Thermoelectric Properties of Layered Anisotropic p-type $PbSb_2Te_4$ Compound and Peculiarities of its Energy Spectrum

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Abstract

The measurements of the transport tensors: electrical σ_{11}, σ_{33} and thermal κ_{11}, κ_{33} conductivity, Seebeck S_{11}, S_{33} and Hall effect R_{123}, R_{321} (11 – along the cleavage plane and 33 - along the trigonal crystal axis) have been made on the high-quality single crystals of the ternary layered p-type $PbSb_2Te_4$ compound in the temperature range 85-350 K. These crystals were grown by Czochralski pulling with melt supply through a floating crucible. The significant anisotropy in thermoelectric properties has been discovered in this compound. The experimental results of Seebeck coefficient and electrical conductivity measuring can be explained in the frameworks of a single-band model of energy spectrum and mixed mechanism of hole scattering. It was suggested that the acoustic phonon scattering was predominant along the cleavage plane and the impurity scattering was predominated in the direction of the trigonal C_3 axis However, an unusual temperature dependence of the components of thermal conductivity tensor and rather strong increasing of both components Hall coefficient tensor at temperature enhancement are not agree with the single-band model. The reason of these effects can be related to a participation of two sorts of holes (heavy and light) having different anisotropy in the carrier mobility in transport phenomena similar to Sb_2Te_3 .

Introduction

The $PbSb_2Te_4$ compound belongs to the large group of layered tetradymite-like chalcogenides with complicated crystal structures and low lattice thermal conductivity [1]. The $PbSb_2Te_4$ unit cell has 21-layer structure with lattice parameters: a=0.4350(1) nm and c=4.1712(2) nm (space group *R3m*). The $PbSb_2Te_4$ unit cell comprises three Te*Sb*Te*Pb*Te*Sb*Te seven layers slabs stacked orderly along the *c* axis. The bonding inside the seven-layer packets has ionic-covalent character while bonds between the slabs are achieved by weak van der Waals forces. The considerable anisotropy in electrical and thermal conductivity, Seebeck and Hall coefficients [2] has been discovered by the measurements of the single crystals parallel and perpendicular to the hexagonal *c* axis.

The objective of this work was the investigation of the anisotropy of transport coefficients and an analysis concerning to the peculiarities of band spectrum and carrier scattering mechanism in this compound.

Experimental

The $PbSb_2Te_4$ perfect single crystals were grown by Czochralski technique with replenishment of the melt from liquid phase through a floating crucible. The compounds were identified by X-ray diffraction (XRD). The X-ray diffraction study was carried out using a DRON-UM automatic diffractometer (CuK_α-radiation, graphite monochromator).

The following independent components of the transport tensors: the thermoelectric power S_{11}, S_{33}; electrical conductivity - σ_{11}, σ_{33}; thermal conductivity - κ_{11}, κ_{33} and Hall coefficients - R_{321}, R_{123} have been measured in the 85-350 K temperature range. In this notation the first index (i) means the direction of measured electrical field, the second index (j) means the direction of the current and the third index (k) – the direction of magnetic field. The thermoelectric properties were measured in two crystallographic directions: parallel and perpendicular to the cleavage planes (i.e. along the trigonal axis C_3). Additional details about the measurement of thermoelectric properties were given elsewhere [3].

Results and discussion

The temperature dependencies of Seebeck coefficient are presented in Fig. 1. Both components of thermoelectric power tensor are enhanced almost linearly at increasing temperature but with different rate. So, the anisotropy of Seebeck coefficient $\Delta S=S_{33}-S_{11}$ is increased proportional to the temperature from $\Delta S=15$ μV/K at 100 K to $\Delta S=80$ μV/K at room temperature.

Temperature dependencies of electrical conductivity are presented in Fig. 2. The anisotropy of electrical conductivity is decreased at increasing temperature from $\sigma_{11}/\sigma_{33}=13.6$ at 85 K to $\sigma_{11}/\sigma_{33}=10.1$ at 300 K.

