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Analysis of heat conductivity mechanisms in PbSnTe solid solutions

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In the paper, a theoretical calculation of the coefficient of thermal conductivity of solid solutions of PbSnTe was carried out. The contribution of phonon scattering on substitution atoms to the effect of reducing thermal conductivity has been established. The composition of the PbSnTe solid solution, characterized by the lowest values of the lattice component of the thermal conductivity coefficient k_{lat}, was determined. The concentration of intrinsic charge carriers in solid solutions is calculated and their influence on the thermoelectric parameters of the material is shown.

Keywords: thermoelectric materials, solid solutions, thermal conductivity coefficient.

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Introduction

A^4B^6 compounds are well-known thermoelectric materials [1-11]. Improvement of their operational parameters can be achieved by creating solid solutions. First of all, this leads to a decrease in the thermal conductivity of the material, which has a positive effect on the thermoelectric factor Z ($Z = S^2\sigma / k$, where S is the Seebeck coefficient, σ and k are electrical conductivity and coefficient of thermal conductivity, T is the absolute temperature). The creation of solid solutions leads to a change in a number of fundamental characteristics of the material, in particular, the width of the band gap, the effective mass of carriers, etc. Thus, it is important to establish the influence of each of these factors on the magnitude of k, which will allow effective implementation of the technique of creating solid solutions to reduce the thermal conductivity of the base material. Since the coefficient of thermal conductivity of conductors can be represented as the sum of the coefficients of the electronic and lattice subsystems ($k = k_{el} + k_{lat}$), the calculation of the coefficient of thermal conductivity k is usually reduced to two separate problems. The calculation of the electronic component is almost always based on the use of the Wiedemann-Franz law ($k_{el} = L_0 T \sigma$, where L_0 is the Lorentz number). Different approximations in the calculation of kel are distinguished by taking into account or not taking into account the degeneracy of carriers in the material, using simplified expressions for calculating the Lorentz number or its sequential calculation through Fermi integrals, correctly taking into account the peculiarities (parabolicity or non-parabolicity) of energy zones. The accuracy of determining the Fermi level is important in these calculations, which will depend on the value of the calculated Fermi integrals and the Lorentz number itself [12].

The calculation of the lattice component of the coefficient of thermal conductivity of solid bodies is based on the use of the "phonon gas" approximation. At the same time, the thermal conductivity coefficient k_{lat} is determined by the formula obtained in the kinetic theory of gases ($k_{lat} = 1/3\, cvl$ or $k_{lat} = 1/3\, cv^2\tau$; c - the heat capacity per unit volume, v - phonon speed, l - phonon free path length, τ - relaxation time). The calculation of the heat capacity is based on the use of the continuous approximation [13]. This approximation is valid for long waves. That is, the features of short waves are ignored (or more precisely, their role is not highlighted). When calculating klat, knowledge of certain parameters is assumed: Debye temperature θ, Grüneisen parameter γ, phase and group of velocity v_p, v_g. The result of calculating the thermal conductivity coefficient is sensitive to the value of these values. And if the data on θ from different sources do not differ significantly, then for γ the spread of values obtained by different authors is large [14]. And work [18] shows 6 methods of calculating the speed of sound in solid solutions, which, respectively, lead to excellent numerical values of the parameters calculated on their basis.

Due to the complexity of calculating k_{lat} of solid solutions, often the analysis of the influence of the composition of the solution on the value of k is reduced to the sequential calculation of the electronic component, and then the calculation of the lattice component of thermal conductivity, by subtracting the theoretically calculated kel in various approximations from the experimental values of k_{exp}. This approach is due to the fact that when creating solid solutions with a change in composition, a number of material parameters necessary for calculation changes, and the numerical values of the changes in these values are not always known with the required accuracy. Moreover, these are not only fundamental parameters, such as the width of the band gap, the effective mass of carriers, etc., but also the above-mentioned Debye temperature, Grüneisen parameter, phase and speed velocity.

In this work, the electronic and lattice thermal conductivity of PbSnTe solid solutions were calculated with a sequential analysis of the influence of the accuracy of the determination of the listed parameters and some model assumptions on the obtained results. One of the main tasks that was set at the same time was to analyze the sufficiency of taking into account the scattering of phonons on phonons and phonons on substitution atoms for the interpretation of experimental data $k(T)$ for PbSnTe solid solutions. This task is due to the fact that other important mechanisms of phonon scattering and the participation of optical phonons in heat transfer processes are often discussed in the literature [18, 19]. In addition, in the work, the concentration of intrinsic charge carriers in solutions was calculated and their influence on the thermoelectric factor was discussed. Knowing the temperature at which intrinsic conductivity begins to dominate is important, as it often determines the upper temperature limit of effective application of materials.

I. Experiment

Solid solutions of $Pb_{1-x}Sn_xTe$ (x = 0, 0.25 and 0.5) for research were obtained by synthesis in vacuumed and specially cleaned quartz ampoules at a temperature of 1290 K. The resulting ingots were crushed and pressed by the SPS method. The single-phase nature of the obtained ingots and samples was confirmed using the Bruker D8 Advance X-ray diffractometer. The parameter of the unit cell of the studied materials corresponded within the error of dependence a(x) = 6.461 – 0.145 x (A) given in the work [17]. The thermoelectric property measurements were performed using NETZSCH SBA458 and NETZSCH LFA457. In more detail, the method of obtaining experimental samples and studying their properties is described in works [17, 20, 21].

The results of the measurements are presented in Figure 1. The numerical values and the qualitative course of the obtained temperature dependences of parameters S, σ, k correspond to literature data, in particular the work [17]. In particular, p-type conductivity is observed for pure PbTe up to a temperature of about 550 K, and n-type at higher temperatures. The addition of tin to the solution leads to the fact that the material is characterized by only p-type conductivity in the entire temperature range. As the Sn content increases, the specific electrical conductivity of the samples increases and the Seebeck coefficient decreases. The thermal conductivity coefficient is the smallest for the composition x = 0.25.

II. Calculation of the electronic component of the thermal conductivity coefficient

Calculation method. Taking into account the Wiedemann-Franz law, we note the electronic component of thermal conductivity ($k_{el} = L0\, T\, \sigma$),

$$k = k_{lat} + k_{el} = k_{lat} + L_0 T \sigma \tag{1}$$

where L_0 is the Lorentz number. For a two-band Kane model, the Lorentz number L_0 is expressed in terms of two-parameter Fermi integrals as follows [12]:

$$L_0(\eta,\beta) = \left(\frac{k_0}{e_0}\right)^2 \left[\frac{I^2_{r+1,2}(\eta,\beta)}{I^0_{r+1,2}(\eta,\beta)} - \left(\frac{I^1_{r+1,2}(\eta,\beta)}{I^0_{r+1,2}(\eta,\beta)}\right)^2\right] \tag{2}$$

