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EFFECT OF THERMOELECTRIC MATERIAL ANISOTROPY ON THE ELECTRIC CONDUCTIVITY AND LATTICE THERMAL CONDUCTIVITY OF ITS CONTACTING PARTICLES

In the framework of a six-ellipsoid Drabble-Wolfe model in the approximation of anisotropic relaxation time depending solely on full energy of current carriers, the electric conductivity was calculated for a physical model – two half-spheres contacting in a circle with regard to electron scattering on the contact boundaries 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 maintained if contact radius exceeds 10.4 of mean free path of electron (hole), i.e. is at least 0.4 μm. This result coincides with that obtained in the isotropic approximation. The reason for this coincidence is a dependence of relaxation time tensor components on full energy of current carriers. The same result is obtained for the radius of contact on which boundaries due to phonon scattering the lattice thermal conductivity of Bi_2Te_3 is reduced by 30 – 40 % as compared to a single crystal. As long as such contacts can arise between particles of radius 40 – 80 μm, it accounts for retention and even some increase of thermoelectric figure of merit when passing from a single crystal to extruded material.

Key words: thermoelectric material, extrusion, figure of merit, electric conductivity, Drabble-Wolfe model, relaxation time, lattice thermal conductivity, contact, boundaries, phonons, scattering, normal processes, Umklapp processes.

Introduction

Bismuth telluride Bi_2Te_3 is a thermoelectric material most commonly used for the manufacture of working members of various thermoelectric instruments and devices [1]. It is characterized by well-expressed electric conductivity and thermal conductivity anisotropy. Taking into account that this crystal possesses *R3m* group symmetry and cleavage planes along which it easily splits, its thermal conductivity and electric conductivity tensors have two independent components each. In particular, in the absence of a magnetic field, electric conductivity tensor has component σ_{11} in cleavage planes and component σ_{33} in a direction normal to them. The ratio σ_{11}/σ_{33} is 2.7 for *p*-type material and 4 ÷ 6 for *n*-type material. Bi_2Te_3 is intermediate in the electric conductivity value between high-resistance semiconductors traditionally used in radio electronics and computer technique, such as germanium and silicon, and semimetals, such as bismuth. The band spectrum of this crystal is anisotropic and described by a six-ellipsoid Drabble-Wolfe model [1].

Due to conductivity anisotropy, thermoelectric modules of solid single crystals Bi_2Te_3 are made so that temperature gradient and electric current are parallel to cleavage planes, where conductivity

value is higher than in the direction perpendicular to them. Alongside with single crystals, extruded materials that may consist of particles with oriented or random cleavage planes are used for the manufacture of thermoelectric modules. With a random arrangement of cleavage planes, the electric conductivity of material in conformity with the Odelevsky formula will make $\sigma = \sqrt{\sigma_{11}\sigma_{33}}$, i.e. will be lower than the largest value. Further electric conductivity reduction can be due to current carrier scattering on the boundaries of small contacts between particles. These factors should have resulted in thermoelectric figure of merit reduction. However, in real practice this reduction is not observed. Hence, a mechanism must exist which assures electric conductivity retention and lattice thermal conductivity reduction at charge carrier and phonon scattering on the boundaries of contacts between the particles. Without a detailed account of electric conductivity anisotropy this mechanism was considered in [2, 3]. Our purpose in this paper is to analyze this mechanism with regard to real anisotropy of band spectrum of charge carrier and electric conductivity, as well as thermal conductivity of Bi_2Te_3.

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

Consider this problem within the framework of a model of two half-spheres of radius R ($r << R$) contacting in a circle of radius r. This model can approximate the shape-forming element of extruded thermoelectric material structure [4]. For this purpose, using the results given in [1], we first write general formulae for single crystal electric conductivity components σ_{11} and σ_{33}. To accomplish this, we predetermine relaxation time tensor components in the approximation of constant mean free paths in the directions of principal axes of ellipsoids by means of full energy of current carriers. These components are:

$$\tau_{1,2,3} = \frac{l_{1,2,3}\sqrt{m^*}}{\sqrt{2\varepsilon}}. \tag{1}$$

In this formula, l_1, l_2, l_3 are charge carrier mean free paths in respective directions, m^* is density-of-state effective mass, ε is full energy of charge carriers. Such an approach corresponds to "nearly isotropic scattering" whose anisotropy is taken into account by means of different lengths l_1, l_2, l_3. Substitution of density-of-state effective mass into formula (1) unambiguously follows from the model assumption of relaxation time tensor components dependence on full energy of charge carriers.

