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Energy spectrum of holes in highly alloyed PbTe

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Abstract. The electrophysical properties of a series of PbTe samples doped with Tl and an additional admixture of Na are investigated. Observed features of temperature dependences of electrical conductivity and Hall's coefficient are explained within the framework of the model of resonant states of thallium, taking into account the complex structure of the valence band. It is shown that the idea of an ideal crystal and a band structure in the framework of the one-electron approximation is insufficient to explain the experimental data on the Hall effect. It is necessary to take into account the modification of the energy spectrum taking into account the statistical distribution of impurities and defects and the additional interaction of particles.

Keywords: PbTe, energy spectrum of holes, TI and Na impurities, Fermi level stabilization, modification of the band spectrum

Introduction

Chalcogenides of elements of groups IV and V of the periodic table are widely used in thermoelectricity. They are the main materials for the manufacture of low-temperature and medium-temperature energy converters. The most studied are the tellurides of lead (PbTe), tin (SnTe) and bismuth (Bi_2Te_3).

From the point of view of the band theory, these materials occupy an intermediate position between classical metals and semiconductors. Like semiconductors, they have a band gap (E_g). At the same time, they are characterized by metallic-type conductivity up to the lowest temperatures. They have electron and hole conductivity due to their own electroactive point defects that do not have levels in the band gap. So the concentration of free carriers in the permitted zones is maintained at low temperatures ($T \to 0$ K) like ordinary metals.

Due to the wide area of homogeneity, these materials are not pure (having only their own conductivity). Typical concentrations of electrons (n) and holes (p) in native unalloyed materials are of the order of 1×10^{18} cm^{-3} in lead chalcogenides, 1×10^{19} cm^{-3} in bismuth telluride and 1×10^{20} cm^{-3} in SnTe and Sb_2Te_3 (Abrikosov et al. 1975; Gol'tsman et al. 1972; Ravich et al. 1968).

Despite numerous studies, the band structure of thermoelectric materials has not been studied sufficiently and is controversial, especially in the field of high Fermi energies (E_F).

According to the results of calculations (Nemov, Ravich 1998; Volkov et al. 1983; 1984), the energy spectrum of the density of electronic states of the valence band *g(E)* of lead and tin chalcogenides has the following form (see Fig. 1).

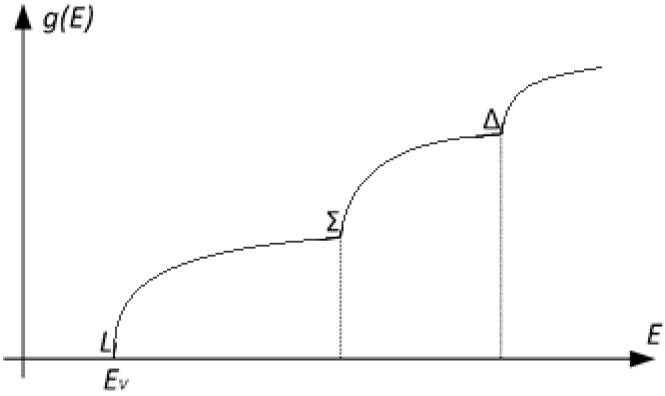

Fig. 1. Qualitative view of the energy spectrum of holes in PbTe and SnTe

The main extremes of the valence band of cubic PbTe and SnTe crystals are located at the L-points of the Brillouin zone. The dependence of the energy E on the quasi-pulse p of charge carriers at these extremes is non-parabolic and, in agreement with experimental data, is well described by the Kane model (Ravich et al. 1968) up to approximately the values of the Fermi energy $E_F \approx 0.15$ eV.

In the monograph (Ravich et al. 1968), the energy spectrum of holes in PbTe is considered in detail experimentally and theoretically in the region of low Fermi energies (up to a hole concentration less than 5×10^{19} cm^{-3}). The experimental data clearly show the contribution to the phenomena of carrier transfer of one kind (light holes) with a small effective mass $m_d \sim 0.1m_0$ (where m_0 is the mass of a free electron).