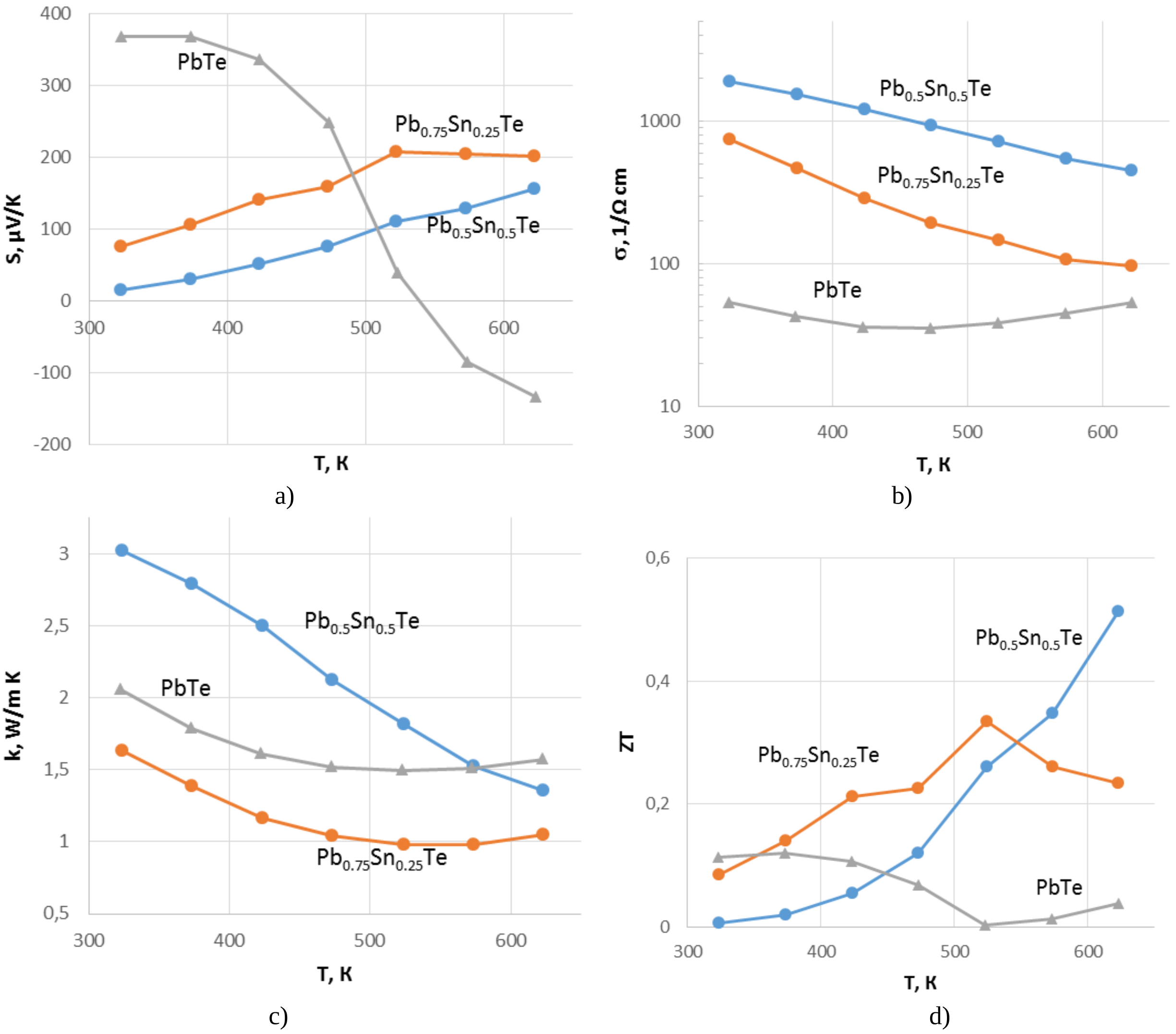
where k_0 is the Boltzmann constant, e_0 is the electron charge, r is the scattering parameter, $\eta = \mu/k_0T$ is the reduced Fermi energy (μ – Fermi energy), $\beta = k_0T/E_g$ is non-parabolic parameter and $I^m_{n,k}(\eta,\beta)$ is the two-parametric Fermi integrals:

$$I^m_{n,k}(\eta,\beta) = \int_0^\infty \left(-\frac{df}{dx}\right) \frac{x^m (x+\beta x^2)^n\, dx}{(1+2\beta x)^k} \tag{3}$$

The reduced Fermi energy η was determined by fitting the Seebeck coefficient:

$$S = -\frac{k_0}{e}\left[\frac{I^1_{r+1,2}(\eta,\beta)}{I^0_{r+1,2}(\eta,\beta)} - \eta\right] \tag{4}$$

That is, for each given T, the value of μ was selected in such a way that the value of S calculated by formula (4) at a given temperature coincided with the experimental value. An important stage of the calculation is the determination of the scattering parameter r. It is known that the dominant mechanism of scattering of charge carriers in A^4B^6 materials is scattering by acoustic phonons, for which the parameter r = 0. If the calculation is carried out for all three possible values of this parameter (r = 0, 1, 2), then only for the case of r = 0 the calculated carrier concentrations (based on previously calculated μ) are realistic (in the range of 10^{18}-10^{21} cm^{-3}). In the case of



a) b) c) d)

Fig 1. Temperature dependence of Seebeck coefficient *S* (a), electrical conductivity *σ* (b), thermal conductivity *k* (c), and the *ZT* parameter (d) of $Pb_{1-x}Sn_xTe$ (x = 0, 0.25 and 0.5) samples.

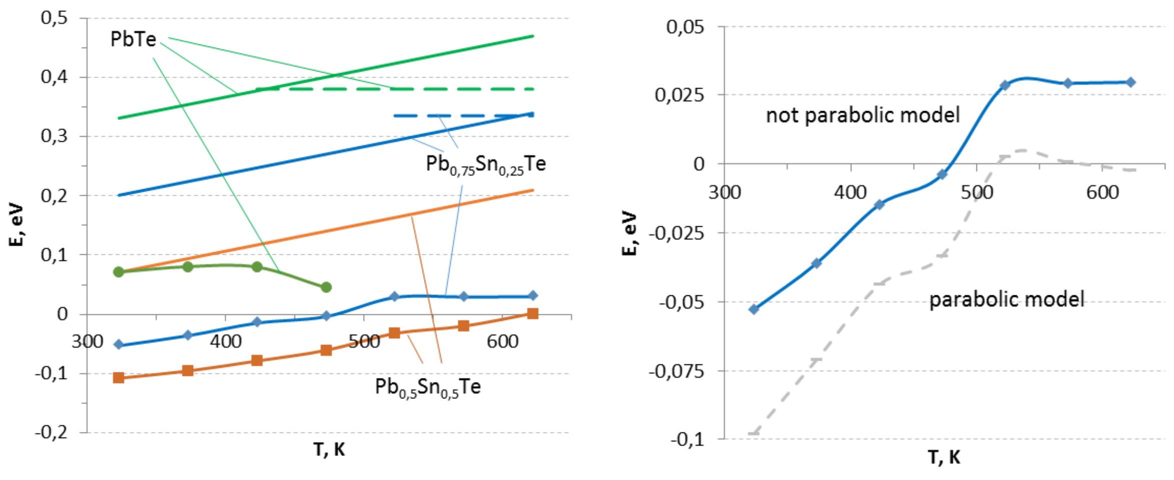
$r = 1$, the calculated chemical potential of electrons for some values of T is over 0.3 eV, and at $r = 2$ – over 1.9 eV, which seems unrealistic and thus confirms the dominance of carrier scattering by acoustic phonons.

Calculation results and their discussion. Values of μ determined under the condition of realization of $r = 0$ are in the vicinity of the ceiling of the valence band or below (Fig. 2). (For the composition $x = 0$, experimental points for lattice thermal conductivity were obtained only up to 450 K, since at higher temperatures two valence bands must be taken into account, which greatly complicates the calculation. First of all, the calculation of the chemical potential of electrons based on experimental data $S(T)$ is meant). The calculation of μ was carried out in the approximation that the zones are non-parabolic. If the non-parabolicity of the valence zone is neglected (for this it is sufficient to consider the parameter β equal to zero in the above formulas), then the determined values will lie deeper in the valence zone (Fig. 2, b).

The zone inversion temperature, at which $E_g = 0\ eV$, is outside the studied temperature range, in the region of lower temperatures (Fig. 2). However, in the vicinity of a temperature of 320 K for the composition x = 0.5 E_g is only ≈ 0.08 *eV* (for $x = 0.25$ – 0.2 *eV*). And although these values increase with increasing *T* (by approximately 0.15 *eV*), we can still expect a significant influence of native carriers on the properties of materials of such compositions.

