The thermal conductivity of the variband crystals of the Bi\textsubscript{1-x}Sb\textsubscript{x} system in the semiconductor region of the composition at the temperature of about 100 K

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The previously observed experimental difference in the thermal conductivity of gradient-inhomogeneous (variband) single-crystal samples of the Bi\textsubscript{1-x}Sb\textsubscript{x} system in the case of parallel and antiparallel directions of the temperature gradients and composition in the semimetallic range of composition values (0.03 <\textit{x}<0.10) under similar temperature conditions was also experimentally confirmed in other samples of this material having a composition in the interval of the semiconductor region (0.11 <\textit{x}<0.19). A theoretical model of the possible mechanism of this effect for the semiconductor region of the composition is proposed.

It is customary to refer to semiconductor materials with a variable in volume or in the direction of the forbidden band as variband. The author offers a broader interpretation of the concept of a variband material, namely: it is a material in which the position of the actual energy extrema of charge carriers on the energy scale changes with at least one spatial coordinate in it.

An experimentally observed dependence of the thermal conductivity \(\kappa\) on the mutual direction of the temperature gradient \(\vec{T}\) and the concentration gradient \(\vec{x}\) of one of the components in a single-crystal sample of the Bi\textsubscript{1-x}Sb\textsubscript{x} binary system was presented in [1]. The composition of this sample changed monotonically with the longitudinal coordinate \(l\) (measured along the heat flux) in the range of \(x\approx0.97\) at \(l=0\) to \(x\approx0.90\) at \(l=15\) mm. The bulk of this interval of values of \(x\) corresponds to a semimetallic state, which is characterized by the presence of a non-direct overlapping of electronic and hole extrema in the space of the wave vector.

The same effect was experimentally confirmed in another variband sample of the same length \(l=15\) mm with a composition change from \(x\approx0.885\) at one end to \(x\approx0.805\) at the other. This composition interval corresponds to the semiconductor state of the material. The composition of the Bi-Sb system in all figures and in the tables of this work is estimated using the percentage of antimony \(C=(1-\textit{x})\times100\%\), not bismuth. Evaluation of the composition with the help of parameter \(C\) is more common for researchers involved in this system. In this case, in the investigated sample, \(C(x=0)=11.5\text{at}\%\), and at \(l=15\) mm \(C(l)=19.5\text{at}\%\). Figure 1 shows a fragment of the composition distribution along the length of a single-crystal ingot, corresponding to the portion of the sample taken from this ingot. The dots indicate the values of the composition measured by the X-ray fluorescence method, and the line indicates spline interpolation.

We used the technology of obtaining the variband single crystals of the Bi-Sb system described in [2]. The thermal conductivity of this sample was measured by a direct method according to the procedure of [3] with an error not exceeding 5%, as in the previous case [1].

The energy spectrum of charge carriers at these values of composition is simpler than in the previous case [1] (fewer actual extrema in the valence band and the conduction band) [4]. Fig. 2 shows the change in the band spectrum of the charge carriers of a given material (homogeneous in volume) with a change in the composition of the samples at three different temperatures. The data for the formation of graphs in Fig. 2, previously not published, were kindly provided to us by the authors of [4,5] and partially were obtained by the author of this work personally. In this figure, the semiconductor region of the material composition is distinguished by background fill at three different temperatures.

If we consider the graphs in Fig. 2, at least on a qualitative level, it can be concluded that the band spectrum of a given material depends both on the composition of \(C\) and on the temperature \(T\). As we know, this conclusion is not disputed by the scientific community.

Since this sample is mainly semiconductor, in order to elucidate the mechanism of this new effect, the author has found it reasonable to apply the foundations of the theory of thermal
conductivity of semiconductors. It is generally accepted that the thermal conductivity $\kappa$ of a semiconductor consists of three components:

$$\kappa = \kappa_f + \kappa_e + \kappa_b,$$

where $\kappa_f$ - phonon, $\kappa_e$ - electronic, and $\kappa_b$ - bipolar components of thermal conductivity. In what follows we shall use the notation $\kappa_{el} = \kappa_e + \kappa_b$, so

**Figure 1.** Dependence of the concentration of antimony $C$ on the longitudinal coordinate $l$ in the sample under study.

