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PECULIARITIES OF HEAT AND ELECTRIC CHARGE TRANSPORT IN "METAL-THERMOELECTRIC MATERIAL-METAL" MINIATURE LAYERS

Phonon thermal conductivity and electric conductivity of miniature thermoelectric structure "metal-thermoelectric material-metal" was calculated. The impact of thickness of thermoelectric material (TEM) layer between metal layers was taken into account. Calculations of thermal conductivity were made in two approximations: constant phonon mean free path and with regard to the frequency dependence of phonon relaxation time with phonon-phonon scattering due to anharmonicity of lattice thermal vibrations. In the latter case, both Umklapp processes and normal processes were considered, capable of modifying electron scattering at the layer boundaries. The electric conductivity was considered with regard to the energy dependence of charge carrier mean free path. By the example of thin layers of $Bi_2Te_{2.7}Se_{0.3}$ it was shown that with reduction of their thickness to 50μm, lattice thermal conductivity is reduced at most by 1.5%, and electric conductivity – at most by 1% as compared to single crystal. Owing to this, the expected growth of thermoelectric figure of merit when passing from a single crystal to a 50 μm layer does not exceed 0.5%.

Key words: lattice thermal conductivity, electric conductivity, phonons, charge carriers, relaxation time, normal processes, Umklapp processes.

Introduction

Microminiature thermoelectric modules are based on thin TEM layers contacting with metal layers. In particular, [1] is dedicated to a thermoelectric microcooler with thermoelements 4 μm high. For such microthermoelements, the impact on heat and electric charge transport of charge carrier energy barriers and diffused phonon scattering at the boundary between TEM and metal was investigated. Based on this approach, the electric and thermal resistances of "TEM-metal" boundary were calculated and their impact on the microcooler characteristics was analyzed. However, in this case no account was taken of the impact of TEM layer thickness on its kinetic coefficients due to commensurability with this thickness of charge carrier and phonon mean free paths.

The purpose of the present wok is to analyze the impact of thickness of single crystal TEM layer on its thermal conductivity, electric conductivity and thermoelectric figure of merit. In so doing, with regard to the fact that the object of study is a layered thermoelectric material, we will consider temperature gradient and electric current to be parallel to crystal layer planes.

Lattice thermal conductivity of a thin layer

Thermal conductivity of a single crystal does not depend on its size in cases when it is much in excess of phonon mean free path caused, for instance, by phonon-phonon scattering due to

anharmonicity of lattice thermal vibrations. However, if the thickness of a single crystal layer becomes commensurate with phonon mean free path, the time of phonon path in a layer becomes commensurate with phonon relaxation time caused by phonon-phonon scattering. In this case, the reverse phonon relaxation time, constant or frequency dependent, should be added to the reverse time of their path in the layer, and the resulting relaxation time is reduced essentially. This reduction has to be taken into account in the calculation of lattice thermal conductivity.

When considering lattice thermal conductivity, we will assume acoustic wave front to be flat and parallel to TEM layer planes. Then, by analogy with [2] that studied the impact of phonon scattering at the boundaries of powder spherical particles and their contacts on lattice thermal conductivity in the approximation of constant mean free path of phonons, we obtain the following expression for the ratio of thermal conductivity κ of a plane layer of thickness d_0 to thermal conductivity κ_{mono} of a single crystal:

$$\kappa / \kappa_{mono} = \frac{d_0}{l_{ph}} \ln\left(1 + \frac{l_{ph}}{d_0}\right), \tag{1}$$

where phonon mean free path $l_{ph} = 3\kappa_{mono} / c_V \rho v_{\|}$, c_V is the specific heat, ρ is the density, $v_{\|}$ is the sound velocity in layer plane. This formula was derived by averaging the expression for thermal conductivity over all phonon mean free paths in a layer, including the shortest. Formula (1) is different from the expressions obtained in [2] only in the method of averaging over possible phonon mean free paths in a layer with regard to its thickness.