With this relaxation time tensor, according to [1], components of electric conductivity tensor for nondegenerate charge carrier gas are equal to:

$$\sigma_{11} = \frac{4e^2 n_0 \sqrt{m_1 m_2 m_3}}{m_2\sqrt{\pi}m^*\left(k_B T\right)^{1/2}}\left(l_2 + \frac{m_2}{m_1}l_1\cos^2\vartheta + \frac{m_2}{m_3}l_3\sin^2\vartheta\right). \tag{2}$$

$$\sigma_{33} = \frac{8e^2 n_0 \sqrt{m_1 m_2 m_3}}{m_2\sqrt{\pi}m^*\left(k_B T\right)^{1/2}}\left(\frac{m_2}{m_1}l_1\sin^2\vartheta + \frac{m_2}{m_3}l_3\cos^2\vartheta\right). \tag{3}$$

In these formulae, m_1, m_2, m_3 are effective masses of charge carriers along the principal axes of ellipsoid, ϑ is the smallest rotation angle of ellipsoid up to coincidence of its long axis with crystal trigonal axis, k_B is the Boltzmann constant, T is absolute temperature, n_0 is charge carrier concentration, the rest of designations are generally accepted or explained above.

In the temperature region relevant for thermoelectric applications scattering mainly occurs on the deformation potential of acoustic phonons. In this region, l_1, l_2, $l_3 \propto T^{-1}$, so finally we get the known dependence $\sigma \propto T^{-3/2}$, which in reality is somewhat distorted by the temperature dependence of respective effective masses.

Thus, formulae (2) and (3) fully determine electric conductivity tensor of Bi_2Te_3 single crystal in the absence of a magnetic field. Account in these formulae of scattering on contact boundaries presents no special problems. However, of crystal parameters in these formulae only all the effective masses and angle ϑ are known with certainty, for they are parameters of band structure which is reliably studied through measurement of de Haas-van-Alphen and de Haas-Shubnikov effects. As to mean free paths l_1, l_2, l_3, they depend on acoustic phonon deformation potential tensor components. The band structure determines only the bulk component of this tensor [5], whereas in crystal with well-expressed cleavage planes the shear and bend components are also essential. So, it is worthwhile to write formulae (2) and (3) in such a form in which unknown parameters could be determined, for instance, from the data on electron and hole mobility.

Passing from the electric conductivity tensor to charge carrier mobility tensor, we write its components as follows:

$$b_{11,33} = \frac{eL_{11,33}\sqrt{2}}{\sqrt{\pi m^* k_B T}}. \tag{4}$$

In these formulae, in conformity with (2) and (3), charge carrier mean free paths determined by known mobility values are equal to:

$$L_{11} = \frac{4\sqrt{m_1 m_3}}{\sqrt{2m^* m_2}}\left(l_2 + \frac{m_2}{m_1} l_1 \cos^2\vartheta + \frac{m_2}{m_3} l_3 \sin^2\vartheta \right). \tag{5}$$

$$L_{33} = \frac{8\sqrt{m_1 m_3}}{\sqrt{2m^* m_2}}\left(\frac{m_2}{m_1} l_1 \sin^2\vartheta + \frac{m_2}{m_3} l_3 \cos^2\vartheta \right). \tag{6}$$

Let us now discuss charge carrier scattering on contact boundaries. Using the summation rule of inverse mean free paths, we find the ratio between mobilities $\tilde{b}_{11}$ and $\tilde{b}_{33}$ determined with regard to scattering on contact boundaries and mobilities determined by formula (4):

$$\tilde{b}_{11,33} \Big/ b_{11,33} = \frac{1}{\pi}\int_0^1 \int_0^{2\pi} \frac{k_{11,33}\sqrt{z^2 + 1 + 2z\cos\varphi}}{1 + k_{11,33}\sqrt{z^2 + 1 + 2z\cos\varphi}} z \mathrm{d}\varphi \mathrm{d}z. \tag{7}$$