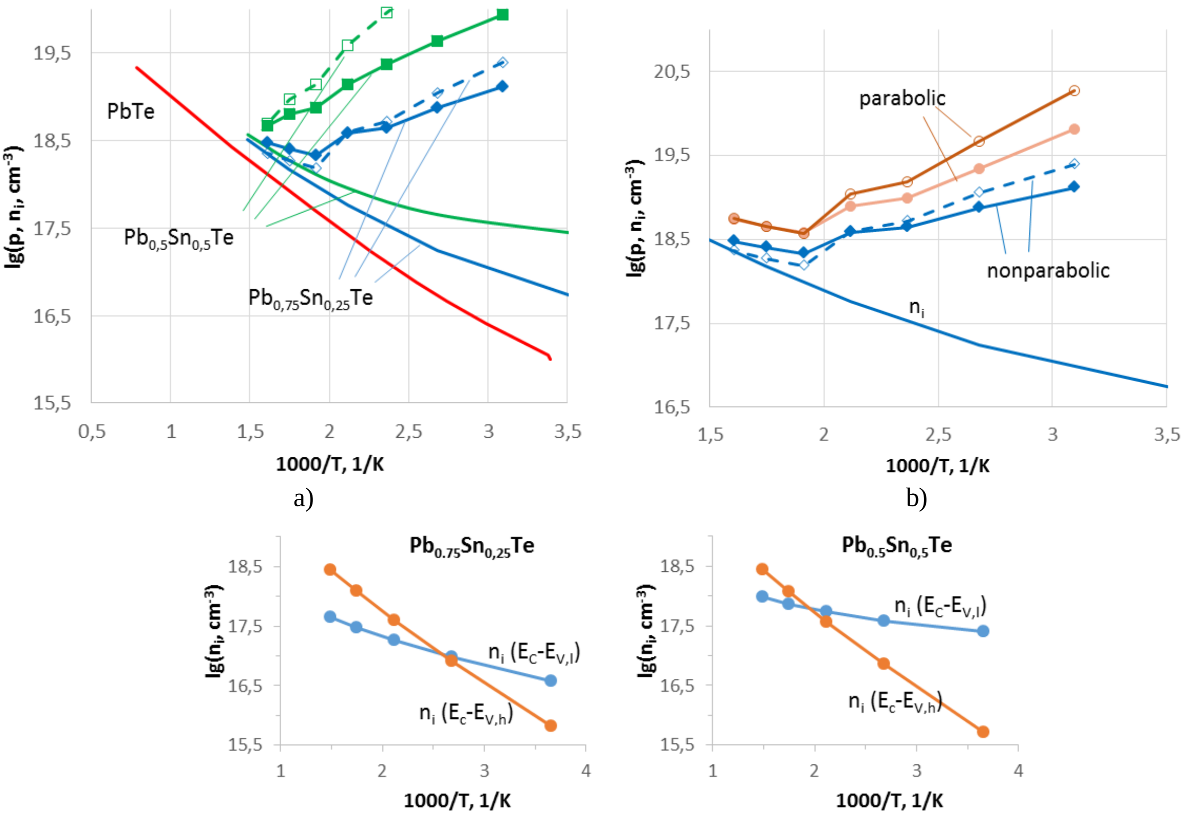
In fig. 3a shows the dependence of the logarithm of the carrier concentration on the inverse temperature calculated on the basis of the determined values of μ. Calculation of *p* was carried out according to the dependence $p = N_V\ exp(-\mu/kT)$. At the same time, two calculations were carried out, in one of which the effective mass was considered independent of the temperature and concentration of the carriers and equal to 0.17 m_0 for $x = 0.25$ [22] and 0.16 m_0 for $x = 0.5$ [22]. In the other case, it was considered that $m^* = m_0 \cdot (1 + 2\ \mu/E_g)$. It was established that, as in the case of taking into account or not taking into account parabolicity, the quantitative changes are not significant, and the qualitative nature of all dependencies is unchanged.

Fig. 3b shows for comparison the carrier concentrations obtained with and without taking into account the non-parabolicity of the valence bands. It can be seen that the qualitative course of the $p(T)$ dependence



a) b)

Fig. 2. a) Fermi energy of carriers for PbTe, $Pb_{0.75}Sn_{0.25}Te$, $Pb_{0.5}Sn_{0.5}Te$ (for $r = 0$) calculated in the approximation of non-parabolic zones based on experimental data $S(T)$ according to formula (4). The figure also shows the values of the energy gaps (forbidden zones) between the conduction zone E_C and the valence zones $E_{V,l}$ and $E_{V,h}$. b) Comparison charts of the calculated dependencies $\mu(T)$ in the approximation of parabolic zones (dashed curve) and non-parabolic zones (solid curve) (for the composition $Pb_{0.75}Sn_{0.25}Te$).



b) d)

Fig. 3. a) - The dependence of the hole concentration p on the inverse temperature for $Pb_{0.75}Sn_{0.25}Te$, $Pb_{0.5}Sn_{0.5}Te$ solid solutions is calculated on the basis of those shown in Fig. 2. values of the Fermi energy. Dashed lines with open symbols show the result of calculating p, taking into account the dependence of the effective mass on the position of the Fermi level. The intrinsic concentration for the specified solid solutions and pure PbTe is also given (solid curves without dots).
b) - Dependence of $p(T)$ in the approximation of parabolic and non-parabolic zones for the composition $x = 0.25$.
c, d) - The dependence of the electron concentration for $Pb_{0.75}Sn_{0.25}Te$ (c) and $Pb_{0.5}Sn_{0.5}Te$ (d) is calculated separately for the zones of light and heavy holes.

does not change. It should be noted that taking into account or not taking into account the non-parabolicity of the E_C conduction zone does not affect the calculation result, since μ is far from the edge of this zone.

Also in fig. 3 a shows the calculated intrinsic concentration of carriers in solid solutions. The calculation of n_i was carried out according to the dependence $n_i = \sqrt{np} = \sqrt{N_C N_V} exp\left(-E_g/2kT\right)$. At the same time, the concentration was calculated separately for $E_g = E_C - E_{V,l}$ and for $E_g = E_C - E_{V,h}$ (Fig. 3 c, 3 d). And presented in fig. 3 and the dependences are the sum of the concentrations obtained in these two calculations. In this case, the non-parabolicity of the zones ($m^*(\mu)$ dependence) was not taken into account, since μ for an intrinsic semiconductor should be near the middle of the band gap. Therefore, according to the calculations, for the composition $x = 0.5$ at low T (around 300 K), the concentration of intrinsic carriers n_i is higher (compared to the composition $x = 0.25$), which is due to the smaller gap width (the difference in the effective masses for of two compositions is not significant: 0.17 m_0 for $x = 0.25$ [22] and 0.16 m_0 for x = 0.5 [22]). As T increases, the difference in n_i concentration for the two compositions decreases and asymptotically approaches the n_i concentration for PbTe.

The dependence of $p(T)$ for the composition $x = 0.5$ is decreasing. For the same composition with $x = 0.25$ at $1/T \approx 2$, there is a deviation from a monotonous decrease in concentration, passing through a minimum and further growth. Moreover, the numerical values of carrier concentration at temperatures above the minimum approximately correspond to the carrier concentration itself. Obviously, it can be stated that the experimentally observed output to the saturation of the $S(T)$ dependence for the composition x=0.25 starting from $T \approx 500$ K is caused by the own carriers. It can also be assumed that the bipolar component of thermal conductivity will have a more significant effect on the total coefficient of thermal conductivity for this component. This is confirmed by the non-monotonic behavior of the experimental dependence $k(T)$ at $T > 500$ K (Fig. 1).

The generation of own carriers is the limiting factor that determines the maximum temperature of the effective application of the thermoelectric material. That is, the material with the composition $x = 0.25$ will be effective (more effective than other compositions) only up to a temperature of about 550 K. A number of factors contribute to the faster manifestation of n_i in the material with the composition $x = 0.25$ (compared to the composition $x = 0.5$). First, for the composition $x = 0.25$ E_g, the influence of the second valence zone (heavy hole zone) begins to appear faster, that is, at lower T. Moreover, for heavy holes, E_g does not change with increasing T. And secondly, in composition 0.5, the impurity concentration of carriers is higher, due to a greater concentration of vacancies compared to composition $x = 0.25$.

However, despite the manifestation of intrinsic conductivity for the composition $x = 0.25$ at lower temperatures, in general, the electronic thermal conductivity is higher for the composition $x = 0.5$ (Fig. 4), which is due to the higher concentration of carriers. For the same reasons, the Seebeck coefficient for this composition is smaller. Thus, from the analysis of the electronic component of thermal conductivity, it can be said that the composition $x = 0.25$ is characterized by a high bipolar component of thermal conductivity, and the composition $x = 0.5$ is characterized by a high electronic component. Therefore, to obtain materials with lower thermal conductivity, it is possible either to dope with donors of composition $x = 0.5$ to reduce the concentration of carriers (which was done in particular in [17]) and, accordingly, the electronic component of thermal conductivity. On the other hand, it is possible to use compositions with x < 0.5, but x > 0.25, so that the effect of the bipolar component must be smaller.