We now consider the lattice thermal conductivity of TEM thin layer with regard to frequency dependence of phonon relaxation time. In this case, by analogy with the results obtained in [2] according to procedure described in [3], the thermal conductivity of a thin layer relative to a single crystal is determined by the following relation:

$$\kappa \Big/ \kappa_{mono} = \int_0^1 \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left(\frac{k_{\|}^* z}{1 + k_{\|}^* Q_{l\|}(x) z} + \frac{2 k_{\|}^* z}{1 + k_{\|}^* Q_{t\|}(x) z} \right) dz dx \left\{ \int_0^1 \frac{x^4 \exp(x/\theta)}{[\exp(x/\theta) - 1]^2} \left(\frac{1}{Q_{l\|}(x)} + \frac{2}{Q_{t\|}(x)} \right) dx \right\}^{-1}. \tag{2}$$

In this formula, $\theta = T / T_D$, T is the absolute temperature, T_D is the Debye temperature of material. A dimensionless parameter $k_{\|}^*$ is calculated as follows:

$$k_{\|}^* = \frac{d_0 \gamma^2 \theta}{\rho} \left(\frac{k_B T_D}{\hbar v_{\|}} \right)^4 \left(\frac{k_B T_D}{v_{\|}^2} \right), \tag{3}$$

where γ, ρ and $v_{\|}$ are the Gruneisen parameter, density and sound velocity in TEM, respectively, k_B is the Boltzmann constant, the rest of designations are common. Index "$\|$" means that the corresponding parameter is taken in the direction parallel to TEM layer plane. Moreover, frequency polynomials $Q_{l\|}(x)$ and $Q_{t\|}(x)$, respectively, are given by:

$$Q_{l\|}(x) = x^4 + 0.082x, \tag{4}$$

$$Q_{t\|}(x) = (0.082 + 3.125\theta^3)x. \tag{5}$$

These formulae take into account both normal processes and Umklapp processes for the longitudinal (*l*) and transverse (*t*) phonon modes. Component 0.082*x* is responsible for Umklapp processes, the numerical coefficient being selected such as to assure matching of theoretical and experimental thermal conductivity values for material based on bismuth telluride in the temperature range 100 to -600K [4] with regard to contribution of electron thermal conductivity to full thermal conductivity. It was also taken into account that phonon scattering due to normal processes takes place differently for the longitudinal and transverse modes, as described by other components in (4), (5).

Calculation of lattice thermal conductivity of a thin layer was done by the example of $Bi_2Te_{2.7}Se_{0.3}$ material with the following parameters: $\gamma = 1.5$ [4], $\rho = 6854\ \text{kg/m}^3$ [1], T_D=157K [5], $v_{\parallel} = 2900\ \text{m/s}$ [1]. The results of calculation of relative lattice thermal conductivity in the approximation of a constant phonon mean free path and with regard to the frequency dependence of phonon relaxation time are given in Fig. 1.