In these formulae, $k_{11} = r/L_{11}$, $k_{33} = r/L_{33}$. Double integrals in them are due to averaging the expression for mobility over phonon mean free paths inside a circle where half-spheres are contacting. From formula (7) it follows that to maintain the mobilities in the form-shaping structural element at a level of 90 % of their values in a single crystal, coefficients k_{11} and k_{33} must be at least 10.4. At T = 300 K for electrons substituting to (6) b_{11} = 1200 cm^2/C·s, $b_{11}/b_{33} = 5$, $m^* = 0.45\, m_0$ [1], we obtain L_{11} = 38.7 nm, L_{33} = 7.7 nm, whence r = 400 nm. Similarly for holes, substituting b_{11} = 510 cm^2/V·s, $b_{11}/b_{33} = 2.7$, $m^* = 0.69\, m_0$ we obtain L_{11} = 20.4 nm, L_{33} = 7.6 nm, whence r = 212 nm. So, finally r = 400 nm. Contacts of such dimensions can appear between particles of diameter 40 ÷ 80 μm.

Let us next consider the possibility of lattice thermal conductivity reduction with phonon scattering on the boundaries of said contact between half-spheres. Comparison of thermal conductivity

and electric conductivity anisotropy figures for Bi_2Te_3 shows that for maintenance of thermoelectric figure of merit of extruded material at a level typical of a single crystal, the lattice thermal conductivity due to phonon scattering on the boundaries of said contact in conformity with the Odelevsky formula must be reduced by $30-40$ % as compared to a single crystal. Consider this opportunity with regard to the following physical circumstances. First, in the region relevant for thermoelectric applications the final lattice thermal conductivity of thermoelectric material in question is largely caused by Umklapp processes at phonon-phonon scattering due to anharmonic component of lattice vibrations, on the one hand, and discrete periodic crystal structure, on the other hand. Second, normal processes, i.e. processes with retention of total pulse of phonon subsystem, making no direct contribution to final lattice thermal conductivity, modify all other scattering processes, including scattering on the boundaries, due to frequency redistribution of scattering probabilities [6, 7]. Thus, in the region relevant for thermoelectric applications, in conformity with the purpose of this paper, in the calculation of lattice thermal conductivity one should take into account three kinds of scattering processes: Umklapp processes, normal processes and scattering on contact boundaries.

Consider first lattice thermal conductivity of Bi_2Te_3 without regard to phonon scattering on contact boundaries. Following [6] and normalizing phonon relaxation time for the time of normal processes, components of lattice thermal conductivity tensor $\chi_{l\parallel,\perp}$ of this material will be written as:

$$\chi_{l\parallel,\perp}=\frac{3\hbar\rho v_{\parallel,\perp}^4}{32\gamma^2 k_B T_D^2\theta^3\pi}\int_0^1\frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{Q_{l\parallel,\perp}(x)}+\frac{2}{Q_{t\parallel,\perp}(x)}\right)dx\,. \tag{8}$$

In this formula, indexes $\parallel$ and $\perp$ refer to respective values in the direction parallel and perpendicular to layers (cleavage planes), ρ is crystal density, ν is sound velocity in it, γ is the Gruneisen parameter, T_D is the Debye temperature, $\theta = T/T_D$, $Q_{l\parallel,\perp}(x)$ and $Q_{t\parallel,\perp}(x)$ is frequency polynomials determined by mechanisms of scattering longitudinal and transverse phonons, respectively, and having in this case the form:

$$Q_{l\parallel,\perp}(x)=x^4+\mu_{\parallel,\perp}x, \tag{9}$$

$$Q_{t\parallel,\perp}=\left(\mu_{\parallel,\perp}+3.125\theta^3\right)x. \tag{10}$$

As regards thermal conductivity dependence on material density, we note that formula (8) in this respect is true for a simple cubic lattice with one atom in a unit cell. The actual Bi_2Te_3 lattice is not of that kind, but we have to replace it by such, provided the real material density is maintained. Coefficient μ was approximately calculated for a simple cubic lattice by Leibfried and Shlemann [6], but, according to experimental data given in [6], even for materials with such a lattice it is not universal. So, we will "derive" coefficients $\mu_\parallel$ from the real values of Bi_2Te_3 thermal conductivity tensor components [1], with the requirement that the latter coincide with the theoretical values (10) with regard to (11) and (12). At $\chi_{l\perp} = 0.58$ W/m·K, $\chi_{l\parallel} = 1.45$ W/m·K, $\rho = 7859$ kg/m^3, $\gamma = 1.5$, $\nu_\parallel = 2952$ m/s, $\nu_\perp = 1867$ m/s, $T_D = 155$ K and $T = 300$ K we obtain $\mu_\parallel = 0.022$, $\mu_\perp = 2.177\cdot10^{-3}$.