Temperature dependencies of the components of Hall coefficient are presented in Fig. 3. Both components of Hall coefficient tensor: R_{321} and R_{123} are characterized by strong abnormal enhancement at temperature increasing. The R_{123}/R_{321} ratio is decreased from the $R_{123}/R_{321}=1.75$ at 85 K to the $R_{123}/R_{321}=1.5$ at 300 K. The R_{123} Hall component is greater than R_{231} one in all temperature range under study what is specific characteristic of the $PbSb_2Te_4$ compound. It is worth to emphasize that the reverse ratio takes place in the binary anisotropic Bi_2Te_3 and Sb_2Te_3 binary compounds [4].

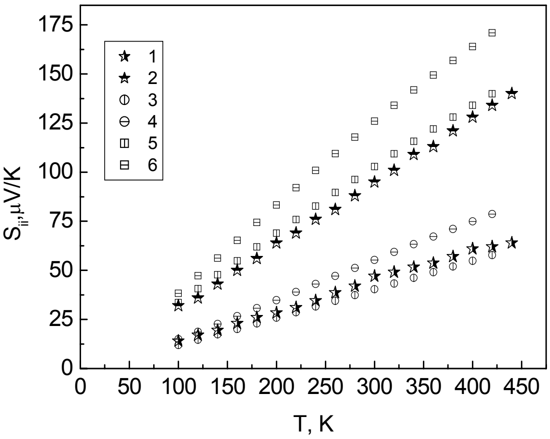

Fig.1. Temperature dependencies of Seebeck coefficient tensor S_{ij}:1(S_{11}), 2(S_{33}) – experimental; (3-6)- calculated values; (3,4) at r=0; 5,6 – at r=2; (1,3,5) – along the cleavage plane; (2,4,6) – along a trigonal axis C_3

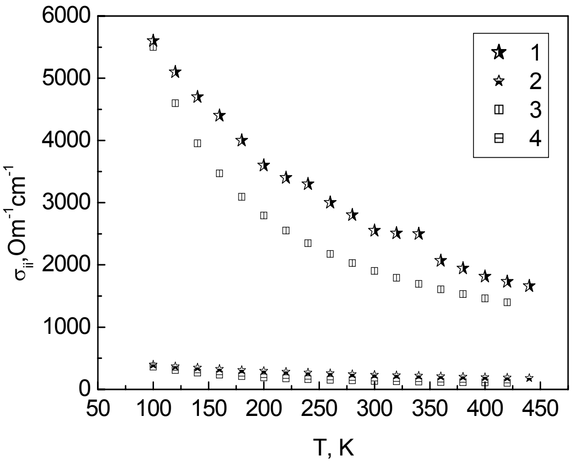

Fig.2. Temperature dependencies of the components of electrical conductivity tensor σ_{ij}: 1(σ_{11}), 2(σ_{33}) – experimental; 3(σ_{11}), 4(σ_{33})-calculated according to double-band model

The experimental results of Seebeck coefficient and electrical conductivity can be explained in the framework of a single-band model of energy spectrum and mixed mechanism of carrier scattering.

1. Single-band model

The estimation of carrier concentration has been made using the largest R_{123} component of Hall coefficient tensor as it is accepted for anisotropic materials:

$$p \approx (eR_{123})^{-1} \approx \frac{6,25\cdot 10^{18}}{0,02} \approx 3\cdot 10^{20}\,cm^{-3} \qquad (1).$$