At high Fermi energies, charge carriers from an additional extremum contribute to the transfer phenomena. The Hall coefficients (R) and Seebeck coefficients (α) grow with temperature. The experimental data are described qualitatively by a two-band model (light and heavy holes with an effective mass of the order of the mass of a free electron). The authors (Nemov, Ravich 1998; Volkov et al. 1984) believe that the second extremum of the valence band is located at the Σ-points of the Brillouin zone and, possibly, is the saddle point.

At even higher hole energies, there is another extremum of the valence band, at Δ-points. It was experimentally observed in solid solutions of $Sn_{0.62}Pb_{0.33}Ge_{0.05}Te$ doped in (Nemov et al. 2000).

Note that high concentrations of holes (Fermi energy) in PbTe are achieved by doping with an acceptor impurity, traditionally with Na, which is the main dopant of the acceptor type in lead chalcogenides. With the help of Na, it is possible to obtain crystals with a concentration of holes up to 1.5×10^{20} cm^{-3} when samples are introduced into the charge about 1–2 at.% Na.

Note that small concentrations of holes in IV-VI materials are achieved due to a deviation from the stoichiometric composition towards an excess of chalcogen. It is significant that despite the change in the doping method (the transition from an excess of chalcogen to an admixture of sodium), the kinetic coefficients monotonically and smoothly change with increasing hole concentration.

An essential feature of lead and tin chalcogenides is the absence of defect levels and major alloying impurities (Na—acceptor, Cl—donor) in the forbidden zone (Ravich et al. 1968).

In the samples of PbTe doped with Na, characteristic features of temperature and concentration dependences of kinetic coefficients are observed, indicating the participation in the transfer phenomena of at least two types of current carriers—light holes from the main L-extremum and heavy holes from the additional L-extremum. Such features are qualitatively interpreted by a two-zone model.

However, it is not possible to describe the experimental data quantitatively in a two-zone model with a single set of additional extremum parameters. There is a significant variation in the parameters of the two-zone model, especially the parameters of the additional extremum (second zone). So we must admit that the model of hard zones applied to doped PbTe does not work when trying to quantify the transfer phenomena. The strong sensitivity of the energy position of the additional extremum and the effective mass of holes to the calculated parameters of the model was also noted in (Volkov et al. 1983; 1984). Therefore, it can be assumed that the appearance of the second zone in the energy spectrum of p-PbTe may be due to the presence of crystal lattice defects, given their large number.

An admixture of thallium in lead telluride (PbTe) behaves in an unusual way. Thallium doping of lead telluride leads to a radical change in the electrophysical properties of PbTe. The following properties are manifested to the greatest extent: stabilization of the hole concentration (pinning of the Fermi level), a change in the type of temperature dependences of the Hall coefficients, a threshold decrease in the mobility of holes and the appearance of a superconducting transition with a critical temperature near 1 K (Shamshur et al. 2008). Moreover, the band of resonant states according to (Volkov et al. 1984) is located near the edge of the assumed extremum at the Σ-points of the Brillouin zone.

Pinning of the Fermi level and stabilization of the hole concentration (p) are due to the presence of partial filling of the density band of resonant states associated with thallium.

The threshold drop in mobility and the increase in the scattering cross section of holes on thallium impurities is explained by the resonant scattering of holes into the Tl band. The occurrence of superconductivity of PbTe samples is observed: Tl when the Fermi level degenerates into a band of resonant states (Kaidanov et al. 1982; Shamshur et al. 2008).

In this paper, in order to experimentally verify the currently used model concepts of the alloying effect of Na and Tl impurities, PbTe samples doped with Na and Tl simultaneously were made, kinetic coefficients were measured and a comparative analysis of the temperature dependences of kinetic coefficients with data for lead telluride samples doped with a single impurity was carried out. Information was obtained on the features of the energy spectrum of the PbTe valence band at Fermi energies greater than 0.15 eV.

Objects of research

The studies were carried out on polycrystalline PbTe samples manufactured using conventional metal-ceramic technology used in industry. They were annealed at a temperature of 650 °C for 120 hours. The synthesis of ingots was carried out from the initial chemical elements of semiconductor purity in evacuated quartz ampoules.

