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Effect of scandium doping and of matrix composition variation on galvanomagnetic properties and electronic structure of $Pb_{1-x-y}Sn_xSc_yTe$ alloys



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ABSTRACT

We synthesize a single-crystal Pb_{1-x-y}Sn_xSc_yTe (x = 0.08, y = 0.02) ingot and investigate the composition and the galvanomagnetic properties of samples cut from it. We find that all samples are single-phase and determine the distribution of tin and scandium along the ingot. As the concentration of scandium increases, we find the *p*-*n*inversion of the conductivity type at the liquid-helium temperature, an increase in the electron concentration, and its saturation at $n \approx 1.0 \times 10^{20}$ cm⁻³, indicating the pinning of the Fermi level by the scandium resonant level located well above the bottom of the conduction band. Using the six-band Dimmock dispersion relation, dependences of the Fermi energy on the scandium and tin content are calculated. A diagram of the electronic structure rearrangement of Pb_{1-x-y}Sn_xSc_yTe upon increasing tin content is proposed; the energy and the compositional coefficient of the scandium level movement with respect to the band edges are estimated.

1. Introduction

It is known that doping of lead telluride and its alloys $(Pb_{1,x}Sn_xTe, Pb_{1,x}Ge_xTe, ...)$ with mixed-valence impurities of 3*d* transition metals (Sc, Ti, V, Cr, Fe) introduces deep impurity levels in both allowed and forbidden bands [1–5] (Fig. 1). Usually, initial undoped crystals are *p*-type, while impurity levels are of donor-type and are located above the Fermi level. As a result, an increase in the impurity concentration results in a decrease of the hole concentration, in an increase of the Fermi energy and, ultimately, in pinning of the Fermi level by the impurity level in heavily doped crystals. Changing the composition of the matrix, temperature, or pressure modifies the positions of impurity levels and of the Fermi level stabilized by them with respect to band edges [5–10].

In recent years, these semiconductors have attracted considerable interest motivated by the development of new thermoelectric materials based on IV–VI semiconductors for the mid-temperature range (500–900 K). First, by tuning the composition of the matrix and the type of impurity, it is possible to control the concentrations of free charge carriers, achieving their optimal values in the operation temperature range. Second, resonant impurity levels in the allowed bands and pinning of the Fermi level within the impurity band can lead to an

increase in the Seebeck coefficient *S* and in the dimensionless thermoelectric figure of merit $ZT = \sigma S^2 T/\kappa$ (σ is the electrical conductivity, *T* is the absolute temperature, and κ is the thermal conductivity). This is due to a distortion and a sharp increase of the density of states at the Fermi level [11–14]. Third, using different doping impurities or the same impurity and different compositions of the matrix, it is possible to achieve pinning of the Fermi level in either conduction or valence band and obtain materials that are suitable for both branches of the thermoelectric *n*-*p*-couple. The practical implementations of these ideas require detailed information about the energy positions of the levels as well as about the nature of their movement with respect to band edges upon changing the composition of the matrix, temperature, or pressure.

Several phenomena were used in experiments conducted on virtually all of the above impurities to arrive at the above conclusions. These include saturation of the charge carrier concentration with the impurity content, transition to the dielectric state or p-n-inversion of the conductivity type upon doping, change in the charge carrier concentration in samples with a stabilized Fermi level when the matrix composition changes or under pressure, a significant (several times) increase in the Hall coefficient with increasing temperature, and other characteristic features in temperature dependences of galvanomagnetic

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Fig. 1. Deep levels of 3d transition metals in the electronic structure of PbTe at the liquid-helium temperature.

parameters and optical absorption spectra. The most studied is the Cr level, for which the compositional, pressure, and temperature coefficients of motion in $Pb_{1-x}Sn_xTe$ [6,7,15] and $Pb_{1-x}Ge_xTe$ [16–18] alloys are known. For V and Fe levels, these coefficients were determined only in $Pb_{1-x}Sn_xTe$ alloys [5,8–10,19] while for Sc and Ti levels they are not known yet. In addition, only the first of the phenomena listed above (namely, the tendency of the Fermi level to saturation as the impurity concentration increases) was used to detect the Sc resonant level and to estimate its energy in PbTe [1].

In the present work, we obtain further evidence of the presence of the resonant scandium level in the conduction band of PbTe and determine the nature of its movement with respect to the band edges upon variation of matrix composition. To this end, we investigate the elemental and the phase composition, the temperature dependences of the galvanomagnetic parameters ($4.2 \le T \le 300 \text{ K}$, $B \le 0.07 \text{ T}$), as well as dependences of the free charge carrier concentration and of the Fermi energy on the impurity concentration and the matrix composition in samples from a single-crystal Pb_{1-x-y}Sn_xSc_yTe (x = 0.08, y = 0.02) ingot.