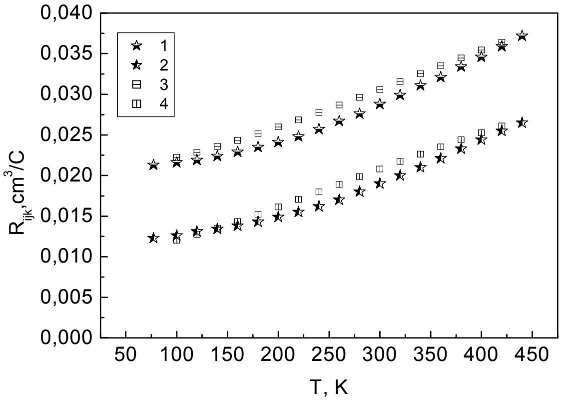

Fig.3. Temperature dependencies of the components of Hall coefficient tensor R_{ij}: 1,2 – experimental; 3,4 – calculated according to double-band model (1,3 – R_{123} – magnetic field (H) is parallel to C_3 trigonal axis; 2,4 – R_{231} – H is perpendicular to C_3 axis)

Such high carrier concentration lets to use equations for transport coefficients which are true for strong degeneration of free carriers. In this case, Seebeck coefficient is equal to the following equation:

$$S = \frac{k_0}{e}\frac{\pi^2}{3}\frac{k_0 T}{\mu}(r+1), \qquad (2),$$

where μ is the Fermi energy, T -the absolute temperature, κ_0 – the Boltzmann constant, *e* – the electron charge, *r* – scattering parameter which is power index in the energetic dependence on the relaxation time: $\tau(\varepsilon)\sim\varepsilon^{r-1/2}$.

The acoustic scattering mechanism with *r*=0 is the most typical for semiconductors in the 77- 400 K temperature range. The parameter characterized the extent of the carrier degeneration $\mu^* = \mu/k_0T \approx 28 >>1$ and the Fermi level of the holes: μ~0.24 eV were estimated using the smallest value of Seebeck coefficient: S_{11}~10 μV/K at 100 K and *r* =0. The determined μ* value confirms the correctness of the Eq. 2 which gives a linear dependence on Seebeck coefficient as a function of temperature in accordance with experiment.

In the heavily doped semiconductors in the 77- 450 K temperature range, except of acoustic scattering, considerable contribution introduces the scattering by ionized impurities and point defects of crystal lattice. The mixed scattering mechanism is probable to be realized in the $PbSb_2Te_4$. Such scattering mechanism may be one of the reasons of the origin of the Seebeck coefficient anisotropy at the assumption that different dominant scattering mechanisms act in-plane and out-of-plane: acoustic scattering is dominant in-plane and the scattering by ionized impurities and point defects acts in the C_3 axis direction. The S_{33}~30 μV/K value at 100 K closed to experimental data was calculated using Eq. 2 and μ* value received earlier suggesting the scattering parameter is equal to *r*=2.

The σ =f(T) dependencies also confirm the mixed scattering mechanism in the $PbSb_2Te_4$ compound. Electrical conductivity in-plane σ_{11} decreases according to $\sim T^{-0.8}$ power law what is closed to the theoretic $\sim T^{-1}$dependence for acoustic scattering in the case of strong degeneration. At the same time, electrical conductivity out-of-plane σ_{33} changes weaker with temperature (σ_{33} ~$T^{-0.3}$) what and must be at the dominant carrier scattering by ions of impurity

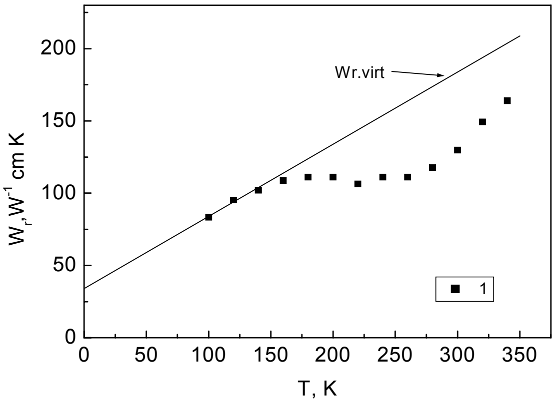

Fig.4. Temperature dependencies of lattice thermal resistivity (W_r=1/κ_{r11}): 1- calculated according to single-band model

Temperature dependencies of lattice thermal resistivity are presented in Fig. 4. The constant value of Lorenz number $L=\frac{\pi^2}{3}\left(\frac{k_o}{e}\right)^2$ is used as the compound is strongly degenerated semiconductor. As seen from Fig.4, the calculated values based on single-band model are deviated from linear dependence in the temperature range higher than 150 K.

