r^2 \right)}. \tag{8}$$

So, the final expression for potential distribution in a half-sphere with a larger potential is as follows:

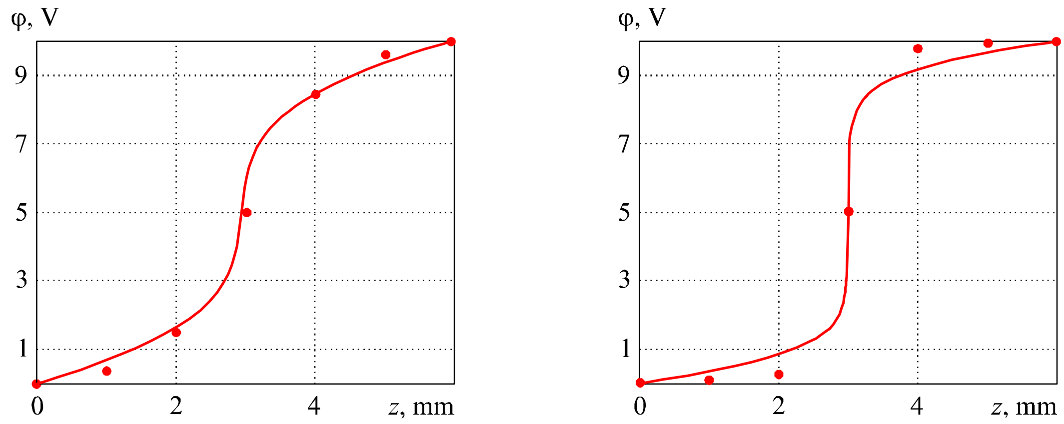
$$\varphi = \varphi_1 - 0.5(\varphi_1 - \varphi_2) \frac{\ln \frac{R+z}{R-z}}{\ln \frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}}}. \tag{9}$$

Whereas in a half-sphere with a smaller potential this expression is given by:

$$\varphi = \varphi_2 + 0.5(\varphi_1 - \varphi_2) \frac{\ln \frac{R + 2\sqrt{R^2 - r^2} - z}{R - 2\sqrt{R^2 - r^2} + z}}{\ln \frac{R + \sqrt{R^2 - r^2}}{R - \sqrt{R^2 - r^2}}}. \tag{10}$$

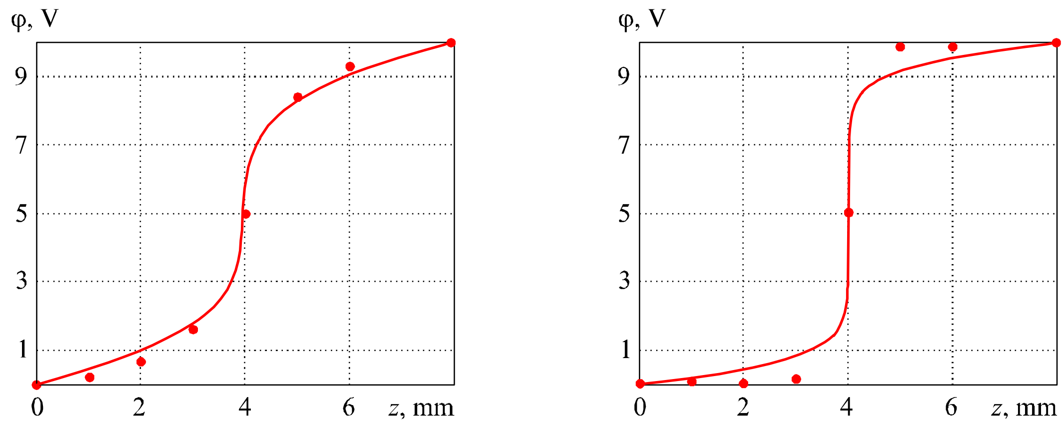
Examples of potential fields in a system of two half-spheres are shown in Figs. 2 and 3. The Z axis is directed as in Fig. 1, i.e. from the base with a smaller potential to that with a larger potential. For simulation the values $\varphi_1 = 10$ V, $\varphi_2 = 0$ V, $R = 3$ and 4 mm, $r = 500$ and 25 μm were taken.