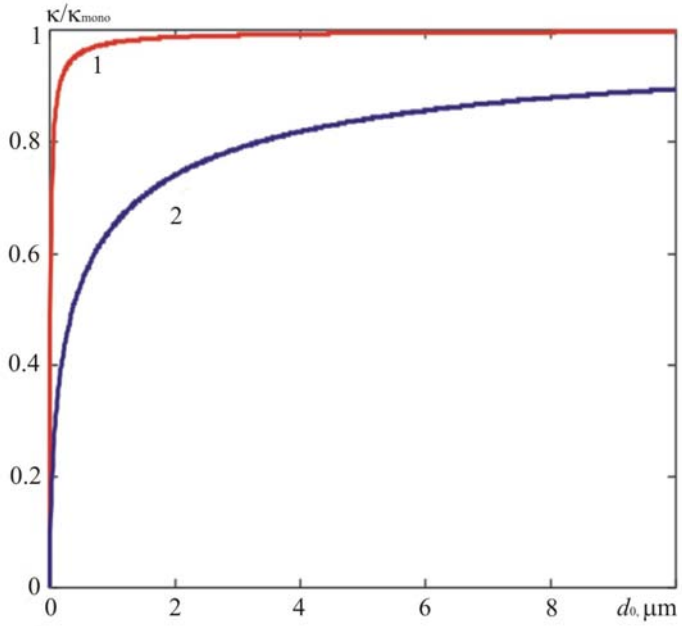
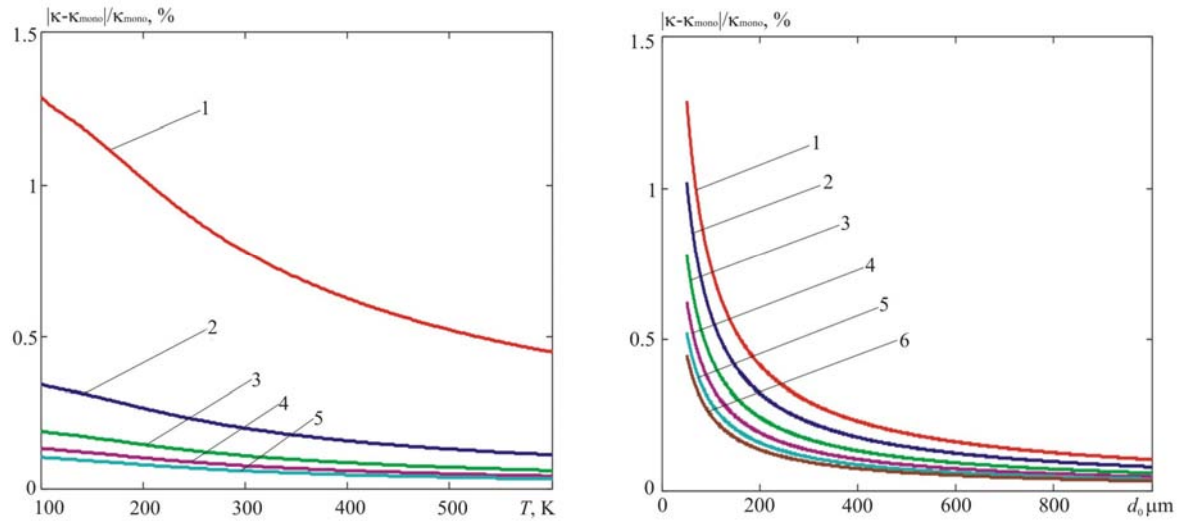


Fig. 1. Dependences of lattice thermal conductivity κ *of a thin layer relative to lattice thermal conductivity* κ_{mono} *of* $Bi_2Te_{2.7}Se_{0.3}$ *single crystal on layer thickness* d_0 *at T = 300K: 1 – in the approximation of a constant phonon mean free path, 2 – with regard to the frequency dependence of phonon relaxation time.*

From the figure it is evident that with a constant mean free path the thermal conductivity of a thin layer tends to the thermal conductivity of a single crystal considerably faster than with regard to the frequency dependence of phonon relaxation time. Thus, in the approximation of a constant relaxation time, the thermal conductivity of a single crystal is achieved already at the layer thickness equal to 2 μm. At the same time, with regard to the frequency dependence of relaxation time even with the layer thickness equal to 10 μm, only 90% of lattice thermal conductivity of a single crystal is achieved.

Dependences of correction to lattice thermal conductivity of $Bi_2Te_{2.7}Se_{0.3}$ single crystal on the temperature and layer thickness are given in Fig. 2*a*, *b*. These dependences were calculated by formulae (2) – (5).



a) *b)*

Fig. 2. Dependences of correction to lattice thermal conductivity κ_{mono} of $Bi_2Te_{2.7}Se_{0.3}$ single crystal: a) on the temperature for layer thicknesses:1 – 50 μm;2 – 250 μm;3 – 500 μm; 4 – 750 μm;5 – 1000 μm; b) on the layer thickness for temperatures:1 – 100; 2 – 200; 3 – 300; 4 – 400; 5 – 500; 6 – 600K.

From the figure it is evident that correction value decreases with temperature due to reduction of phonon mean free path, and that correction decreases with increasing layer thickness due to the fact that phonon relaxation time ceases to be limited by the layer thickness. In the temperature range 100 to 600K for the layers more than 50 μm thick correction to thermal conductivity of a single crystal does not exceed 1.5%. Hence, the thickness of TEM layer exceeding 50 μm scarcely affects the lattice thermal conductivity.