Thus, an unusual temperature dependence of the components of thermal conductivity tensor and rather strong increasing both components Hall coefficient tensor at temperature enhancement are not agree with the single-band model. Therefore, more complicated models of energy spectrum must be attracted for explaining these anomalies.

2. Double-band model

The reason of the described effects can be related to a participation of two sorts of holes (heavy and light) having different anisotropy in the carrier mobility in two crystallographic directions suggesting that transport phenomena are similar to Sb_2Te_3 [4]. As the $PbSb_2Te_4$ band structure is not known, the estimation of transport coefficients has been performed in the frameworks of phenomenological theory developed in [4].

Seebeck effect

The anisotropy in Seebeck coefficient is probably related to the appearance of the second type carriers. The temperature dependence of Seebeck coefficient can be used for the estimation of energy gap between main (1) and additional (2) valence bands. In the temperature range, where the contribution of additional band into the conductivity only is begun, the ΔS value is expressed by the following equation:

$$\Delta S \sim \nu \sim \exp(-\Delta\varepsilon_V/k_0T) \qquad (3),$$

where $\nu=p_2/p_o$ is the ratio of the light hole concentration to total carrier concentration: $p_0=p_1+p_2$. The energy gap between main and additional valence bands is estimated to be equal to $\Delta\varepsilon_V$~0.24 eV.

The calculation of the temperature dependencies of the Seebeck coefficient tensor has been performed in the frameworks of double-band model for two scattering parameter: *r*=0 for acoustic scattering (Fig.1, curves 3,4) and *r*=2 for the scattering by ionized impurities (Fig.1, curves 5,6).

As seen, double-band model does not describe quantitatively the experimental temperature dependencies S=f(T). Apparently, like to single-band model, different predominant mechanisms of carrier scattering act in different crystallographic directions: the acoustic scattering is predominant along the cleavage planes and the impurity scattering is predominated in the direction of the trigonal C_3 axis.

Hall effect

The temperature dependencies of R_{123} and R_{321} components of Hall coefficient tensor have been calculated on base of the phenomenological theory [4] using the parameters presented in Table 1 and 2

Table 1.The energy gap between two sub-bands (ε_v), the density-of-states effective masses (m_{dp1}, m_{dp2}), carrier mobilities (u_{a10}- along the cleavage plane, u_{c10} – along a trigonal C_3 axis)

$\Delta\varepsilon_{v,}$ eV	m_{dp1}	m_{dp2}	u_{a10}, см^2/Vs	u_{c10}, см^2/Vs
0.24	0.7	0.2	114	7.5

Table 2. The ratio of carrier mobilities for first and second sub-bands along the cleavage plane $b_a=u_{a1}/u_{a2}$ and along a trigonal C_3 axis $b_c=u_{c1}/u_{c2}$; Hall factors A_{c1}, A_{a1}; the ratio of Hall factors of first and second sub-bands along a trigonal axis $\chi_c=A_{c1}/A_{c2}$ and along the cleavage plane - $\chi_a=A_{a1}/A_{a2}$

$b_a=$ u_{a1}/u_{a2}	$b_c=$ u_{c1}/u_{c2}	A_{c1}	A_{a1}	$\chi_c=$ A_{c1}/A_{c2}	$\chi_a=$ A_{a1}/A_{a2}
1/10	1/30	1.0	0.5	1.0	1.0

The energy gap $\Delta\varepsilon_v$=0.24 eV and its temperature coefficient (α=-1.0 10^{-5} K^{-1}) were estimated from Seebeck coefficient analysis. Other values summarized in Table 1,2 are fitting parameters. As seen from Fig.3, the double-band model lets to explain the enhancement of the components of Hall tensor as well as the fact that R_{123} component is greater than R_{231} one in all temperature range under study. The model is characterized by different anisotropy of carrier mobilities in first and second sub-bands suggesting that the carrier mobility in additional band (2) is higher than that in the main band (1).

