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**CALCULATION OF THERMAL CONDUCTIVITY OF GeBiTe SOLID SOLUTIONS BASED ON ZONE MODELS**

Solid solutions based on germanium telluride are considered to be among the most efficient medium-temperature p-type thermoelectric materials to date [1]. High thermoelectric figure of merit has been achieved for GePbBiTe solid solutions, where the figure of merit is approximately 2.3 at T = 700 K [2]. This value can be further increased, in particular by optimizing doping and further improving the material growth technology. Improving the composition and structural properties, such as grain size and dislocations, can contribute to increasing the efficiency of the material for thermoelectric applications over a wider temperature range.

In the study of hard GePbTe and GeBiTe solutions, an approximation was used to calculate the electronic component of thermal conductivity, in which it was assumed that a non-parabolic zone of light holes is located higher in the energy spectrum. As a result, important conclusions were obtained regarding the location of the Fermi level [3], on the basis of which an increase in the thermoelectric figure of merit ZT was explained when lead (Pb) and bismuth (Bi) atoms were added to GeTe.

Due to differences in the numerical values of the band parameters specified in [1-2] and used in [3], this work calculates the Fermi level and the electronic component of the thermal conductivity coefficient based on experimental data [3]. The main objective of the study was to identify possible differences in the numerical values of these parameters due to the choice of a specific model of the GeTe band structure. The work also focuses on the effect of doping on changes in the conduction band parameters, which allows for more accurate optimization of the thermoelectric properties of materials for use in thermocouples.

The first step in calculating the electron component of thermal conductivity is to determine the chemical potential of electrons (the Fermi level). As a rule, these values, including in works [1-3], are obtained from experimental dependences of the Seebeck coefficient S(T). In this calculation, a model of a parabolic and non-parabolic valence band was used, considering the possible degeneracy of charge carriers.

The results of the Fermi level calculations are shown in Fig. 1. It can be observed that the parabolic model predicts a deeper location of the Fermi level compared to the non-parabolic model. For the non-parabolic band, at two different values of the band gap Eg(T) (according to [2] and [4]), the Fermi level μ differs by approximately 0.02 eV, which, at a temperature of 500 K, corresponds to about 40%. In the temperature range corresponding to the cubic phase, the difference between the μ values decreases, as the Eg values obtained in [2] and [4] are close in this temperature range.

These differences in the Fermi level position are crucial for modeling the electronic and thermal properties of materials, as they affect conductivity and thermoelectric characteristics. The correct choice of the model is essential for accurately predicting the material's properties and optimizing its applications in thermoelectric devices (Fig. 1).

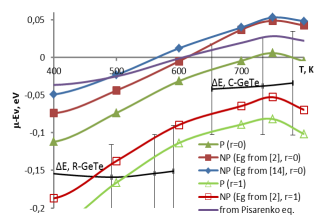


Fig. 1. The temperature dependence of the Fermi energy of Ge0.96Bi0.4Te was determined from the experimental dependence S(T) from [3] for different models (▲,∆ – parabolic valence band model; ■, □ – non-parabolic valence band model (Eg(T) – [2]); ♦ – non-parabolic valence band model (Eg(T) – [4]); curve without markers – parabolic band model and without taking into account carrier degeneracy).

Special attention should be paid to the analysis of another important parameter of the theoretical calculation – the mechanism of scattering of charge carriers. In most studies concerning the interpretation of the properties of GeTe and solid solutions based on it, it is believed that holes are scattered by acoustic phonons, and the parameter rrr is taken to be zero. For most compounds of the A4B6 type, this approach is justified. However, as shown in [1], for solid solutions of GePbBiTe, only up to a temperature of approximately 400 K does the dependence μ(Т) ~ T-3/2, which is typical for the mechanism of scattering by acoustic phonons. For pure GeTe, this interval can be conditionally taken to be up to 500 K. However, at higher temperatures, the deviation of experimental data from such an approximation becomes significant. The obtained results indicate that to describe the scattering mechanism at high temperatures it is necessary to take into account additional factors that can have a significant impact on the behavior of charge carriers, such as scattering by optical phonons or crystal lattice defects.

Solid solutions based on GeTe are weakly degenerate semiconductors, whose electronic properties – such as Fermi energy and the electronic component of thermal conductivity – depend on the chosen band structure model and band gap value, especially in the non-parabolic band model. Further experimental studies are needed to confirm the relative positions of light and heavy hole bands, determine the dominant carrier scattering mechanism, and refine effective mass values.

**References**

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