2. Material and methods

A single-crystal $Pb_{1-x-y}Sn_xSc_yTe$ ingot with nominal tin content x = 0.08 and scandium content y = 0.02 was grown approximately along < 111 > crystallographic direction using the modified vertical Bridgman–Stockbarger technique from a mixture of pre-synthesized PbTe, SnTe and Sc₅Te₈ compounds. Initial compounds were obtained

by reacting the pure elemental Pb (99.9999 %), Sn (99.9999 %) or Sc (99.9 %) with the vacuum distilled Te (99.9999 %).

Using pre-synthesized binary compounds serves two purposes: a) the minimization of the charge components oxidation, since PbTe, SnTe and Sc₅Te₈ oxidize in air much slower than Pb, Sn and Sc; b) the improvement of the solubility of Sc, since despite the fact that the full *T-x* diagram of the Sc-Te system has not yet been constructed, it is known that the melting points of scandium tellurides (~1000 °C) are much lower than those of the metallic Sc (1541 °C) [20]. The synthesis of Sc₅Te₈ was carried out for two weeks at different temperatures in custom made graphite containers placed in quartz ampoules evacuated to 10^{-5} Torr. The maximum synthesis temperature of Sc₅Te₈ reached 1270 °C.

To preserve the stoichiometry of $Pb_{1.x-y}Sn_xSc_yTe$, excess tellurium from Sc_5Te_8 was compensated by corresponding molar amount of Sn. Crystallization of an ingot from the melt was carried out in a vacuumed quartz ampoule at a temperature gradient of 35 °C/cm and a crystallization temperature front velocity of 1.5 mm/h. Preparation of initial components, the modes of synthesis, as well as the single-crystal growth procedure are described in detail in Ref. [21].

Using string cutting, the ingot was cut perpendicular to the growth axis into 26 discs, each about 1.5 mm thick. Serial numbers of disks are used below to identify the investigated samples. Large numbers (e.g. 26, 24) correspond to the beginning of the ingot, while small numbers (e.g. 4, 2) correspond to the end of the ingot.

To determine the phase and the elemental composition of solid solutions, at the temperature of liquid nitrogen samples with dimensions of about 1–2 mm were chipped from the disks. The homogeneity of samples and the distributions of Sn and Sc along the ingot were investigated on the cleaved sample surfaces by the X-ray fluorescence microanalysis using the scanning electron microscope LEO SUPRA 50 VP (LEO Carl Zeiss SMT Ltd, Germany) with the microanalysis system INCA Energy+ (Oxford Instruments, England).

For the study of galvanomagnetic effects by using the electric discharge machine, samples in the shape of rectangular parallelepipeds with typical dimensions $4.0 \times 0.7 \times 0.7$ mm were cut. They were subjected to etching in a solution of bromine in hydrobromic acid and were thoroughly washed in ethanol and distilled water. All contacts to the samples were made of copper wires tinned with indium or platinum wires 0.03-0.05 mm thick. Current contacts were soldered by a microsoldering iron to sample ends with In + 4% Ag + 1% Au alloy, and potential and Hall contacts were welded using an electric spark unit. A four-contact *dc* method was used to measure the temperature dependences of the resistivity, the Hall coefficient, and the Hall mobility in weak magnetic fields ($4.2 \le T \le 300$ K, **B** ≤ 0.07 T).

3. Results and discussion

3.1. Phase and elemental composition of samples

Fig. 2 shows microphotographs of cleaved surfaces and X-ray emission spectra from the marked areas for two samples from the beginning and the end of the ingot, respectively (numbers in the photographs correspond to disk serial numbers). We find that, within the experimental error, all samples are rather homogeneous. All the studied samples contain no noticeable inclusions of second phases, which is likely to indicate that the solubility limit of the scandium impurity was not exceeded.

Tin concentration increases monotonously from the beginning to the end of the ingot, covering a wide range of *x* values from 0.045 to 0.175 (Fig. 3). This behavior is normal for all doped alloys based on IV–VI semiconductors [22,23] and was observed in all previously investigated Pb_{1-x}Sn_xTe alloys with transition metal impurities (Cr, V, Fe) [7,8,10]. At the same time, as in the case of Pb_{1-y}Sc_yTe [1], the distribution of scandium along the ingot is inverted: its concentration increases from the end to the beginning of the ingot (see Fig. 3). As far as



Fig. 2. Scanning electron microscope images of the cleaved surfaces (*a*, *b*) and the X-ray emission spectra (*c*, *d*) obtained from selected areas of the investigated Pb_{1-x}. _vSn_xSc_vTe samples 20 and 2.



