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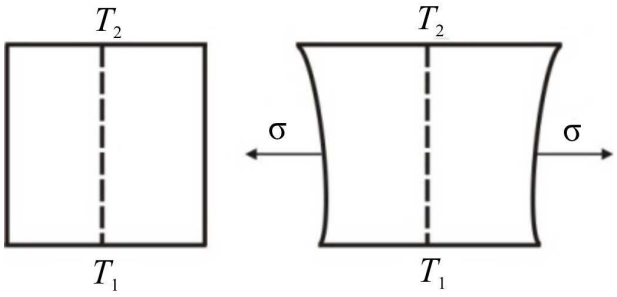
THEORETICAL MODELS OF LATTICE THERMAL CONDUCTIVITY OF SINGLE-CRYSTAL BISMUTH TELLURIDE

In the isotropic approximation, the effect of the real density of phonon states on the lattice thermal conductivity of single-crystal bismuth telluride is taken into account within the framework of two model approaches. First, the problem is considered in the isotropic approximation, and then the layered structure and anisotropy are roughly taken into account. It is shown that the real density of phonon states almost does not change the temperature dependence of the lattice thermal conductivity of bismuth telluride both in the plane of the layers (cleavage) and perpendicular to it compared to the Debye density of phonon states. This weakness is explained by the fact that the change in the differential heat capacity contribution to thermal conductivity caused directly by the density of phonon states is compensated by the effect of this density on scattering, which is caused by the nonlinear dependence of the wave vector on the frequency, the difference between the group velocity of sound and the phase velocity, and a significant increase in the Umklapp coefficient. The obtained results are not only in qualitative, but also in satisfactory quantitative agreement with the theoretical studies of previous authors and the experiment. This allows us to hope that the real density of phonon states will not have a significant effect on the thermomechanical deformations of thermoelectric legs in comparison with the Debye density of phonon states. Bibl. 7, Fig. 2.

Key words: cyclic stability of thermoelements, reliability of thermoelectric legs, thermomechanical stresses, thermal conductivity, real and Debye densities of phonon states, normal processes, Umklapp processes.

Introduction

The efforts of material scientists today are mainly aimed at increasing the thermoelectric figure of merit and efficiency of thermoelectric materials. At the same time, one of the main ways of such an increase is considered to be a decrease in thermal conductivity, in particular its lattice component. But such a way is in a certain contradiction with the considerations of mechanical reliability of thermoelectric materials. This contradiction can be explained on the basis of the physical model depicted in Fig. 1.



а) $T_1 = T_2$ *б) $T_1 < T_2$*

Fig.1. Physical model of temperature deformation of thermoelectric leg

If there is no temperature gradient, then thermomechanical stresses do not occur. But in the presence of a temperature gradient, stresses do not arise only when a thermoelectric leg expands freely. But in reality, it is attached by the end faces to the anti-diffusion layer, interconnect and ceramic plates. If the fastening is absolutely rigid, then in accordance with Hooke's generalized law [1], there is a bending stress equal to:

$$\sigma = \frac{E\alpha_T \Delta T}{1-\nu} \ , \tag{1}$$

where E, α_T, ν are Young's modulus, coefficient of linear expansion and Poisson's ratio of thermoelectric material, respectively, ΔT is temperature difference on the leg. This bending stress should not exceed the cracking strength of the crystal σ_f [2]. On the other hand, for the same heat flow, the temperature difference is the smaller, the higher the thermal conductivity κ. Therefore, the so-called thermal shock resistance criterion [2] is introduced, which is equal to:

$$R = \frac{E\alpha_T}{(1-\nu)\kappa\sigma_f} \ . \tag{2}$$

It is believed that it should be as small as possible. On the other hand, high figure of merit of a thermoelectric material implies a low value of κ, that is, a high value of R. This explains the contradiction mentioned at the beginning of the article, which determines the relevance and the very setting of this study, because the task of finding ways to achieve a safe "compromise" value of κ arises. From this follows the object and subject of research.

The object of research is single-crystal bismuth telluride. The subject of research is the influence of the real density of phonon states and the anisotropy of the phonon spectrum on its lattice thermal conductivity.