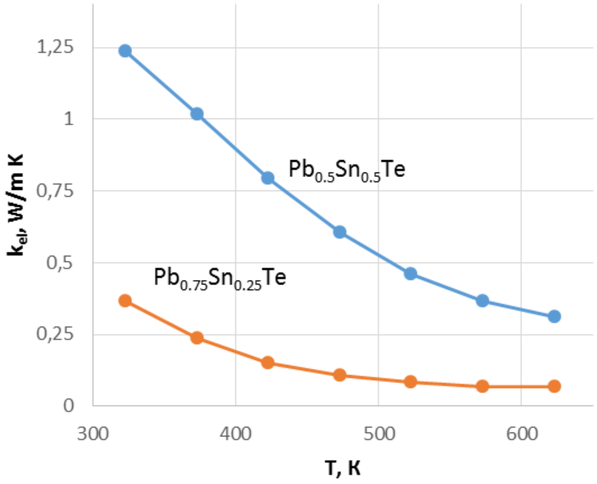


Fig. 4. Temperature dependence of the electronic component of $Pb_{0.75}Sn_{0.25}Te$, $Pb_{0.5}Sn_{0.5}Te$ solid solutions.

III. Calculation of the lattice component of the thermal conductivity coefficient

Calculation method. The theoretical calculation of the coefficient of lattice thermal conductivity can be carried out based on the following dependence [19, 23-24]:

$$k_{lat} = \frac{1}{3}\int_0^{\omega_D} c_V(\omega) v_S(\omega) l(\omega) d\omega$$

or

$$k_{lat} = \frac{1}{3}\int_0^{\omega_D} c_V(\omega) v_g(\omega)^2 \tau(\omega) d\omega \qquad (5)$$

Here, c_V is the specific heat (одиниці об’єму), v_s is the speed of sound, v_g is the group of speed of sound, τ is the relaxation time for phonons, ω_D is the Debye frequency. The specific heat at high temperatures ($T > \theta$) can be found as follows:

$$c_V(\omega) = \frac{3k_0\omega^2}{2\pi^2 v_s^3} \qquad (6)$$

The main scattering mechanism that determines the order of magnitude of the thermal conductivity coefficient of single-crystal materials is phonon-phonon scattering. U- and N-processes are distinguished in phonon interaction. It is believed that the coefficient of thermal conductivity is determined mainly by U-processes, since the total quasi-momentum of interacting phonons does not change during *N*-processes [25] [26]. (that is, *N*-processes do not create thermal resistance). In the case of *U*-processes, a decreasing dependence of $k(T) \sim 1/T$ is assumed. With *N*-processes, $k(T)$ can grow [25]. Since $k(T) \sim 1/T$ is observed experimentally, this is the basis for neglecting *N*-processes when calculating the thermal conductivity coefficient in most works on the calculation of k.

Relaxation time for phonon-phonon Umklapp scattering [19]:

$$\tau_U(\omega) = \frac{\left(6\pi^2\right)^{1/3}}{2}\frac{Mv_s^3}{k_0V^{1/3}\gamma^2\omega^2T} \qquad (7)$$

where M is the average atomic mass (ting into aczont that stanium and plumbum octsupi the nodes of the same sublattice in $Pb_{1-x}Sn_xTe$, M was counted as $1/M = 1/M_{Te}+(1-x)/M_{Pb+x}/M_{Sn})$ V is the atomic volume (determined how a^3/N, N – is the number of atoms in the unit cell, a is the unit cell parameter; for PbSnTe $N = 8$, a (x) = 6.461 - 0.145 x (A) [17]), and γ is the Gruneisen parameter.

For solid solutions, phonon scattering on substitutional atoms is also significant. For this mechanism [19]:

$$\tau_{PD}(\omega) = \frac{4\pi v_s^3}{V\omega^4}\left(\sum_i f_i\left(1-\frac{m_i}{m}\right)^2 + \sum_i f_i\left(1-\frac{r_i}{r}\right)^2\right)^{-1} \qquad (8)$$

This $f_i = x(x-1)$, where x is the atomic fraction of impurity atoms, m_i/m is the ratio of atomic masses between impurity and matrix atoms, r_i/r is the ratio of atomic radii between impurity and matrix atoms. Here it is important to note that for small x, the approximation $f_i = x$ is often used, which is incorrect for large x.

The analysis of expression (7) for the relaxation time during phonon-on-phonon scattering leads to known requirements for thermoelectric materials, which must be characterized by a low value of k_{lat}. Such materials should have a low Debye temperature θ and a high value of the Gruneisen parameter γ. In addition, a small reduced mass M and a large value of the volume per atom V. A detailed analysis of these requirements leads to the conclusion that their simultaneous implementation is difficult. Thus, in particular, smaller values of the reduced mass will usually correspond to smaller values of V. This pattern can be circumvented in the case of using materials with very hollow structures (small packing coefficient), such as $Ba_8Ga_{16}Ge_{30}$ or some others presented, in particular, in [19]. The paper [19] also demonstrated the dependence of the thermal conductivity coefficient on the number of atoms in the unit cell N. In the case of phonon scattering by phonons, $k_{lat} \sim N^{-1/3}$, and in the case of phonon scattering at grain boundaries, $k_{lat} \sim N^{-1}$. This regularity is determined by the expression relating the speed of sound and the Debye frequency: $\omega_D \sim N^{-1/3}\, v_s$ (appendix 1, formula 3A). This representation shows a tendency to decrease the volume per atom in structures with large unit cells. This representation shows a tendency to decrease the volume per atom in structures with large unit cells.

A more fundamental relationship between the parameters θ and γ. Both of these parameters, despite the fact that they can be experimentally determined independently, are related to each other through the dispersion dependences for phonons $\omega(k)$ (here k is the wave number) and their temperature dependence. In particular, according to [13] there is an unambiguous relationship between them: $\theta \sim V^{-\gamma}$; and therefore, when optimizing material properties, in particular when creating solid solutions, it is worth taking into account their change, firstly, simultaneously, and secondly, preferably within the framework of one approximation. From the analysis of the given proportionality, it also follows that larger values of the parameter γ will correspond to smaller values of θ. Taking into account the fact that $k \sim \theta^3/\gamma^2$, it can be argued that anharmonicity in general will contribute to a decrease in the coefficient of thermal conductivity. Interesting conclusions regarding the relationship between these parameters were obtained in [27]. In it, based on ab initio calculations on the example of lithium, sodium, and potassium oxides, it is shown that an increase in temperature leads to an increase in γ and a decrease in θ (That is, an increase in T additionally decreases k, not only due to an increase in the scattering of phonons by phonons). But an increase in pressure leads to an increase in γ and a decrease in θ. That is, more compact structures will be characterized by a higher coefficient of thermal conductivity, which was already mentioned above.

It also follows from the analysis (8) that for the intensification of phonon scattering processes in solid solutions, the masses of matrix atoms and substitution atoms, as well as their radii, should differ as much as possible.

Some additional details and model assumptions of the klat calculation method and parameter selection are given in appendix 1.

Calculation results. The numerical values of the Gruneisen parameter, Debye frequency, and sound speed for different values of x, required for the numerical calculation of the coefficient of thermal conductivity of $Pb_{1-x}Sn_xTe$ solid solutions, as in other similar works, in particular [17], were obtained by linear interpolation of the corresponding parameters for the binary compounds PbTe and SnTe. The calculated coefficient of thermal conductivity for compositions $x = 0$ and $x = 0.25$ is presented in Fig. 5. The obtained $k(T)$ curves agree relatively well with the experimental data. In the range of temperatures $T > 500$ K, an increase in the experimental values of k is observed due to the manifestation of bipolar thermal conductivity. Since the working model does not take this into account, the correlation of the theoretical curve with the experimental points in this area deteriorates. According to the calculation results, the contribution of phonon scattering on point defects, although not decisive, is significant (Fig. 6). In particular, for the composition $x = 0.25$ at around 300 K, its inclusion changes the numerical value of the thermal conductivity coefficient by about *a* quarter. From fig. 7. it can be seen that the calculated dependence of $k_{lat}(x)$ at 320 K quite accurately coincides with the experimental value of k_{exp} at $x = 0$, however, as x increases, the theoretical curve lies above all the experimental data presented in the figure.