The choice of sample compositions was due to the following considerations. Na doping allows a wide range of changes in the concentration of holes in PbTe. However, in the quantitative analysis of data on transfer phenomena in PbTe:Na samples there is a large variation in the parameters of the two-band model, in particular, the effective mass of holes in the additional extremum. It should be noted that thallium doping does not allow to achieve such high concentrations of holes as in the case of using a sodium impurity. However, there is a stabilization of the concentration of holes in relation to the introduction of excess components and additional dopant Na. In this case, the Fermi level moves within the additional peak of the density function of states (associated with thallium doping) and exits it at high concentrations of additional acceptor impurity (Na).

Thus, the double doping of PbTe with thallium and sodium makes it possible to study the spectrum of electronic states in the valence band.

Since the solubility of impurities in PbTe reaches 1–2 at.%, we introduced a small amount of Tl, sufficient to stabilize the Fermi level, and varied the Na impurity content within wide limits in order to shift the Fermi level deep into the valence band.

Experiment

Measurements of kinetic coefficients were carried out by the probe method on direct current using copper-constantane thermocouples in the temperature range of 77–450 K in a constant magnetic field of 1.6 T.

The temperature dependences of the main kinetic coefficients—specific electrical conductivity (σ) and Hall (R) were investigated. On a series of PbTe:(Tl, Na) polycrystals with a fixed thallium (N_{Tl}) content of 0.3, 0.5 and 2 at.%. The sodium content varied from 0 to 2.5 at.%.

Results and discussions

The Hall coefficient in p-PbTe samples obtained by deviation from the stoichiometric composition towards an excess of tellurium or the introduction of an impurity of Na monotonically increases with increasing temperature. However, from helium temperatures (4.2 K) to about 150 K, the Hall coefficient retains a constant value. Therefore, the concentration of holes p in lead chalcogenides is determined from the value of the Hall coefficient at a temperature of 77 K by the formula:

$$P = (eR)^{-1}$$

Then, with a further increase in temperature, the Hall coefficient gradually increases and reaches a maximum in highly doped samples at approximately 430 K (Ravich et al. 1968). The position of the maximum is almost independent of the concentration of holes. A decrease in the Hall coefficient is observed long before the onset of intrinsic conductivity and cannot be explained by the latter. The observed behavior of the Hall coefficient is traditionally associated in semiconductor physics and in PbTe with the complex structure of the valence band and explained in the framework of a two-band model (Ravich et al. 1968).

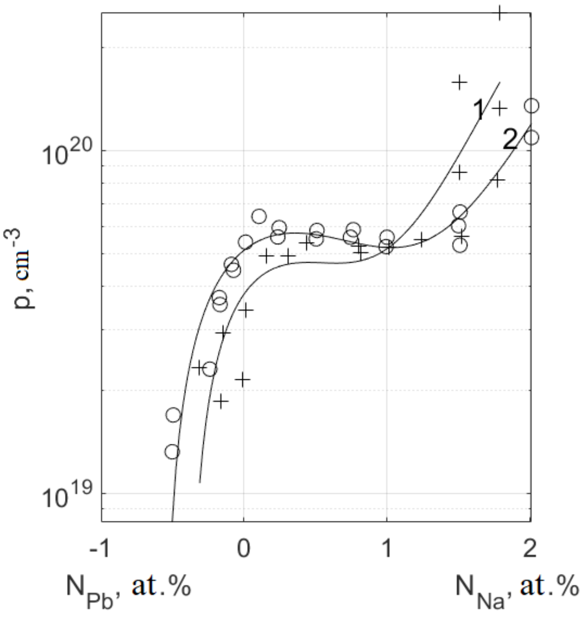

Fig. 2. Dependence of the hole concentration on the amount of additional impurities introduced into PbTe:Tl

Consider the experimental data we have obtained, shown in Figs. 2–4. As can be seen from Fig. 2, in a series of images with relatively small (0.3 and 0.5 at.%) with thallium content, there is indeed a fairly wide area of stabilization of the concentration of holes. When an additional dopant—excess Pb (donor)—is added to the charge of PbTe:Tl samples, the concentration of holes in the valence band decreases. The Fermi level shifts to the ceiling of the valence band. When Na acceptor impurity in the amount of $N_{Na} \geq 2N_{Tl}$ is added to the charge, the hole concentration begins to grow and the Fermi level leaves the band of resonant states. This result correlates with the electrical conductivity data.