Impact of charge carrier scattering at the boundaries of thin layers on the electric conductivity

Let us assume that the mean free path of charge carriers in a bulk material depends on their energy by the power law $l_e \propto \varepsilon^q$. We take into account that restriction of layer thickness affects charge carrier relaxation time for the same reason and in the same way as on the phonon relaxation time. Then, by analogy with [6 – 8] that considered electron scattering at the boundaries of powder particles on the contacts between them, we obtain the following formula for the electric conductivity σ of a thin single crystal layer of TEM relative to single crystal electric conductivity σ_{mono}:

$$\frac{\sigma}{\sigma_{mono}} = \frac{1}{\Gamma(q+2)} \int_0^{\infty} \int_0^{1} \frac{k^* z x^{q+1} \exp(-x)}{x^q + k^* z} \mathrm{d}z\mathrm{d}x, \qquad (6)$$

where $k^* = [\Gamma(q+1.5)/\Gamma(1.5)](d_0/l_e)$, l_e is the average charge carrier mean free path, q is the power exponent in the law of mean free path energy dependence. Formula (6) differs from similar formulae derived earlier in [6] only in the method of averaging over possible charge carrier mean free paths.

The results of calculation of the electric conductivity of a thin single crystal layer of $Bi_2Te_{2.7}Se_3$ relative to a bulk single crystal are given in Fig. 3.

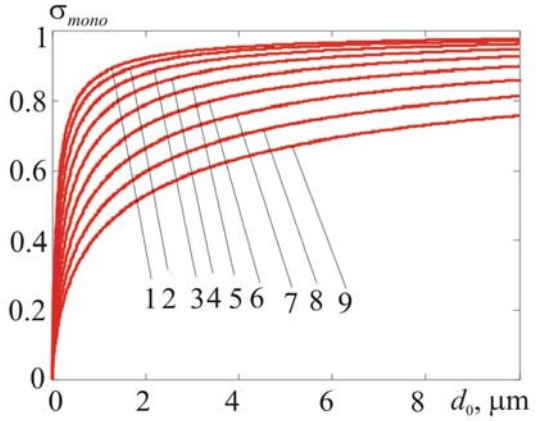


Fig. 3. Dependences of electric conductivity σ of a thin layer of $Bi_2Te_{2.7}Se_{0.3}$ relative to a single crystal σ_{mono} on the layer thickness d_0 at 300K. Dependences 1 – 9 were built for q values in the range of 0 – 4 s with an increment 0.5.

From the results of calculation it follows that for power exponent $q = 0$ that is most common in semiconductor TEM in the temperature range relevant to use, the thickness of a plane layer needed to keep the electric conductivity at a level of 90% relative to single crystal at 300 K, is about 1.5 μm.

Note that due to the Casimir effect [3] the lattice thermal conductivity (Fig. 1) and electric conductivity (Fig. 3) of a thin layer are always less than the respective characteristics of a single crystal.

To calculate the electric conductivity of a single crystal layer versus its thickness, preliminary estimate of electron mean free path in $Bi_2Te_{2.7}Se_3$ material was made and the lattice component of thermal conductivity was separated from the electron component. It was done from the data on electron concentration n_0, effective mass of electron states density m_e^* and electric conductivity σ_{mono} at 300K by known relationships [4] on the assumption that electron mean free path does not depend on energy, hence, scattering factor used in [4], r = –0.5. This assumption is justified on condition of electron scattering both on acoustic phonon deformation potential and on impurities, at least at high doping levels. The only difference is that with acoustic phonon scattering the electron mean free path is inversely proportional to temperature, and at impurity scattering it is temperature independent.