For comparison, crosses on the same plots are used to show the results of a numerical solution of Laplace's equation for a system of two half-spheres with the aid of "Comsol Multiphysics" program. The distinctions are mostly due to the error of difference approximation of differential operators with a numerical solution of second-order differential equations in partial derivatives by method of networks.



a) *b)*

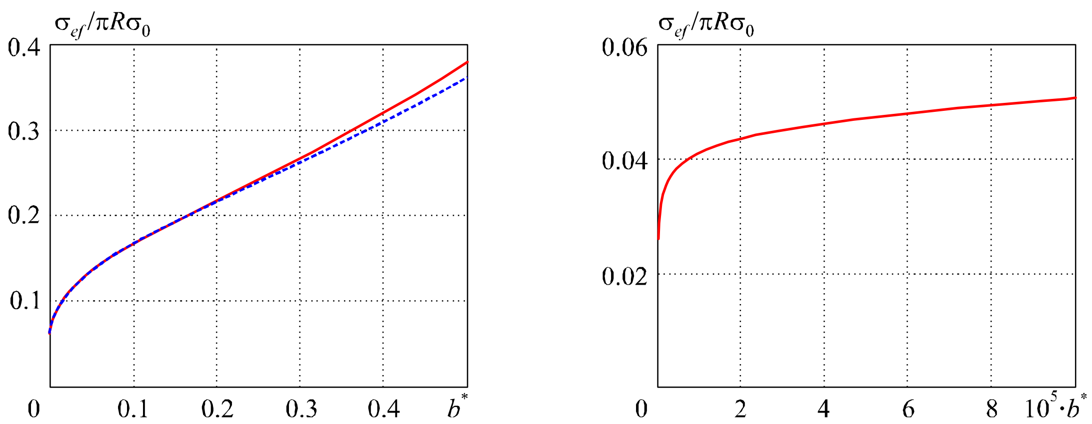
Fig. 2. Results of a correlation between the numerical and analytical solutions at R = 3 mm and r = 500µm (a), 25 µm (b).



a) *b)*

Fig. 3. Results of a correlation between the numerical and analytical solutions at R = 4 mm and r = 500 µm (a) and 25 µm (b).

Dependence of current through the system (and its effective electric conductivity) on the ratio $b^* = r/R$ with a fixed radius of half-spheres is shown in Fig. 4.



a) *b)*

Fig. 4. Dependence of effective electric conductivity of the system (and current through it) on the relative contact radius for moderate (a) and particularly small (b) radii. The dashed curve in Fig. 4 a is constructed by a simplified formula (8).

Thus, it follows from the results of phenomenological consideration of the problem that by virtue of similarity between thermal conductivity and electric conductivity effects, no gain in thermoelectric figure of merit can be obtained due to purely "geometric" factor, hence, it is necessary to consider the microscopic mechanism of system electric conductivity retention with a reduction of its thermal conductivity. In this case we will consider purely drift mechanism, thus far leaving aside quantum tunneling.

Consideration of the problem of electrons (holes) scattering on sample boundaries in the approximation of power dependence of relaxation time on energy

Consider this problem within a model of two half-spheres contacting in a circular spot of radius r . In the bulk material the mean free path l_{cc} of electron or hole depends on energy by the power law $l_{cc}(\varepsilon) = A\varepsilon^q$, where A is a certain coefficient of proportionality, q is power exponent. The values of these quantities are defined by specific scattering mechanism, where q, according to general concepts of quantum mechanics varies from 0 at low to 4 at high energies. Therefore, for the electric conductivity of the bulk sample in the isotropic approximation in the case of a nondegenerate gas of current carriers the following expression is valid:

$$\sigma_0 = D(kT)^{q+1}\int_0^\infty \exp(-x)x^{q+1}\mathrm{d}x = D(kT)^{q+1}\Gamma(q+2). \quad (11)$$

In this formula, $D = ABC\exp(\zeta/kT)$, B is coefficient of proportionality between the density of states of current carriers and the square root of their energy, C is coefficient of proportionality between the rate of current carriers and the square root of their energy, ζ is chemical potential, T is temperature, $\Gamma(x)$ is gamma-function.

For carrier scattering on the contact spot boundaries the following expression for the resulting mean free path of current carriers is valid:

$$l_{cct}(\varepsilon) = \frac{l_{cc}(\varepsilon)L}{L + l_{cc}(\varepsilon)}. \quad (12)$$

In this formula, $l_{cc}(\varepsilon)$ is mean free path of current carrier (electron or hole) in material determined by all scattering mechanisms, except for the contact spot boundaries, L is effective mean free path of current carrier determined by the sample boundaries. Now we introduce the mean free path of current carrier, for instance, electron, by the formula:

$$l_e = \frac{\int_0^\infty l_{cc}(\varepsilon) f_0(\varepsilon) g(\varepsilon)\mathrm{d}\varepsilon}{\int_0^\infty f_0(\varepsilon) g(\varepsilon)\mathrm{d}\varepsilon}. \quad (13)$$