Results of research and their discussion

In this work, research was carried out for single-crystal bismuth telluride, and when calculating the lattice thermal conductivity, the influence of normal scattering and scattering with mutual phonon Umklapp was taken into account. The latter is important because it is what provides the finite value of thermal conductivity. In the case of purely normal scattering, the total energy and total quasi-momentum of each triplet of phonons, and, consequently, the momentum of the phonon subsystem of the crystal as a whole are preserved. Thus, a kind of "super thermal conductivity" takes place, which is to some extent analogous to superconductivity, and hence the lattice thermal

conductivity will be infinite if there are no other phonon scattering mechanisms. In the presence of Umklapp processes, the energy is preserved, and the quasi-momentum is preserved, as is customary to say, with the accuracy of the inverted lattice vector. But the very concept of an inverted lattice has meaning only when taking into account the atomic structure of matter. In a "truly" continuous medium, the phonon thermal conductivity should be infinite if there are no other phonon scattering mechanisms.

The article [3] gives general formulae for the thermal conductivity of a crystal lattice in the case when the law of dispersion of acoustic phonons is linear, and the isofrequency surface of phonons is a sphere, and therefore the density of phonon states is described by the Debye model, that is, it is a quadratic function of frequency. At the same time, they were derived for a simple cubic lattice with one atom in the unit cell. We need to modify these formulae for the case of an arbitrary structure of the crystal lattice, an arbitrary energy spectrum of phonons, and, therefore, an arbitrary frequency dependence of the density of phonon states. At the same time, having information not about the phonon spectrum as a whole, but only about the frequency dependence of the density of phonon states, we can do this in the isotropic approximation. This approximation, despite the anisotropy of the bismuth telluride crystal, is quite often used in calculating its thermoelectric characteristics. We are forced to do this also because the correspondence between the phonon spectrum of a crystal and the corresponding density of phonon states is not one-to-one. This means that, knowing the phonon spectrum of a crystal, you can always find the corresponding density of phonon states. But in the general case it is impossible to unambiguously perform the reverse operation. But it can be implemented in the isotropic case, when the is of requency surface is a sphere.

So, we will start the modification of the corresponding formulay by restoring the energy spectrum according to its density of states. In the isotropic case, the following formula for the radius of the isofrequency surface corresponding to the frequency ω follows from the requirement of conservation of the number of phonon states:

$$k_0(\omega) = \sqrt[3]{\frac{3}{4\pi}\int_0^x g_{ph}(\omega)\,d\omega}\,. \tag{3}$$

In the so-called normalized form, this ratio can be presented as follows:

$$K(x) = \sqrt[3]{3\int_0^x f(y)\,dy}\,, \tag{4}$$

where x – is the phonon frequency normalized to their maximum frequency, $f(x)$ – is the density of phonon states normalized to their maximum value according to the Debye model, $K(x)$ – is the phonon quasimomentum normalized to its value corresponding to the maximum phonon frequency according to the Debye model. In addition, let us take into account that both in the general formula for lattice thermal conductivity and in the formulae given in the article [3] for the probabilities of normal scattering of phonons and their scattering with Umklapp, not only the frequency and wave vector of phonons appear, but also the velocity of sound in the crystal, which, is obviously the group velocity. On the other hand, it is not the group but the phase velocity of sound that is directly related to the

elastic constants of the crystal. Therefore, we still need the group velocity of sound normalized to the phase velocity of sound in the Debye model for the real phonon spectrum. From relation (2), it is not difficult to obtain the following expression for the normalized group velocity of sound:

$$v_g(x) = \frac{f(x)}{K^2(x)}. \tag{5}$$

Taking into account the above and modifying accordingly the formulae known from [3] for the probabilities of normal scattering of phonons and their Umklapp scattering, we obtain the following formula for the thermal conductivity of a single crystal with a real phonon spectrum in the isotropic approximation:

$$\kappa_l = \frac{3h^2\rho s^4\omega_{\max}}{16\gamma^2k^2T^3}\int_0^1 \frac{f^2(x)x^2\exp(x/\theta)}{K^2(x)\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{Q_l(x)}+\frac{2}{Q_t(x)}\right)dx, \tag{6}$$