The temperature dependence of the specific electrical conductivity of the studied PbTe:(Tl, Na) samples has a metallic character, and is characterized by lower values compared to PbTe:Na crystals. Estimates show that the cross-section of the scattering of holes on Tl impurities is about an order of magnitude higher and has a threshold character depending on the concentration of holes. This is due to the strong resonant scattering of holes (Kaidanov, Nemov 1981; Shamshur et al. 2008) in the band of resonant states arising against the background of the resolved states of the PbTe valence band when doped with its admixture of thallium (Kaidanov, Nemov 1981). The dependences of the resistivity on the amount of additional impurities in all series of samples with a fixed thallium content are similar and have

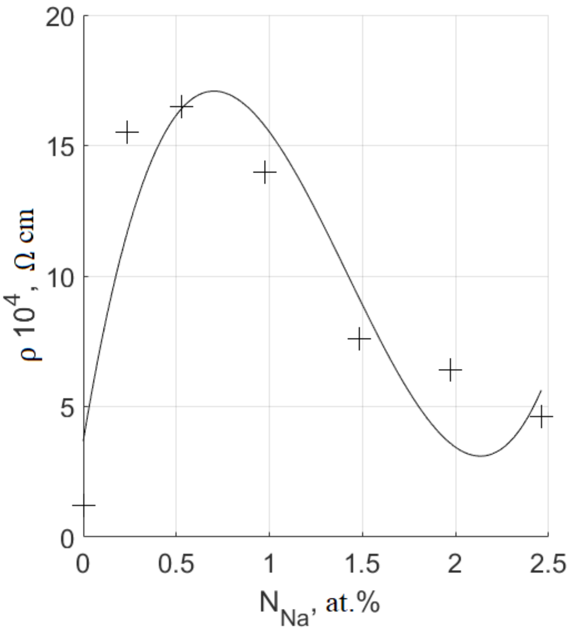

Fig. 3. Dependence of the specific electrical conductivity on the concentration of sodium impurity

the form of a curve with a maximum, which is consistent with the ideas of resonant scattering of holes into the thallium band. Fig. 3 shows data for a series of samples with 2 at.% thallium content, since a large amount of impurities compared to the concentration of intrinsic defects using the neutrality equation allows us to estimate the degree of filling of impurity states with electrons with holes (or electrons) according to the formula:

$$k = 0.5 + \frac{\left(N_{\mathrm{Na}} - p\right)}{2N_{\mathrm{Tl}}}.$$

The two in the formula takes into account the presence of two electronic states per thallium atom. It turns out that the maximum resistance corresponds to approximately half the filling of the resonance state band, and the initial points correspond to crystals doped with a single admixture of thallium grown by the Bridgman-Stockbarger method. They have a value of $k \approx 0.3$, that is, in samples with a high thallium content of 1–2 at.%, the thallium strip is about 2/3 filled with electrons and 1/3 with holes. For large N_{Na}, the coefficient $k \approx 0$, which is consistent with the concepts of resonant scattering and the passage of the peak of resonant states by the Fermi level.

Consider the Hall effect data. As can be seen from Fig. 4, in PbTe:(Tl, Na) samples, the character of the temperature dependence of the Hall coefficient radically changes. From the Hall coefficient $R(T)$ growing with temperature to PbTe:Na it changes the sign of the $\mathrm{d}R/\mathrm{d}T$ derivative in the low temperature region and becomes decreasing over the entire temperature range (up to 450 K).

Moreover, what is significant, even in samples with a significantly higher (almost an order of magnitude) content of additional impurity Na (up to 2 at.%) than Tl (0.3 at.%), the temperature dependences of the coefficient $R(T)$ do not match the dependences characteristic of PbTe:Na samples with the same hole concentration and Fermi level. This means that PbTe:(Na) and PbTe:(Tl, Na) samples in the region of high Fermi energies at the same concentrations of holes have different values of the density function of states, i. e. crystals with the same crystal lattice, but with different impurities have a different energy spectrum. This conclusion is supported by the significant variation in the band parameters of the second zone of sodium-doped PbTe crystals noted in the literature.