Taking into account the fact that both the parameters γ and θ can be determined through the speed of sound, it is possible to calculate $k(T)$ using only the experimental values of the longitudinal and transverse components of the sound speed: v_L and v_T.

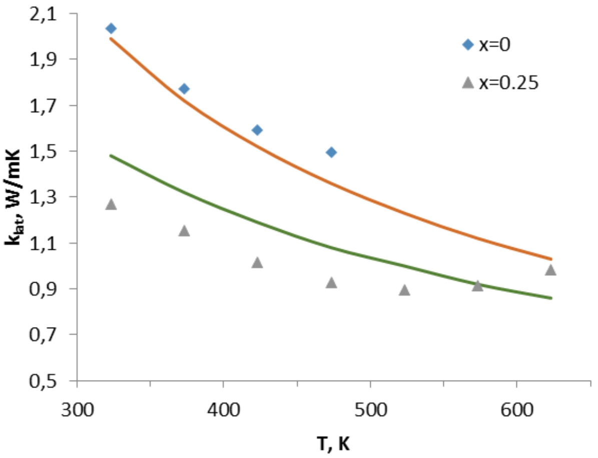


Fig. 5. Temperature dependence of the lattice component of the thermal conductivity coefficient for PbTe and $Pb_{0.75}Sn_{0.25}Te$. Points - experimental data defined as k_{tot} - k_{el}, curves - calculation.

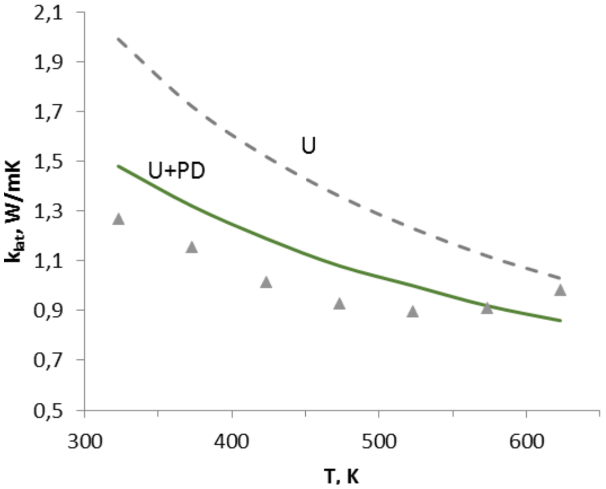


Fig. 6. Temperature dependence of the lattice component of the thermal conductivity coefficient for $Pb_{0.75}Sn_{0.25}Te$ taking into account the scattering of phonons on phonons (dashed curve) and phonons on phonons and phonons on substitution atoms (solid curve).

The Debye frequency was determined according to (3A, Appendix 1), vs according to (5A, Appendix 1), and the Gruneisen parameter was determined as $\gamma=3/2\cdot(1+\eta)/(2-3\eta)$, where $\eta=1/\,2\cdot((v_L/v_T)^2-2)/((v_L/v_T)^2-1)$ is Poisson's ratio. At $v_L = 3050$ m/s and $v_T = 1730$ m/s [17], η = 0.26 is obtained for PbTe, which is in good agreement with the data [28]. As in the previous version of the calculation, we used the values of v_L and v_T for PbTe and SnTe from [17] and approximated them with a linear dependence to obtain the corresponding values for different compositions. The values of k calculated in this way for the composition x=0 are smaller than when using the approach used above (Fig. 7). However, in the range of compositions x = 0.25-0.6, the theoretical curve $k_{lat}(T)$ lies much closer to the experimental points.

The differences observed between the two theoretical curves can have several explanations. But first of all, this indicates a significant impact on the result of calculating the numerical values of parameters γ, θ, v_S. Regarding the specific reasons for the disagreements. First, this may indicate the shortcomings of the linear approximation when determining the parameters γ, θ, v_S for intermediate compositions of the solution. Although, for the unit cell parameter, such a dependence has been experimentally confirmed. However, this does not mean that it will also be valid for other values.

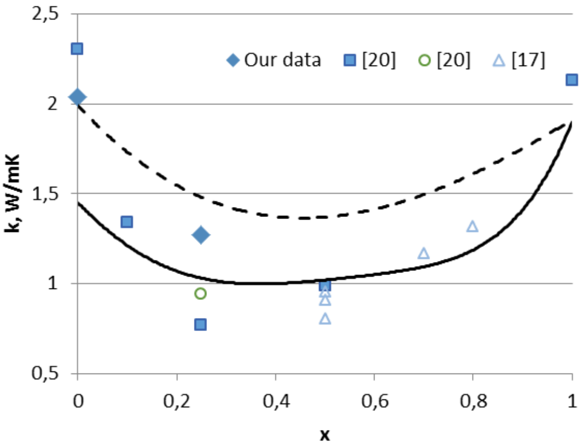


Fig. 7. Concentration dependence of the lattice component of the thermal conductivity coefficient at 320 K for two calculation options: dashed curve – parameters θ, γ, v_S are taken from separate experimental studies; solid curve – parameters θ, γ were calculated using experimentally measured v_L and v_T.

Secondly, it is worth considering the approximation of the formula for the relaxation time during scattering on substitutional atoms τ_{PD} (8). It is worth mentioning that the proportionality of $\tau_{PD} \sim 1/\omega$ was obtained in the long-wave approximation [29-30]. Also, this formula was not theoretically derived, but "constructed" (here we mean specifically the factor in brackets in formula (8)) based on assumptions about possible factors that will affect the intensity of phonon scattering when impurities are introduced. The first versions of this formula took into account only the mass factor (m_i/m) [30]. Further, to improve the correlation of calculations with the experiment, the size factor (r_i/r) was also introduced [30]. A significant improvement could be the introduction of an additional multiplier that will take into account the charge state of the substitution atoms. In particular, it was shown in [31] that ionized impurities in PbTe scatter phonons much more effectively due to the greater polarization of the crystal lattice in the vicinity of the impurity defect. In particular, for a thallium impurity in PbTe in the neutral state, the phonon scattering cross section is 0,74, and in the ionized state it is 4,7. In PbSnTe solid solutions, steel atoms are in a neutral state. However, the possibility of formation of metal vacancies with -1, -2, -4 charge states [32] may indicate significant redistribution of the electron density around atoms, which will lead to an increase in the scattering cross section.

It should be noted that the formula for the relaxation time during the scattering of phonons on phonons also at high T and high frequencies may differ from (7). First of all, the indicator of the degree of frequency is meant. According to works [33-35], the equality of this quantity "2" is not chosen on the basis of strict derivations using a generalized model and is sometimes not fulfilled.

With such a discrepancy between the curves obtained as a result of the use of different numerical values and methods of calculating the parameters γ, θ, vs, it is difficult to assert the presence or absence of additional mechanisms of phonon scattering, in particular the participation of optical phonons. Appendix 2 also discusses other factors that may affect the accuracy of the calculation. However, it can be unequivocally stated that the contribution of phonon scattering on substitutional atoms is significant and its consideration is necessary for a quantitatively correct description of the experimental dependences of k_{lat}(T).

Conclusions

The experimental thermal conductivity for a PbSnTe solution can be satisfactorily explained by taking into account the scattering of phonons on phonons and phonons on point defects. Errors in the experimental data k, as well as the accuracy of the calculation of k_{lat}, due to both model assumptions and the accuracy of determination of individual crystal parameters, do not allow us to unambiguously establish the presence or absence of the influence of optical phonons on thermal conductivity. But its influence is definitely not decisive.

The generation of own carriers is the limiting factor that determines the maximum temperature of effective use of PbSnTe thermoelectric materials: for composition $x = 0.25$ such temperature is about $T \approx 550$ K, and for composition $x = 0.5$ this temperature consist $T \approx 650$ K.

Given that: 1) composition $x = 0.25$ is characterized by a low temperature of the onset of intrinsic conductivity; 2) composition $x = 0.5$ has a high concentration of carriers and, accordingly, high electronic thermal conductivity; 3) According to calculations, composition $x = 0.4$ has the lowest lattice thermal conductivity; then we should probably expect optimal values of ktot for compositions around $x \approx 0.4$. (possibly with additional doping to optimize μ).