where ρ, s, ω_{max}, γ, T the crystal density, the phase velocity of sound, the maximum phonon frequency, the Gruneisen parameter and the temperature $\theta = T/T_D$, T_D – the Debye temperature, the rest of notations are explained above, or they are generally accepted. Moreover:

$$Q_l(x) = f(x)K^2(x) + \mu\frac{x^2}{K(x)}, \tag{7}$$

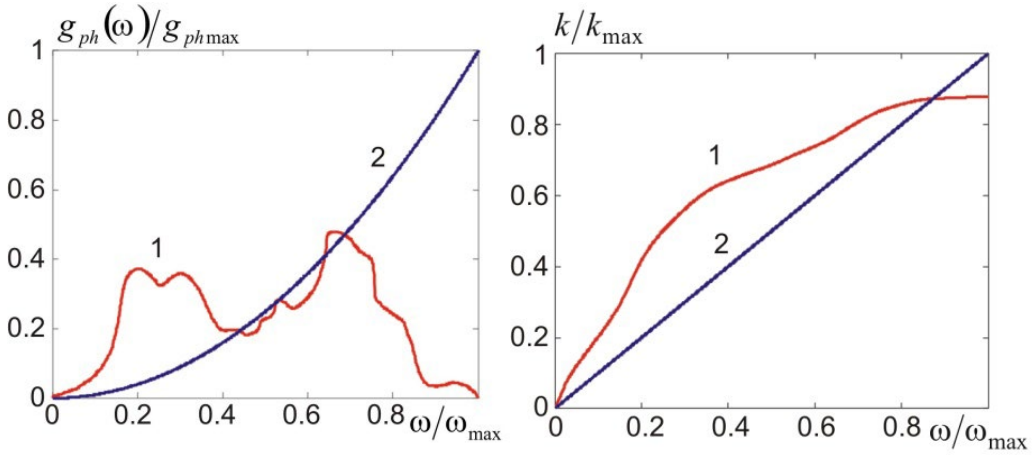
$$Q_t(x) = 3.125\theta^3\frac{f^4(x)}{K^7(x)} + \mu\frac{x^2}{K(x)}, \tag{8}$$

μ – the Umklapp coefficient, which is selected so that the theory coincides with experiment, since its theoretical estimate, made only for a simple cubic lattice with one atom in the unit cell, is not even suitable for all substances with such a lattice. This coefficient was also selected by the authors of work [4]. In this case, expressions (5) and (6) describe mutual scattering of longitudinal and transverse phonons, inherent in a single-crystal material, due to the anharmonicity of thermal vibrations of the lattice, and the terms in them that do not contain the Umklapp coefficient describe normal processes. They influence the overall thermal conductivity due to the renormalization of the time between phonon collisions.

In the Debye model, formula (4) will acquire the form:

$$\kappa_l = \frac{3h^2\rho s^4\omega_{\max}}{16\gamma^2k^2T^3}\int_0^1 \frac{x^4\exp(x/\theta)}{\left[\exp(x/\theta)-1\right]^2}\left(\frac{1}{x^4+\mu x}+\frac{2}{(3.125\theta^3+\mu)x}\right)dx. \tag{9}$$

The real [5] and Debye densities of phonon states for bismuth telluride and the corresponding dependence of the wave vector on the frequency in accordance with (2) are shown in Fig. 1.



a) *b)*

Fig.1. a) real (curve 1) and Debye (curve 2) densities of phonon states in bismuth telluride; b) the corresponding dependences of the wave vector on frequency

But there is another question, which phase velocity of sound should appear in formulae (4) and (7). The answer to this question is as follows. Since the Debye temperature is experimentally determined on the basis of calorimetric measurements and is a scalar, the velocity that makes sense to be called calorimetric should appear as the phase velocity of sound. It does not necessarily have to be related by any one-to-one relationship to crystal elastic constants, but must be unambiguously related to the number of phonon states in the Debye model. Let's establish this relationship for bismuth telluride.