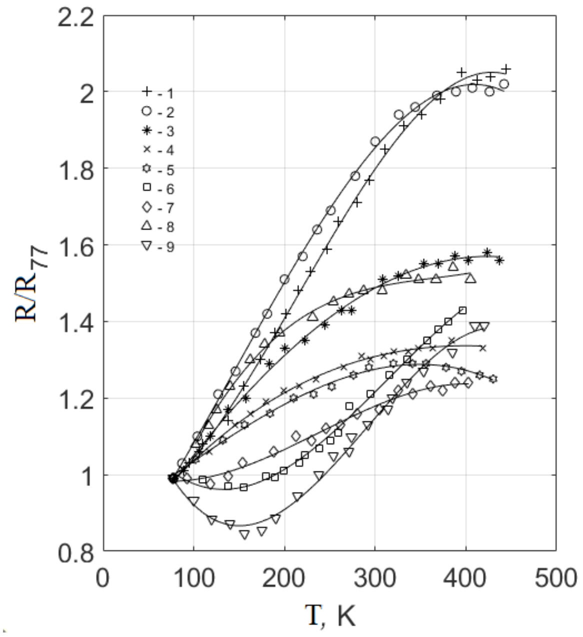

Fig. 4. Temperature dependence of the Hall coefficient in PbTe:(Tl, Na) samples

It should be noted that the presence of a peak in the density of states associated with Tl against the background of the resolved states of the valence band in PbTe:(Tl, Na) is confirmed by superconductivity data. An estimate of the density of states per spin can be made using the formulas:

$$N(0)=4.8*10^{14}\frac{H_{c_2}(0)}{\rho_N T_c},$$

$$N(0)=2.8*10^{14}\rho_N^{-1}\left|\frac{\partial H_{c_2}(T)}{\partial T}\right|_{T\to T_c},$$

where H_{c_2} is the second critical magnetic field, ρ_N is the resistivity of the sample in the normal state, $H_{c_2}(0)$ is an extrapolation of the dependence of $H_{c_2}(T)$ to T = 0 K. The estimates made in this way showed that the density of states in the valence band of PbTe doped with Tl and Na exceeds its value in samples of PbTe doped with Na in samples with such a concentration of holes. In this regard, the authors (Kaidanov et al. 1982) suggested that superconducting electrons are in hybridized band-impurity states.

Thus, based on the results obtained in the work and the available literature data, it must be admitted that the hard zone model does not work in PbTe doped samples with sodium and thallium. The energy spectrum of holes depends on the grade and amount of impurities. Moreover, in the one-electron approximation, it is not possible to combine the appearance of a peak of resonant states in thallium-doped PbTe with two energy compounds per thallium atom. Within the framework of the classical theory of BCS, there is no explanation for the occurrence of a superconducting transition in PbTe:Tl with a high critical temperature for semiconductors $T_c \approx 1$ K.

Conclusions

Thus, the experimental data obtained in the work on transfer phenomena in conjunction with the literature indicate that the ideas of an ideal crystal in the one-electron approximation and the band theory are insufficient to describe the electrophysical properties of PbTe and other compounds of group IV–VI.

This is understandable, since they are synthesized with a noticeable deviation from the stoichiometric composition with a large number of intrinsically electrically active defects (about 0.1–1 at.%) In addition, the materials used in thermoelectricity contain alloying impurities in an amount exceeding the concentration of intrinsic defects, distributed statistically. In such cases, using the example of III–V semiconductors, A. Yu. Zakharov showed (Zakharov 2015) that it is necessary to take into account the approximation of solid solutions and the approach with renormalization of the electron energy spectrum.

It should be noted that this problem is common for compounds A^{IV} B^{VI} and $A_2^V B_3^{VI}$.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All the authors discussed the final work and took part in writing the article.

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