Let us now turn to calculation of material lattice thermal conductivity on condition of phonon scattering on contact boundaries. Using summation rule of inverse relaxation times, we obtain the following ratio between material thermal conductivity χ_l^{ef} at scattering on contact boundaries and single crystal thermal conductivity:

$$\chi^{ef}_{l\|,\perp}\Big/\chi_{l\|,\perp}=\pi^{-1}\int_0^1\int_0^1\int_0^{2\pi}\frac{zx^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{k^*_{\|,\perp}\sqrt{z^2-2z\cos\varphi+1}}{1+k^*_{\|,\perp}Q_{l\|,\perp}(x)\sqrt{z^2-2z\cos\varphi+1}}+\right.$$
$$\left.+\frac{2k^*_{\|,\perp}\sqrt{z^2-2z\cos\varphi+1}}{1+k^*_{\|,\perp}Q_{t\|,\perp}(x)\sqrt{z^2-2z\cos\varphi+1}}\right)\mathrm{d}\varphi\mathrm{d}z\mathrm{d}x\left\{\int_0^1\frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{Q_{l\|,\perp}(x)}+\frac{2}{Q_{t\|,\perp}(x)}\right)\mathrm{d}x\right\}^{-1}. \quad (11)$$

In this formula, an additional designation is introduced

$$k^*_{\|,\perp}=\frac{r_{\|,\perp}\gamma^2}{\rho}\left(\frac{k_BT_D}{\hbar v_{\|,\perp}}\right)^4\left(\frac{k_BT_D}{v^2_{\|,\perp}}\right). \quad (12)$$

From formula (11) it follows that for lattice thermal conductivity reduction by 30 – 40 % due to phonon scattering on contact boundaries, $k_{\|}^{*}$ should make 69.6 ÷ 167.7, and $k_{\perp}$ – 1008 ÷ 2691. Therefore, contact radius should make 0.4 ÷ 1.1 μm. In its lowest value this result coincides with the minimum contact radius necessary for maintenance of electric conductivity of shape-forming element of extruded material structure at a level of 90 % of single crystal electric conductivity. Thus, when passing from a single crystal to extruded material, its thermoelectric figure of merit should not drop, and with size optimization of shape-forming element of material structure this figure of merit can even increase.

Conclusions and recommendations

1. In the drift approximation with regard to charge carrier scattering on acoustic phonons and the boundaries of contact between material particles, as well as a real anisotropy of band spectrum and electric conductivity of material it is shown that when passing from a single crystal to extruded material, the electric conductivity of shape-forming element of material structure is maintained at a level not less than 90 % of its value in a single crystal, if contact radius between half-spheres is at least 10.4 of electron (hole) mean free path.
2. As applied to Bi_2Te_3 at a temperature of 300 K it means that contact radius should be at least 0.4 μm, and such contacts can appear between particles of diameter 40 ÷ 80 μm.
3. Retention or little change of thermoelectric figure of merit when passing from a single crystal to extruded material can be attributed to the fact that at phonon scattering on the boundaries of contact between half-spheres of shape-forming element, its thermal conductivity drops, whereas electric conductivity even with regard to charge carrier scattering on contact boundaries is maintained at the previous level.
4. Coincidence of these results with the results obtained in the isotropic approximation is due to the fact that charge carrier relaxation time, though considered anisotropic, depends on their full energy, rather than on each quasi-pulse component separately.
5. The same estimate for contact radius necessary for lattice thermal conductivity reduction due to phonon scattering on its boundaries by 30 to 40 % as compared to a single crystal results if alongside with scattering on the boundaries, one will consider normal processes together with Umklapp processes related to phonon-phonon scattering.

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