Thermal conductivity (Lorenz number)

In the frameworks of double-band model, the total thermal conductivity in the range of extrinsic conductivity can be expressed by the following equation [5]:

$$k_{tot}=k_r+k_e=k_r+L_1\sigma_1T+L_2\sigma_2T+\frac{T\sigma_1\sigma_2}{\sigma_1+\sigma_2}(|S_1|-|S_2|)^2 \qquad (4)$$

where k_r - lattice thermal conductivity, k_e - electronic thermal conductivity, L_1, L_2, σ_1, σ_2, S_1, S_2 - Lorenz number, electrical conductivity and Seebeck coefficient for sub-bands (1) and (2).

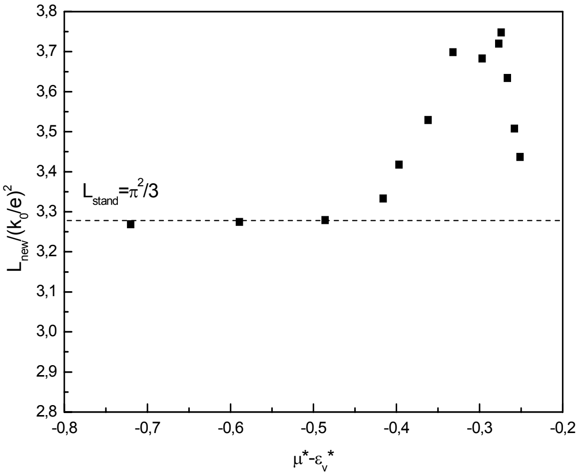

Fig.5. The appearance of the influence of additional band on Lorenz number at temperature increasing

According to [5], Lorenz number increases or decreases sharply as compared to usual value for single-band model $L = \frac{\pi^2}{3}\frac{k_o}{e}$ when strong carrier degeneration takes place in the band (1) and when the chemical potential level is approached to the top of the second sub-band. In the present work, the influence of an additional band on Lorenz number has been studied. It is supposed that the thermal resistivity W_r changes linearly with temperature. Then, the extrapolation of W_r low-temperature values to high-temperature range was performed. The new Lorenz number (L_{new}) was estimated using the equation (4). Fig. 5 demonstrates the influence of additional sub-band on the Lorenz number L_{new}. The dependence of the L_{new} on the ($\mu^* - \varepsilon_v^*$) value is presented in Fig.5 where μ^* is calculated using the parameters from Table 1,2. As seen, the Lorenz number is considerably increased at approaching the level of the chemical potential to the edge of the additional sub-band. It can be concluded that the character of temperature dependence of thermal conductivity is not contradicted to the assumption about the existence of additional sub-band in the $PbSb_2Te_4$ energy spectrum.

Conclusions

The p-type $PbSb_2Te_4$ compound is characterized by an extremely large anisotropy in the electrical and thermal transport properties measured in two crystallographic directions: parallel (out-of-plane) and perpendicular (in-plane) to the trigonal axis. The following independent components of the transport tensors: the thermoelectric power S_{11}, S_{33}; electrical conductivity σ_{11}, σ_{33}; thermal conductivity κ_{11}, κ_{33} and Hall coefficients R_{321}, R_{123} have been measured in the 85-350 K temperature range. The results are analyzed in the frameworks of single-band and double-band models of the $PbSb_2Te_4$ energy spectrum. It is concluded that temperature dependencies of both components of Hall effect and thermal conductivity qualitatively can be explained by complicated constitution of the $PbSb_2Te_4$ valence band.

Acknowledgments:

This work supported by the Russian Foundation for Basic Research, grant no. 07-03-00146 and by the Presidium of Russian Academy of Sciences through the program # 8 *Synthesis of Substances with Controlled Properties and Fabrication of Related Functional Materials.*

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