If the calorimetric Debye temperature is equal to T_D, then $\omega_{max} = 2\pi k T_D / h$, and, hence, the radius of the Debye sphere is equal to

$$k_D = \frac{2\pi k T_D}{hs}. \tag{10}$$

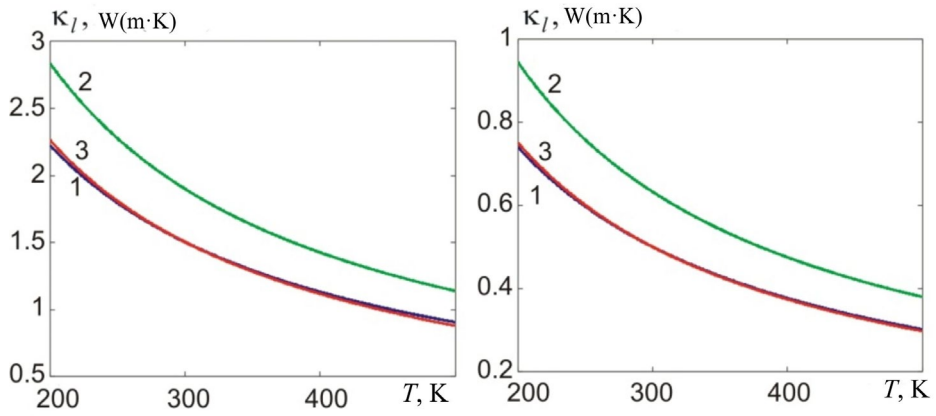
Then the volume of this sphere should be equal to the number of phonon states per unit volume of the crystal. And this number is the number of degrees of freedom per unit volume of the crystal. Given the fact that the bismuth telluride molecule consists of five atoms, it has 6 degrees of freedom. Thus, we obtain the following relation for determination of s:

$$\frac{4}{3}\left(\frac{2\pi k T_D}{hs}\right)^3 = \frac{6 N_A \rho}{M}, \tag{11}$$

where M is a molecular mass of bismuth telluride, other notations are explained above or they are generally accepted. Therefore,

$$s = \frac{2\pi k T_D}{h}\sqrt[3]{\frac{M}{4.5 N_A \rho}}. \tag{12}$$

The temperature dependences of the lattice thermal conductivity of bismuth telluride corresponding to the two considered models in cleavage planes and perpendicular to them are shown in Fig. 2.



a) *b)*

Fig. 2. Temperature dependences of lattice thermal conductivity in the isotropic approximation: a) in cleavage planes, b) perpendicular to them: 1 – in the Debye model; 2 – for the real phonon spectrum, with regard to its influence only on the heat capacity differential contribution to thermal conductivity; 3 – for the real phonon spectrum, with regard to its influence both on the heat capacity differential contribution and on mutual phonon scattering due to the anharmonicity of lattice thermal vibrations

It can be seen from the figure that for both models of the density of phonon states, one of which, namely, shown by curve 1 in Fig. 1, was determined experimentally, the thermal conductivities both in the cleavage planes and perpendicular to them in the entire investigated temperature interval are weakly different from each other, although in the Debye model, at low temperatures, both components of the thermal conductivity tensor are somewhat smaller, and at high temperatures, they are somewhat larger than for the real phonon spectrum. But these differences are so insignificant that they cannot have a significant impact on thermomechanical stresses in thermoelectric legs. At first glance, such minor differences may seem incomprehensible. But it should be borne in mind that the difference in the differential heat capacity contributions to the thermal conductivity for the specified models is compensated by the difference in the manifestations of mutual phonon scattering, which is caused by: 1) the nonlinear relationship between the frequency and the wave vector for the real model of the density of phonon states; 2) the difference between the group sound velocity and the phase velocity for a real model of the density of phonon states; 3) the difference in Umklapp coefficients in the real and Debye models of the density of phonon states. This can be seen from the comparison of curves 1 and 3 with curve 2 in each of the figures. On the other hand, if the real density of phonon states affected only the heat capacity differential contribution to the thermal conductivity, then the thermal conductivity would be approximately 1.27 - 1.5 times higher than in the Debye model. And this would allow us to hope for a certain reduction of thermomechanical stresses in thermoelectric legs, albeit at the expense of some loss of thermoelectric figure of merit and the efficiency of material.