**Figure 2.** The change in the band spectrum in the Bi$_{100-x}$Sb$_x$ system with the change in the parameter $C$. Number 1 corresponds to the motion line of the extremum $L$ of the conduction band, number 2 corresponds to the $T$-extremum of the valence band, and number 3 corresponds to the $H$-extremum of the valence band. The $L$-extremum of the valence band existing in the system is not shown here, since it is well below the forbidden energy interval and is not relevant.
\[ \mathcal{K} = \mathcal{K}_f + \mathcal{K}_{el} \]  

At the same time, based on the values of the thermal conductivity measured outside the magnetic field and in the transverse magnetic field \( B \) up to \( B \approx 1200 \text{ mTl} \), we can separate the phonon thermal conductivity and the sum of the electron and bipolar components of the thermal conductivity (see Table I).

| Table 1. | \( \kappa \), Wt/m·K |
|---|---|
| \( \nabla T \uparrow \uparrow \nabla C \), \( T_0 = 89,4\text{K} \), \( T_1 = 102,5\text{K} \). Heat flux density \( q=1,907 \text{ mWt/mm}^2 \). | \( \nabla T \downarrow \downarrow \nabla C \), \( T_0 = 101,5\text{K} \), \( T_1 = 87,6\text{K} \). Heat flux density \( q=1,798 \text{ mWt/mm}^2 \). |
| Experiment | Calculation | Experiment | Calculation |
| \( \kappa \) | \( \kappa_{fon} \) | \( \kappa_{el} \) | \( \kappa_{el} \) | \( \kappa \) | \( \kappa_{fon} \) | \( \kappa_{el} \) | \( \kappa_{el} \) |
| 4,526 | 2,344 | 2,182 | 2,181 | 4,108 | 2,356 | 1,752 | 1,944 |

From the data of Table I it is seen that the phonon component is practically independent of the mutual direction of the composition and temperature gradient (the difference in the third significant digit). It follows that the mechanism of the observed effect should be sought in the theory of the electronic component of thermal conductivity \( \mathcal{K}_{el} = \mathcal{K}_e + \mathcal{K}_b \), the electronic part \( \mathcal{K}_e \), which is determined only by thermal diffusion and the bipolar part \( \mathcal{K}_b \) associated with the generation (recombination) of electron-hole pairs in the process of thermal diffusion [6, 8]. According to publications [6, 8], for the total electronic thermal conductivity of a semiconductor the following is valid:

\[
\mathcal{K}_{el} = T \cdot L \cdot \left[ \left( \sigma_p + \sigma_n \right) \cdot A + \left[ \frac{E_g}{kT} + (r+2) \cdot \left( F_{r+1}(\mu_p) / F_r(\mu_p) + F_{r+1}(\mu_n) / F_r(\mu_n) \right) \right] \times \left[ \sigma_p \cdot \sigma_n / \left( \sigma_p + \sigma_n \right) \right] \right] \]

or

\[
\mathcal{K}_{el} = T \cdot \left[ \left( \sigma_p + \sigma_n \right) \cdot A \cdot L + \left( \alpha_p - \alpha_n \right)^2 \cdot \sigma_p \cdot \sigma_n / \left( \sigma_p + \sigma_n \right) \right] . \tag{2}
\]

Here \( T \) - the temperature, \( L = (k / e)^2 \) - the Lorentz number, \( k \) - the Boltzmann constant, \( \sigma_p \) and \( \sigma_n \) - the partial conductivity of holes and electrons, respectively, \( \alpha_p \) and \( \alpha_n \) - the partial thermoelectric power of holes and electrons, respectively, \( E_g \) - the width of the forbidden band, \( r \) - is an indicator of the degree of the dependence of the free path length of charge carriers on energy, \( \mu_{n,p} \) - presented charge carrier chemical potential (of the electron or hole), \( F_{r}(\mu_{i}) \) - the Fermi integral of degree \( k \) with respect to the energy of the \( i \)-th carrier. The dimensionless coefficient \( A \) in the expressions (2) is as follows:

\[
A = \frac{r+3}{r+1} \cdot \frac{F_{r+2}(\mu)}{F_r(\mu)} - \frac{(r+2)^2}{(r+1)^2} \cdot \frac{F_{r+1}^2(\mu)}{F_r^2(\mu)} . \tag{3}
\]

To calculate the chemical potential of electrons and holes on the basis of the principle of electroneutrality, the value of the ratio of the effective mass in the valence band to the effective mass in the conduction band is necessary. The meaning of this value varies from 5 to 13 in different authors. This is especially true for the range of values of \( C \), in which the value of \( E_g \) decreases with increasing \( C \), and where the extremum in the direction of the point \( H \) of the Brillouin zone is actual. For this
extremum, the dispersion law for holes is poorly studied. We used the value $m_p/m_n \approx 7$. The topology of the Brillouin zone of the Bi-Sb system can be found in [7].