Calculation of the coefficient of thermal conductivity requires correct consideration of θ, γ, v_S. But since these parameters are interconnected by analytical dependencies, it is possible to use a model in which the only (one instead of three) parameter is the transverse and longitudinal speed of sound. This method of calculating k is quite a practical approach, since it is the most easily measured of all three parameters, and the accuracy of measurements is not critical for subsequent calculations.

Acknowledgments

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Appendix 1

The formula for the coefficient of thermal conductivity includes three parameters: specific heat capacity, group of velocity and relaxation time. Analytical expressions and numerical values of parameters for their calculation are obtained in certain approximations. Their clear understanding is necessary for correct interpretation of calculation results and adequate selection of numerical values of model parameters (primarily γ, θ, v_S).

Specific heat capacity. The specific heat capacity (6) is defined in the Debye approximation. The main assumptions of this theory are the use of the continuum approximation and the use of the assumption of a quadratic dependence of the density of states on the frequency with some maximum possible value of ω_D (Debye frequency). The first approximation of the theory assumes a linear functional dependence of the frequency on the wave number: $\omega = v_S\, k$ (here k is the wave number). The second approximation is analytically presented as [25]:

$$\sum_{\alpha=1,2,3} g(\omega) = \frac{3V_{кристала}}{2\pi^2 v_s^3}\omega^2 , \omega \le \omega_D \tag{1A}$$

The limiting Debye frequency is found from the condition of the equality of the number of modes and the number of phonons:

$$\int_0^{\omega_D} \sum_{\alpha=1,2,3} g(\omega) = 3N \tag{2A}$$

Taking into account the previous form of the function g and carrying out the integration, we get

$$\omega_{max} = \omega_D = \left(\frac{6\pi^2}{V}\right)^{1/3} v_S \tag{3A}$$

The value of ω_D is an important parameter not only in view of its fundamental meaning. The numerical value of ω_D determines the upper limit of integration in (5), and therefore significantly affects the accuracy of the thermal conductivity coefficient calculation.

The complete expression for heat capacity in the Debye approximation [19, 25]:

$$c_V(\omega) = \frac{3\hbar^2}{2\pi^2 k_B T^2} \int_0^{\omega_{max}} \frac{\omega^4\, exp(\hbar\omega / kT)}{v_s^3 \left(exp(\hbar\omega / kT) - 1\right)} d\omega \tag{4A}$$

Despite the fact that the obtained expression for the heat capacity takes into account the acoustic spectrum of phonons rather approximately and does not take into account the peculiarities of the spectrum of optical phonons (Fig. 1A), this approximation explains quite well a wide range of experiments and is widely used to calculate, in particular, the thermal conductivity coefficient. Such a result is a consequence of the use of certain model parameters, primarily the limiting frequency, by varying which it is possible to achieve a good correlation between the theory and the experiment.

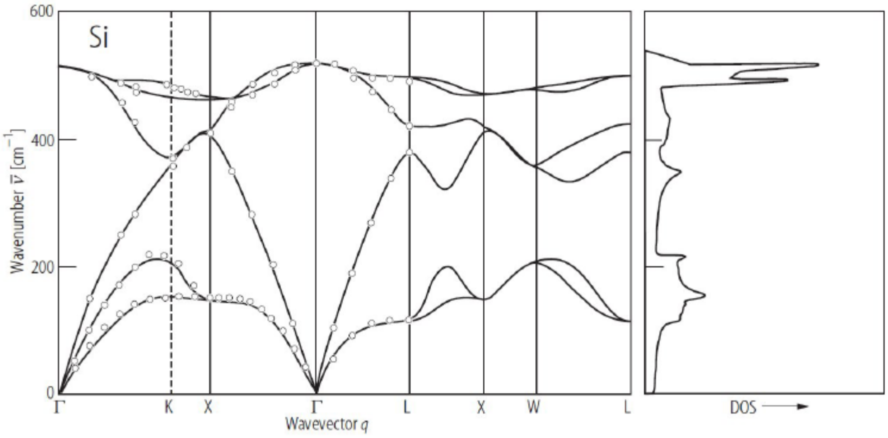

Fig. 1A. A typical experimental phonon spectrum of solids and the corresponding density of states (on the example of a silicon crystal [36]). It can be seen that only in the region of small k the dependence $\omega(k)$ can be considered linear. Similarly, for the density of states only in the region of low frequencies, the density of states ~ ω^2.

It should be noted that the presented formula for c_V takes into account the presence of three acoustic branches in the phonon spectrum - two transverse and one longitudinal [13, 25]. In the general case, these three branches are not identical (do not coincide), so each of them should be characterized by its speed of sound. Instead, the Debye model involves using an averaged value. That is, v_s is some characteristic (model) parameter of the theory. Moreover, according to (3A), this value v_s is uniquely related to another parameter of the model – the Debye frequency.

The Debye frequency can be determined through the Debye temperature ($k_0\theta = \hbar\omega_D$), which in turn can be determined in different ways. Most often, it is chosen in such a way as to match the theoretical dependence of the specific heat capacity of the material on temperature with the experimental one. For PbTe according to [37] this temperature is about 120-125 K, and according to [38] – 130 K. With such values of θ, using the above formula, the value of the Debye frequency is $1.64{\cdot}10^{13}$ Hz.

Another way to determine θ is by measuring the speed of sound. Sound speed measurements are usually carried out by the Papadakis method [39] at frequencies in the megahertz range and below. That is, in the region of linear approximation $\omega = v_s k$ (here k is the wave number), where the speed of sound should not depend on the frequency. At the same time, its longitudinal and transverse components are measured separately, and then the calculation is made according to the dependence [40]:

$$1/v_s^3 = 1/v_L^3+2/v_T^3. \tag{5A}$$

At v_L = 3050 m/s and v_T = 1730 m/s [17] v_s = 1333.71 m/s. And the actual Debye frequency determined by formula (11) is $\omega_D = 1.64{\cdot}10^{13}$ Hz.

That is, from two different experiments (through the Debye temperature and through the transverse and longitudinal speed of sound) one and the same value of the Debye frequency is obtained. But here it is important to pay attention to the correctness of the calculation of the speed of sound, which should be included in the calculation formulas, in particular in (3A). It should be calculated exactly as (5A), which is the average value of the speed per one acoustic branch [40]. Often, the calculation of vs is carried out using a formula similar to the one given above, but in the numerator to the left of the equals sign there is a multiplier of 3. That is, it can be roughly said that the calculation is not carried out for one line, but "for three". Then When v_L = 3050 m/s and v_T = 1730 m/s [17] v_s = 1920 m/s. And the actual Debye frequency determined by formula (11) is $\omega_D = 2.31{\cdot}10^{13}$ Hz, which does not agree with the calculation based on the Debye temperature. If we further calculate the Debye temperature at this frequency, the obtained values will be ≈ 180 K, which differs from the experimental 120-130 K [37]. The reason for the appearance of this multiplier lies in whether to consider the number of modes in equation (10) equal to N or $3N$. In the second case, we get expression (5A), in the first case, expression (5A) with an additional factor. There are other formulas for calculating vs through longitudinal and transverse components ($1/v_s^2 = 1/v_L^2+2/v_T^2$; $3/v_s^2 = 1/v_L^2+2/v_T^2$; $3v_s = v_L + 2v_T$). However, with their use, it is not possible to obtain a Debye frequency that would agree with the calculation based on the Debye temperature.

Group of velocity $v_g(\omega)$. In the second factor under the integral in the expression for k, it is necessary to use the explicit dependence vg(ω) determined experimentally or theoretically calculated. However, this approach significantly complicates the task of finding the thermal conductivity coefficient. In [41], the authors investigated the influence of methods of approximating the real dispersion dependence $v(k)$ (here k is the wave number) by various functions on the result of calculating the thermal conductivity coefficient. However, this does not lead to a significant simplification of the k calculation procedure. In view of what has been said, usually, the speed of sound included in the second (and third for similar reasons) coefficients of the expression under the integral is chosen the same as for the heat capacity, neglecting the frequency dependence. It is well known that this approach gives good results. But if in the expression for heat capacity, the choice of a constant numerical value of the speed of sound is theoretically justified and its effectiveness is experimentally confirmed, then here it is worth separately justifying the neglect of the contribution of short waves (high frequencies) and, in general, the frequency dependence of $v_g(\omega)$.