Note that when constructing the graphs, we used the following values of Bi_2Te_3 parameters: $\rho = 7850$ kg/m^3, $M = 801$, $T_D = 155$ K, $\gamma = 1.4$. The anisotropy of thermal conductivity at 300 K was assumed equal to [6] and for both models of the density of phonon states it was taken into account solely due to the anisotropy of Umklapp coefficient.

Regarding a more complete comparison of the results of our calculations with experiment, we note that the calculated value of the thermal conductivity of bismuth telluride at 200 K that we obtained differs from the experimental value, which, in accordance with the data of [6, 7] is 2.1 W/(m K), by approximately 5.7 % upward, which can be considered satisfactory. However, on this

occasion it is appropriate to make the following remark. There is no direct experimental technique for separating the lattice part of thermal conductivity from the thermal conductivity caused by free charge carriers. Therefore, this separation is performed purely by calculation on the basis of certain assumptions about the band spectrum of the material and the mechanisms of scattering of free charge carriers in it. We did not analyze the reliability of this kind of assumptions made in paper [7].

Conclusions

1. In the isotropic approximation, it is shown that the real density of phonon states, compared to the Debye density, has a weak effect on the lattice thermal conductivity of single-crystal bismuth telluride in the temperature range between 200 and 500 K both in the cleavage planes and perpendicular to them. Small differences between the Debye and real densities of phonon states from the point of view of their influence on thermal conductivity can be explained by the fact that the differences in the differential heat capacity contributions to thermal conductivity due to the considered densities of phonon states are compensated by differences in the group sound velocities and the characteristics of mutual phonon scattering, both normal and Umklapp.
2. The Umklapp parameter is anisotropic and depends on the form of the density of phonon states, but does not depend on temperature.
3. When calculating thermal conductivity, the phase velocity of sound, which is determined by the Debye temperature and the number of degrees of freedom of the phonon subsystem, should be taken into account.
4. Differences in the densities of phonon states between the real and Debye models cannot lead to significant differences in the expected values of thermomechanical stresses in thermoelectric legs.
5. The results of calculations are not only in qualitative, but also in satisfactory quantitative agreement with experimental data.

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ТЕОРЕТИЧНІ МОДЕЛІ ГРАТКОВОЇ ТЕПЛОПРОВІДНОСТІ МОНОКРИСТАЛІЧНОГО ТЕЛУРИДУ ВІСМУТУ

В ізотропному наближенні враховано вплив реальної густини фононних станів на граткову теплопровідність монокристалічного телуриду вісмуту у рамках двох модельних підходів. Спочатку задачу розглянуто у ізотропному наближенні, а потім наближено враховано шарувату структуру та анізотропію. Показано, що реальна густина фононних станів майже не змінює температурної залежності граткової теплопровідності телуриду вісмуту як в площині шарів(спайності) так і перпендикулярно до неї порівняно з Дебаївською густиною фононних станів. Ця слабкість пояснюється тим, що зумовлена безпосередньо щільністю фононних станів зміна диференціального теплоємнісного внеску у теплопровідність компенсується впливом цієї щільності на розсіювання, який зумовлений нелінійною залежністю хвильового вектора від частоти, відмінністю групової швидкості звуку від фазової та істотним зростанням коефіцієнта перекидання. Отримані результати перебувають не лише у якісній, а й у задовільній кількісній згоді з теоретичними дослідженнями попередніх авторів та експериментом. Це дозволяє сподіватись, що реальна густина фононних станів не справлятиме істотного впливу на термомеханічні деформації термоелектричних гілок у порівнянні з Дебаївською густиною фононних станів. Бібл. 7, Мал. 2.

Ключові слова: *циклічна стійкість термоелементів, надійність термоелектричних гілок, термомеханічні напруги, теплопровідність, реальна і Дебаївська щільності фононних станів, нормальні процеси, процеси перекидання.*

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