Using the experimental data of conductivity $\sigma(T, C)$ and thermopower $\alpha(T, C)$ obtained by the authors of [4,5], as well as personally obtained by the author of this work, the heat conductivity of the material was calculated. The calculation was carried out by numerical methods in the approximation $r = 0$, which corresponds to the preferential scattering of charge carriers on the neutral impurity.

Fig. 3 shows in the polynomial approximation the graph of the dependence on the temperature $T$ and composition $C$ of the value of the forbidden band, referred to the energy of thermal motion, $\eta = E_g(T, C)/k \cdot T$ and Fig. 4, also in the polynomial approximation, shows the graph of the dependence on the temperature $T$ and the longitudinal coordinate $l$ for the calculated thermal conductivity $\kappa_{el}(T, l) = \kappa_{el}(T, C(l))$.

![Graph](image)

**Figure 3.** The graph of the dependence of the presented width of the the forbidden band on the temperature $T$ and the amount of antimony $C$ in the Bi$_{100-x}$Sb$_x$ system.

| Table 2. | The ratio of electron (together with bipolar) thermal conductivity $\kappa_{el}$ at $\bar{\nabla}T \uparrow \uparrow \bar{\nabla}C$, $T_0 = 89.4K$, $T_f = 102.5K$ to the electronic thermal conductivity (together with bipolar) at $\bar{\nabla}T \uparrow \downarrow \bar{\nabla}C$, $T_0 = 101.5K$, $T_f = 87.6K$. |
|-----------|-------------------------------------------------------------|
| Experiment| Calculation                                                |
| 1,245     | 1,123                                                      |

Using the obtained dependence $\kappa(T, l)$, the temperature is calculated at equidistant fifteen points along the entire length of the sample by numerically solving the differential equation of the heat balance of the type:
\[
\frac{dT}{dl} = \kappa(l, T)^{-1} \cdot q.
\]  
(4)

On the basis of the tabulated temperature, the heat conductivity averaged over the length of the sample is calculated for the case \(\nabla T \uparrow \nabla C\) and \(\nabla T \downarrow \nabla C\) case (see Table I and Table II). The calculated difference in thermal conductivity in these two cases turned out to be noticeably less than that obtained with direct measurement. Such a discrepancy between the measured and the calculated difference in thermal conductivity when the direction of the heat flow changes in very close temperature intervals is, probably, connected with the fact that the smooth polynomial approximation of the function \(E_g(T, C)\) was used for calculation. In fact, judging by Fig. 2 this function in parameter \(C\) should consist of a combination of two approximately rectilinear functions with a jump in the value and a sign of the angle of inclination at the point of the largest value of \(E_g\). The underestimation of the result of the calculation could also be affected by ignoring the dependence for the ratio of the effective masses of the \(m_p/m_n\) carriers on the composition (coordinates) and the inaccuracy of its absolute value.

**Figure 4.** Dependence of the calculated electronic thermal conductivity \(\kappa_{el}\) (together with the bipolar one) on the temperature \(T\) and on the longitudinal coordinate \(l\) in the sample under study.

It should be noted that the author also carried out calculations for the case when the dependence of the width of the forbidden band on temperature was ignored, and only the dependence on the composition was preserved. In this case, the calculation gave an almost complete coincidence of the thermal conductivity before and after the change in the direction of the heat flux in a given temperature interval. The difference in this case was the third and even the fourth significant figure. It follows that the experimentally observed effect of the change in the thermal conductivity when the direction of the heat flux changes in the \(Bi_x-Sb_{1-x}\) system with a variable volume \(x\) is determined by the fact that the energy spectrum of the charge carriers depends both on the composition and on the temperature, and the phonon component of thermal conductivity does not contribute to this effect.
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