A reasonable approach to choosing a constant value of the sound speed for the second and third multipliers could be to use the value determined at some average phonon frequency $v_g(<\omega>)$ as the sound speed. In fig. Figure 2 shows the dependence of the product of the density of states and the distribution function (Bose-Einstein) $f(\omega)g(\omega)$. In fact, this is the dependence of the number of phonons on the frequency. It can be seen that this function is non-monotonic with a maximum at a frequency above the Debye frequency. The position of the maximum depends on the temperature. However, it is always at a frequency higher than ωD. Thus, the number of phonons with increasing frequency (i.e., short-wave phonons) increases in the entire frequency range. Importantly, the Debye frequency can also be a function of temperature. However, the order of magnitude does not change when this dependence is taken into account.

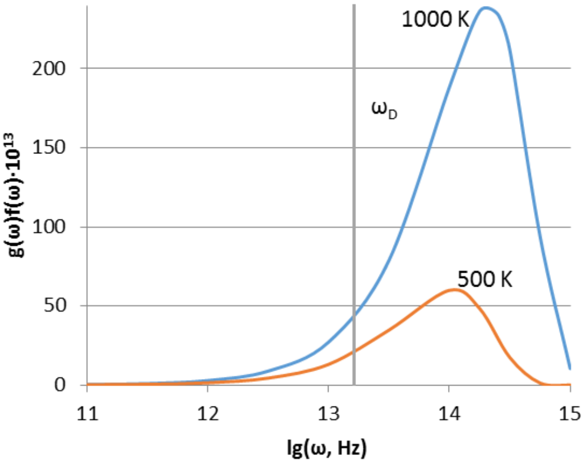

Fig. 2A. The product of the density of states (f-la (9)) on the Bose-Einstein distribution function for PbTe crystals at temperatures of 500 K and 1000 K. The vertical line shows the Debye frequency ($1.64\cdot10^{13}$ Hz).

If you find the average value of the phonon frequency according to the dependence:

$$<\omega>=\frac{\int_0^{\omega_D}\omega\, f(\omega)\, g(\omega)\, d\omega}{\int_0^{\omega_D} f(\omega)\, g(\omega)\, d\omega},$$

where

$$f(\omega)=\frac{1}{exp\left(\frac{\hbar\omega}{kT}\right)-1} \qquad (6A)$$

The obtained average value of the phonon frequency is <ω> = 1.08 1013 Hz. If we take into account that short-wave phonons are scattered more intensively than long-wave phonons by multiplying the integral expressions in the numerator and denominator by the relaxation time □U (when scattering phonons on phonons), then the average value of the frequency decreases by two orders of magnitude <ω> ≈3 10^{11} Hz. (the calculation was carried out for T = 1000 K). This value corresponds to the average frequency of phonons present in the crystal. However, the thermal conductivity cannot be estimated by this value, since different frequencies will give different contributions to the heat capacity of the crystal. Therefore, it is more correct to look for the average value of the frequency for the entire expression k:

$$<\omega>=\frac{\frac{1}{3}\int_0^{\omega_D}\omega\cdot c_V(\omega)v_g(\omega)^2\tau(\omega)d\omega}{\frac{1}{3}\int_0^{\omega_D}c_V(\omega)v_g(\omega)^2\tau(\omega)d\omega} \qquad (7A)$$

Since we are interested in temperatures above the Debye temperature, it is convenient to use expression (6) to determine the heat capacity, according to which $c_V \sim \omega^2$. The relaxation time is taken for the case of scattering of phonons on phonons (U-processes). In this form, it is easy to see that the frequency dependence of the integral expression for k is completely determined by the frequency dependence of the second factor - the group speed of sound (since the relaxation time is inversely proportional to the square of the frequency τ ~ 1/ω2, and $c_V \sim \omega^2$).

For acoustic phonons, the group velocity decreases with increasing frequency from some constant value at $k\rightarrow0$ (often in the literature, $v_s = (E/\rho)^{1/2}$ is used to estimate it, where E is Young's modulus, ρ is density [42]) to zero at the edge of the Brillouin zone (that is, such phonons do not participate in heat transfer at all.). The phase velocity at k→0 coincides with the group velocity, and as k increases, it decreases more slowly than the phase velocity and is not equal to zero at the edge of the zone. Obviously, when using the phase speed in the expression for the average value of the frequency (7A), we will get a larger value of $<\omega>$. Therefore, we will use this value for the above estimate. As an analytical expression for vs(ω), we can take the expression obtained for the model of a linear chain, which predicts a decrease in speed with an increase in frequency according to the law [42]: $v_p/v_s = ((\omega/(\omega_D))/\arcsin(\omega/\omega_D))$. The average value of the phonon frequency calculated in this way is $<\omega> \approx 7\cdot10^{12}$ Hz.

Thus, as the average value of the speed of sound in the crystal to estimate the coefficient of thermal conductivity, it would be worth taking the value measured at a frequency of about 10 THz. This is approximately half the Debye frequency. Why, then, does the substitution of sound speed values measured at MHz frequencies in (5) give a satisfactory result in explaining the experimental data $k(T)$? It is known that the speed of sound decreases not even by an order of magnitude with a change in frequency. In particular, in the case of a linear chain, the numerical value $v_p(\omega)$ within the first Brillouin zone decreases by ≈ 30%. In fig. 3A shows a graph of such dependence. It can be seen that up to a frequency of $7\cdot10^{12}$ Hz, the speed of sound decreases by no more than 3% from the values obtained for k → 0. Thus, due to the weak frequency dependence of the speed of sound, the values of vs measured in the MHz range do not lead to significant errors in the estimation values of k. And, therefore, the value obtained at ultrasonic frequencies at the MHz level can be used as the speed of sound.

It is important to note that this result was obtained under the condition that phonon scattering is dominated by phonons. In the case of dominance of phonon scattering on substitution atoms, the relaxation time is inversely proportional to the fourth power of the frequency. In this case, the average value of the frequency determined by (7A) will be $<\omega> \approx 2\cdot10^6$ Hz. However, it should be noted here that for this scattering mechanism, the exact value of the average value will significantly depend on the lower limit of integration. That is, from the minimum frequency of phonons, which will be determined by the size of the crystal ωmin = vs/L, where L is the size of the sample. When $L \approx 1$ m, and $v_s \approx 10^5$ *m/s* $\omega_{min} \approx 10^5$ Hz. The above value corresponds to just such a minimum frequency. If $L \approx 1$ mm, and $v_s \approx 10^5$ m/s, then $\omega_{min} \approx 10^8$ Hz and $<\omega> \approx 1\ 10^9$ Hz.

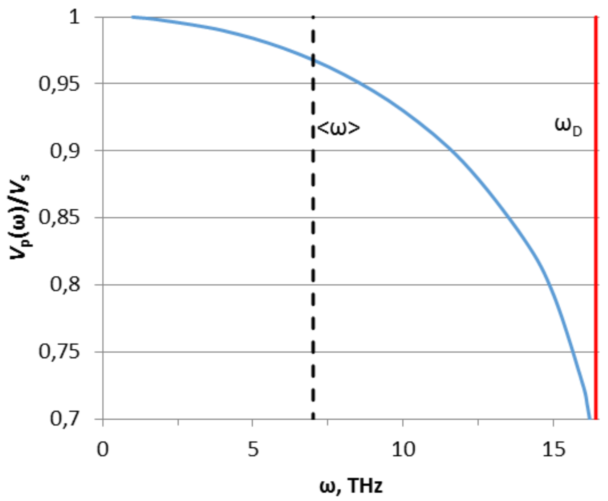

Fig. 3A. Dependence of phase speed on frequency (relative change $v_p/v_s = ((\omega/(\omega_D))/\arcsin(\omega/\omega_D))$ for the linear chain model. Vertical dashed line – $<\omega>$, vertical solid line – ω_D.