In this formula, $f_0(\varepsilon)$ is the Maxwell-Boltzmann distribution function, $g(\varepsilon)$ is the electron density of states. From (12) follows the following relation for A:

$$A = l_e \frac{\Gamma(1.5)}{(kT)^q\,\Gamma(q+1.5)}. \quad (14)$$

In the case of a circular contact which is small as compared to half-sphere diameters, it can be considered that a drag of current carriers, for instance, electrons, takes place only in the area of this contact. Moreover, all contact points are equivalent due to its symmetry. Therefore, a general formula for electric conductivity [7] with regard to (12) and (14) yields the following expression for the ratio between the electric conductivity of a system of half-spheres to the electric conductivity of the bulk sample:

$$\frac{\sigma_{bs}}{\sigma_0} = \frac{1}{\pi\Gamma(q+2)} \int_0^{\infty}\int_0^1\int_0^{2\pi} \frac{k^* \sqrt{y^2+1-2y\cos\varphi}\, y x^{q+1} \exp(-x)}{x^q + k^* \sqrt{y^2+1-2y\cos\varphi}} \mathrm{d}\varphi \mathrm{d}y \mathrm{d}x . \quad (15)$$

In this formula, σ_{bs} is the electric conductivity of the system, $k^* = [\Gamma(q+1.5)/\Gamma(1.5)](r/l_e)$. As it must be, at $k^* = 0$ formula (13) gives zero, and at $k^* \to \infty$ – the electric conductivity of the bulk sample. The results of this calculation are depicted in Fig. 5.

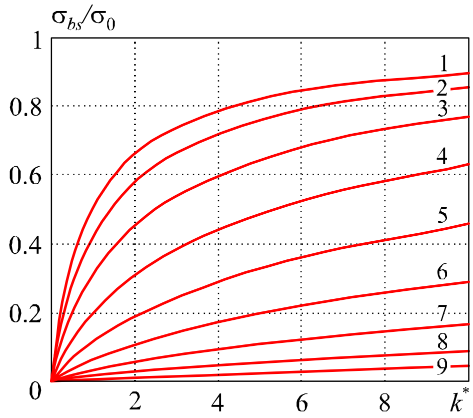


Fig. 5. Dependence of the electric conductivity of a system of two half-spheres contacting in a circular spot on its radius. Curves 1 – 9 are constructed for the values of q from 0 to 4 with a step of 0.5.

Dependence of r/l_e ratio on q following from considerations of retention of at least 90 % of the electric conductivity of the bulk sample is depicted in Fig. 6.

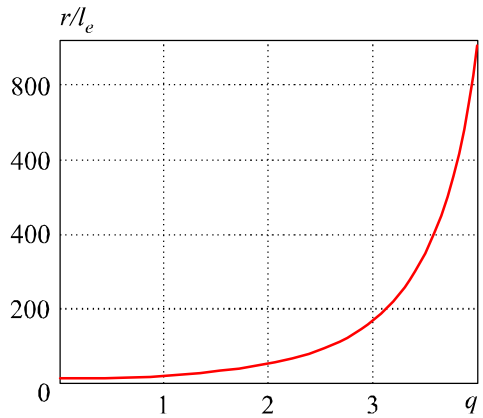


Fig. 6. Dependence of r/l_e ratio on q following from considerations of retention of at least 90 % of the electric conductivity of the bulk sample.

From this figure it is evident that with increase in q after the value equal to 2, r/l_e ratio is rather drastically increased. However, in semiconductors the most frequent q values are equal to 0, which corresponds to approximation of constant mean free path, or 0.5, which corresponds to approximation of constant relaxation time. In the temperature range of 300 K and above which is relevant for thermoelectricity it can be considered that $q = 0$. In this case the mean free path of current carriers, i.e. electrons (holes) l_{cc} at temperature T is expressed through their mobility b and density-of-state effective mass m^* as follows:

$$l_{cc} = \sqrt{\frac{\pi}{2}} \frac{b}{e} \sqrt{m^* kT}. \quad (16)$$

Therefore, the estimate of mean free paths at this temperature, based on the mobilities and density-of-state effective masses of electrons and holes [7], yields $l_e = 38.7$ nm, $l_h = 20.4$ nm. Minimum contact radius at $q = 0$, necessary for the retention of 90 % of electric conductivity, is 10.4 of the mean free path of electron or hole. And this corresponds (with a larger path) to 0.4 μm.

Conclusions and recommendations

1. In the isotropic drift approximation with regard to charge carrier scattering on the acoustic phonons and contact boundaries it is shown that in going from single crystal to extruded material the electric conductivity of shape-forming material structural element at least 90 % is retained, if the radius of contact between half-spheres is at least 10.4 of the mean free path of electron (hole).
2. As applied to Bi_2Te_3 at a temperature of 300 K it means that contact radius must be not less than 0.4 μm, and such contacts can occur between particles of diameter 40 to 80 μm.
3. Retention or slight change of thermoelectric figure of merit in going from single crystal to extruded material is attributable to the fact that at phonon scattering on the boundaries of contact between half-spheres of shape-forming element its thermal conductivity drops, while the electric conductivity even with account of charge carrier scattering on the contact boundaries remains the same.

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