At first, in the temperature range 100 to 600 K an equation was solved that determines normalized to thermal motion energy chemical potential η of electron gas and has the form:

$$n_0 = \frac{4\left(2\pi m_e^* k_B T\right)^{3/2}}{\sqrt{\pi} h^3} F_{1/2}(\eta). \qquad (7)$$

Following that, the mean free path l_e was estimated on the basis of relation for single crystal electric conductivity:

$$\sigma_{mono} = \frac{2 n_0 e^2 l_e \sqrt{\pi} F_0(\eta)}{3\Gamma(1.5)\sqrt{2 m_e^* k_B T} F_{1/2}(\eta)}, \qquad (8)$$

where $F_r(\eta)$ are the Fermi integrals of respective indices determined by the relation:

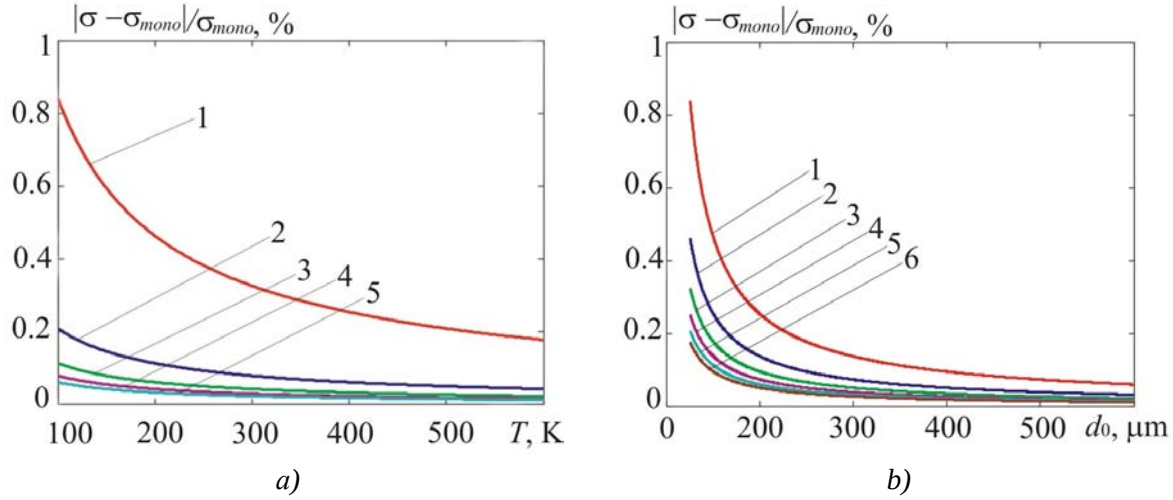
$$F_r(\eta) = \int_0^\infty \frac{x^r \mathrm{d}x}{\exp(x-\eta)+1}. \qquad (9)$$

Taking into account that for $Bi_2Te_{2.7}Se_{0.3}$ single crystal $n_0 = 3\cdot 10^{19}$ cm^{-3}, $m^* = 1.25 m_0$, $\sigma_{mono} = 1100\,\Omega^{-1}$cm^{-1}, we obtain l_e=21 nm at a temperature of 300 K. Then, with regard to relations (7) – (9), the temperature dependence of electric conductivity of $Bi_2Te_{2.7}Se_{0.3}$ single crystal was calculated.

Dependences of correction to electric conductivity of *n*-type single crystal $Bi_2Te_{2.7}Se_{0.3}$ on the temperature and layer thickness are presented in Fig. 4. These dependences were calculated by formula (6), assuming that $q = 0$ and electron mean free path is proportional to temperature [4], i.e. the relation is valid:

$$l_e(T) = \frac{300 l_e(300)}{T}, \tag{10}$$

where $l_e(300)$ is mean free path at a temperature of 300 K.



a) *b)*

Fig. 4. Dependences of correction to the electric conductivity of $Bi_2Te_{2.7}Se_{0.3}$ single crystal: a) on temperature at layer thicknesses, μm: 1 – 50; 2 – 250; 3 – 500; 4 – 750; 5 – 1000; b) on layer thickness at temperatures, K: 1 – 100; 2 – 200; 3 – 300; 4 – 400; 5 – 500; 6 – 600K.