But, in fact, although the effect of phonon scattering on point defects must be taken into account for the correct quantitative interpretation of experimental data, phonon scattering on phonons is still decisive. If you compare the relaxation times τ_U and τ_{PD}, you can see that at a temperature of 500 K and frequencies around 10^{10} Hz, the difference is 6 orders of magnitude. At higher T, this difference increases. In the range of frequencies of 10^{13} Hz, the orders of these two quantities are the same, but τ_U is still half as small.

Table

Values of relaxation times for phonon-on-phonon and phonon-on-substitution atom scattering at two different frequencies and temperatures.

T, K	$\omega = 10^{10}$, Hz		$\omega = 10^{13}$, Hz	
	τ_U, c	τ_{PD}, c	τ_U, c	τ_{PD}, c
500 K	$1{,}11\cdot10^{-6}$	2,16	$1{,}11\cdot10^{-12}$	$2{,}16\cdot10^{-12}$
1000 K	$5{,}56\cdot10^{-7}$	2,16	$5{,}56\cdot10^{-13}$	$2{,}16\cdot10^{-12}$

Gruneisen's parameter. Choosing the numerical value of the Grüneisen parameter requires special attention when calculating the thermal conductivity coefficient. The parameter γ is determined by the non-parabolicity of the interatomic interaction potential *U(r)*, which leads to anharmonicity of atomic vibrations and thermal expansion of the crystal lattice. This, in turn, leads to a change in the dispersion dependences *ω(k)*. And therefore the parameter γ can be defined as [13]: $\gamma = -\frac{d\ ln(\omega)}{d\ ln(V)}$ This equation was proposed by Gruneisen and determines the change in vibration frequencies with a change in crystal volume due to thermal expansion.

Experimentally, the value of γ can be determined through the interatomic interaction potentials. In particular, in [17], this value was determined from EXAFS. The obtained values, in particular for PbTe, are 1.54. You can also calculate the value theoretically. In particular, [15] presents this theoretically calculated parameter, which is 2.18. Such a significant difference is not a consequence of method errors, but is caused by the method of parameter calculation. These values differ by $\approx 3^{1/3}$ due to the fact (as in the case of sound speed) that the first value ($\gamma = 1.54$) is calculated as the average for one acoustic line of oscillations, and the second ($\gamma = 2.18$), apparently, "on 3 branches".

It is worth noting that in general it is possible to enter Gruneisen parameters and Debye temperatures (Debye frequencies) separately for transverse *T* and longitudinal *L* phonons. In addition, it is also possible to take into account the temperature dependences for γ(T), θ(T) for each of these branches [13, 25]. However, in this case, the model becomes much more complicated and the number of parameters increases. Therefore, one usually operates with one value averaged over branches for both γ and θ.

Appendix 2

In addition to the factors discussed in the main part that determine the accuracy of the *k*(T) calculation, in the detailed analysis of heat transfer processes, it is worth taking into account a number of other factors that can be significant under certain conditions.

First of all, it is worth paying attention to two basic model questions: first, the correct analysis of the contribution of N-processes to the thermal properties of the crystal; secondly, the adequacy of the 3-phonon interaction model in heat transfer processes.

Regarding the first. This issue was studied in [34]. Accurate determination of the ratio between the number of *N*- and *U*-processes is a difficult task [34]. From the dependencies derived in the work, it follows that if $\tau U \to \infty$ is assumed in the formulas (that is, *U* processes are absent, and only *N* is present), then the thermal conductivity coefficient will go to infinity $k \to \infty$. That is, the obtained dependences clearly confirm the fact that *N*-processes do not transfer heat.

And this is the basis for neglecting *N*-processes in most works. But, according to [43], *N*-processes lead to the redistribution of momentum between phonons, which contributes to the emergence of new phonons (with large *k*, for example), which will contribute to the activation of *U*-processes. According to [43], at $T < \theta$, the contribution of *N*-processes (to thermal conductivity) in BiSb can be up to 40%. Also, according to [43], the intensification of phonon scattering on defects in solid solutions increases the role of *N*-processes (the author, however, studied the temperature range up to 100 K, and, according to [43], at high *T* the contribution of *N*-processes decreases). That is, in the case of highly doped materials or solid solutions, this effect can have a significant impact on the formation of the numerical value of the quantity *k*. The importance of taking into account *N*-processes to obtain numerical values of k that agree well with experimental ones is demonstrated in [44] on the example of interpreting the thermal conductivity of Si crystals. The authors also established the dominance of *U* processes at high frequencies at the *T*Hz level and above, and *N* processes at lower frequencies. The calculation was carried out for *T* = 300 K by the ab initio method.

Regarding the second. The criterion of the adequacy of the 3-phonon approximation is the analytical dependence $k \sim 1/T$, which is obtained for the model of dominance of 3-phonon *U*-processes. Most of the experimental data within the limits of measurement errors correspond to just such a dependence. Deviation from such regularity is usually considered as a consequence of the influence of additional mechanisms of phonon scattering. However, according to [29], when $T > \theta$, the role of 4-phonon interaction processes can be significant. However, there are practically no works in which such a model would be analyzed.

Among other factors that can significantly influence the processes of phonon scattering and the formation of the numerical value of *k*, it is first of all worth noting optical phonons. The Debye theory, and therefore the expression for the heat capacity (6 or 4A) included in equation (5), does not distinguish their independent role in the formation of thermodynamic properties. That is, the Debye theory does not separate optical and acoustic phonons. An argument in favor of not taking optical phonons into account is their low group velocity (at least lower than the velocity of acoustic phonons, which is very well illustrated, in particular, in [19]). Accordingly, optical phonons can often be neglected to estimate the value of *k*. However, in the case of materials with a large number of atoms in the unit cell, the role of optical phonons in forming the numerical value of *k* increases, as the number of optical branches in the phonon spectrum increases [19].

When analyzing the participation of optical phonons, it is worth considering that they will not only contribute to heat transfer. Acoustic phonons will scatter on optical phonons. Thus, these two effects will partially compensate each other. Accordingly, *k* will not change as significantly as one might expect [18]. However, this influence is there. And, in particular, in work [45], on the basis of a theoretical calculation, the importance of taking this effect into account is shown on the example of silicon and diamond crystals. Moreover, as shown in the work, this interaction intensifies with increasing temperature. The authors also conclude that in materials with a small band gap between acoustic and optical phonons, the coefficient of thermal conductivity is lower (PbTe is given as an example in particular).

In [18], the weight ratio of the cation and anion mass M_1/M_2 is considered to be the criterion for the importance of the contribution of optical phonons to heat transfer processes. At the same time, if this ratio is less than 3, then optical phonons can scatter acoustic phonons, reducing the value of *k*. If it is more, then the interaction of acoustic and optical phonons becomes insignificant, but under such conditions optical phonons can make a significant contribution to heat transfer. In particular, the authors showed that for PbSe the ratio of optical to acoustic phonons is ≈ 30%. For PbTe, this contribution is predicted to be smaller.

Another element of the sequential analysis of thermoelectric coefficients, including the coefficient of thermal conductivity, is the consideration of the electron-phonon interaction. However, as shown in [46], for degenerate semiconductors, this contribution is not significant (in the numerical values of α, σ, k). Therefore, it can be expected that for weakly degenerate semiconductors, which are usually effective thermoelectric materials, it will be even smaller and can be neglected in the first approximation. A similar conclusion was obtained in [47] during the experimental study of Ge:P. The author shows that the phonon scattering effect on electrons is important at *T*=1-5 K.

In addition to the mechanism discussed above, the possibility of phonon scattering on dislocations is often analyzed. However, as shown in particular in [48], their influence, as well as the influence of the electron-phonon interaction, can be significant only at very low *T*.

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Аналіз механізмів теплопровідності у твердих розчинах PbSnTe

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В роботі проведено теоретичний розрахунок коефіцієнта теплопровідності твердих розчинів PbSnTe. Встановлено внесок розсіювання фононів на атомах заміщення на ефект зниження теплопровідності. Визначено склад твердого розчину PbSnTe, що характеризується найнижчими значеннями граткової складової коефіцієнта теплопровідності k_{lat}. Розраховано концентрації власних носіїв заряду у твердих розчинах та показано їх вплив на термоелектричні параметри матеріалу.

Ключові слова: термоелектричні матеріали, тверді розчини, коефіцієнт теплопровідності.