Dependences of correction to single crystal electric conductivity on temperature and layer thickness are determined by the same factors as the temperature and thickness dependences of lattice thermal conductivity, namely a reduction of electron mean free path with a rise in temperature and gradual leveling the role of scattering at the layer boundaries with its thickness increase. In the temperature range 100 to 600 K for layers more than 50 μm thick a correction to single crystal electric conductivity does not exceed 1%. Therefore, TEM layer thickness over 50 μm scarcely affects its electric conductivity.

Thermoelectric figure of merit of thin layers

Consider now the temperature and thickness dependences of thermoelectric figure of merit of a thin layer relative to single crystal. We take into account that in the approximation of constant relative to energy mean free path, charge carrier scattering at the layer boundaries does not affect thermopower. Indeed, a general formula for the Seebeck coefficient in the case of a quadratic and isotropic law of electron dispersion is given by:

$$\alpha = \frac{1}{eT} \frac{\int_0^\infty \tau(\varepsilon)\varepsilon(\varepsilon-\zeta) f_0'(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon}{\int_0^\infty \tau(\varepsilon)\varepsilon f_0'(\varepsilon)\sqrt{\varepsilon}\,d\varepsilon} \tag{11}$$

where $f_0'(\varepsilon)$ is a derivative of the Fermi-Dirac distribution function with respect to energy. For relaxation time $\tau(\varepsilon)$ on condition of constant with respect to energy mean free path l^* of charge carriers the following relation is valid:

$$\tau(\varepsilon)=\frac{l^*\sqrt{m^*}}{\sqrt{2\varepsilon}}, \tag{12}$$

where l^* is determined by scattering both in the bulk and at the layer boundaries, i.e. by the formula:

$$l^* = l_e\left\langle\frac{L^*}{l_e+L^*}\right\rangle, \tag{13}$$

where l_e is electron mean free path in a single crystal, L^* is mean free path due to scattering at the layer boundaries, angular brackets denote averaging over layer thickness. Therefore, l^* appears in the numerator and denominator of formula (11) as a constant multiplier which is taken out of the integral and does not affect thermopower. Hence, thermopower is not affected by scattering at the layer boundaries.

The electron component of single crystal thermal conductivity κ_{emono}, needed to calculate the figure of merit of material, is found from the Wiedemann-Franz ratio:

$$\kappa_{e\,mono} = L\sigma_{mono}T\,, \tag{14}$$

where the Lorentz number L is

$$L=\left(\frac{k_B}{e}\right)^2\left[\frac{3F_2(\eta)}{F_0(\eta)}-\frac{4F_1^2(\eta)}{F_0^2(\eta)}\right]. \tag{15}$$

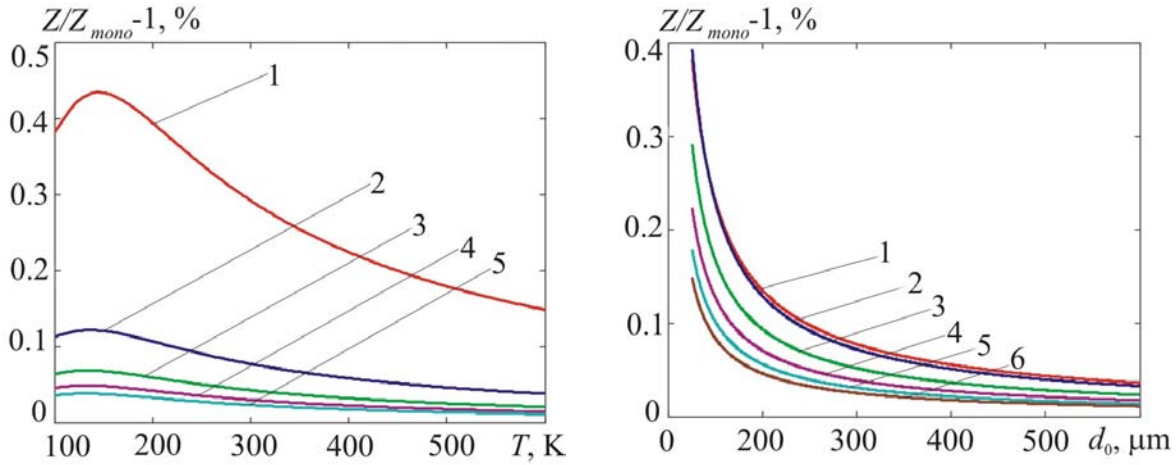
We now turn directly to calculation of thermoelectric figure of merit of a thin layer relative to a single crystal with regard to electron thermal conductivity contribution. For this purpose we will use a subsidiary expression written with regard to relations (2) and (6) as follows:

$$Z_a=\left(\int_0^1\frac{d_0l_e^{-1}(T)z}{d_0l_e^{-1}(T)z+1}\mathrm{d}z\right)\left[\int_0^1\int_0^1\frac{x^4\exp(x/\theta)}{[\exp(x/\theta)-1]^2}\left(\frac{k_{\parallel}^*z}{1+k_{\parallel}^*Q_{l\parallel}(x)z}+\frac{2k_{\parallel}^*z}{1+k_{\parallel}^*Q_{t\parallel}(x)z}\right)\mathrm{d}z\mathrm{d}x\right]^{-1}\left\{\int_0^1\frac{x^4\exp(x/\theta)}{[\exp(x/\theta)-1]^2}\left(\frac{1}{Q_{l\parallel}(x)}+\frac{2}{Q_{t\parallel}(x)}\right)\mathrm{d}x\right\}. \tag{16}$$

Taking into account that scattering at the layer boundaries does not affect thermopower and electron thermal conductivity and electric conductivity in case of electron mean free path independence of energy depend on layer thickness through the same multiplier, we obtain the following final expression for thermoelectric figure of merit Z of a thin layer relative to single crystal Z_{mono}:

$$Z/Z_{mono}=\frac{1+\kappa_{e\,mono}/\kappa_{mono}}{Z_a^{-1}+\kappa_{e\,mono}/\kappa_{mono}}. \tag{17}$$

The thickness and temperature dependences of the figure of merit of $Bi_2Te_{2.7}Se_{0.3}$ thin layer are given in Fig. 5.



a) *b)*

Fig. 5. Dependences of the figure of merit Z of a thin layer of $Bi_2Te_{2.7}Se_{0.3}$ relative to a single crystal Z_{mono}: a) on temperature at layer thicknesses, μm:1 – 50; 2 – 250; 3 – 500; 4 – 750; 5 – 1000; b) on layer thickness at temperatures, K:1 – 100; 2 – 200; 3 – 300;4 – 400; 5 – 500; 6 – 600K.

From the figure it is seen that with a rise in temperature and layer thickness, the figure of merit of a layer tends to the figure of merit of a single crystal. The temperature and thickness dependences of the figure of merit of a layer relative to a single crystal are determined by reduction in electron and phonon mean free paths, as well as by leveling of scattering at layer boundaries with its thickness increase. In the thickness range 50 to 1000 μm at temperatures 100 to 600 K the expected figure of merit increase of thin layers of *n*-type $Bi_2Te_{2.7}Se_{0.3}$ relative to a single crystal does not exceed 0.5%.

It should be noted that depending on the ratio between charge carrier and phonon mean free paths the figure of merit of TEM in going from a single crystal to a thin layer can be both increased and decreased.

Conclusions

1. The impact of phonon and charge carrier scattering at the boundaries of microminiature layers on the electric conductivity and lattice thermal conductivity is most essential at thicknesses less than 10 μm.
2. Account of the frequency dependence of phonon relaxation time and the energy dependence of charge carrier mean free path increases the impact of scattering at the boundaries of micromimiature layers on their kinetic coefficients.
3. A stronger reduction of lattice thermal conductivity as compared to electric conductivity creates prerequisites for TEM figure of merit improvement in going from the bulk single crystals to microminiature layers.
4. With the thicknesses exceeding 50 μm and the temperatures 100 – 600 K the expected figure of merit increase of thin layers of *n*-type $Bi_2Te_{2.7}Se_{0.3}$ relative to a single crystal does not exceed 0.5%.

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