Fig. 3. Distributions of tin and scandium along the $Pb_{1-x-y}Sn_xSc_yTe$ (x = 0.08, y = 0.02) ingot obtained by the X-ray fluorescence microanalysis. The solid curves represent the approximations (1) and (2) for Sn and Sc distributions, the dashed curve is the approximation of Sc distribution in $Pb_{1-y}Sc_yTe$ (y = 0.01) [1].

we know, in IV–VI semiconductors such anomalous distribution of a 3*d* transition metal impurity was observed earlier only in $Ge_{1-x}Sn_xTe$ doped with Mn [22,23].

It should be noticed that in contrast to other studied impurities of 3*d* transition metals with mixed valence, the concentration of scandium in almost all our samples significantly exceeds the measurement uncertainty. It monotonously increases along the ingot, reaching a record value of more than 3 mol %, and decreases slightly only at the very beginning of the ingot. The distributions of Sn and Sc along the ingot are well approximated by empirical formulas for the distribution of substitution impurities in IV–VI semiconductors [22,23] (see solid lines

in Fig. 3):

$$x = x_0 + A_1 \exp(L/t_1) + A_2 \exp(L/t_2)$$
(1)

$$y = y_0 + B_1 \exp(-L/t_3) + B_2 \exp(-L/t_4)$$
(2)

Here $L = h/h_0$ is a dimensionless coordinate, *h* is the distance from the beginning of the ingot to the middle of a disk, h_0 is the total length of the ingot, and x_0 , y_0 , $A_{1,2}$, $B_{1,2}$, $t_{1,2,3,4}$ are dimensionless fit parameters.

The distribution of scandium along the Pb_{1-x-y}Sn_xSc_yTe ingot is similar to that previously measured for Pb_{1-y}Sc_yTe [1]. The area under the solid curve y(L) in Fig. 3, which should correspond to the integral concentration of the impurity in the ingot, is only 5% less than the concentration of scandium on loading into the growth furnace (y = 0.02), and just twice the value for Pb_{1-y}Sc_yTe (y = 0.01) (see the dashed curve in Fig. 3). From our point of view, these numbers are outstanding in comparison with all other previously studied impurities of 3*d* transition metals (Ti, V, Cr, Fe). They witness a very high solubility of scandium in the investigated alloys.

Tin and scandium concentrations along the ingot are well described by theoretical fits obtained by the least squares method. Therefore, in the further discussion of experimental results we will assume that the concentrations of tin and scandium in the alloys change monotonously along the ingot in accordance with the theoretical curves in Fig. 3.

3.2. Temperature dependences of galvanomagnetic parameters

The study of galvanomagnetic properties of our samples in weak magnetic fields shows that at the liquid-helium temperature, their main parameters consistently vary along the ingot both with the increase in the concentration of scandium impurity and with the variation in the concentration of tin in the alloy (Fig. 4). It is clearly seen that the weakly doped samples are characterized by the *p*-type conductivity (see Fig. 4a). As the impurity concentration increases (and the tin content decreases), the Hall coefficient R_H increases monotonically by about an



Fig. 4. Compositional dependences of galvanomagnetic parameters in $Pb_{1.x.y}Sn_xSc_yTe$ alloys at the liquid-helium temperature. The concentrations of tin and scandium in the studied samples 2–24 are: 2 - x = 0.175, y = 0.004; 4 - x = 0.101, y = 0.005; 6 - x = 0.082, y = 0.007; 7 - x = 0.075, y = 0.008; 8 - x = 0.070, y = 0.009; 10 - x = 0.062, y = 0.011; 12 - x = 0.056, y = 0.013; 14 - x = 0.052, y = 0.016; 16 - x = 0.049, y = 0.015; 18 - x = 0.047, y = 0.023; 20 - x = 0.045, y = 0.024; y = 0.038.

order of magnitude (from sample 2 to sample 7), which obviously corresponds to a decrease in the concentration of free holes in the alloys. Then, a *p*-*n*-inversion of the conductivity type, a monotonous decrease in the absolute value of the Hall coefficient, and an increase in the electron concentration $n = 1/e|R_H|$ (*e* is the elementary charge) by about two orders of magnitude take place in the samples from 8 to 14. Finally, in the heavily doped samples 16–24 (y > 0.015) the Hall coefficient tends to saturate at a level corresponding to the electron concentration of about 1.0 × 10²⁰ cm⁻³.

At the same time, for almost all studied samples, the resistivity ρ at T = 4.2 K varies along the ingot rather weakly and sharply increases by more than two orders of magnitude only in the immediate vicinity of the *p*-*n*-conversion point (in samples 7 and 8). For this reason, the dependence of the Hall mobility $\mu_H = R_H/\rho$ at the liquid-helium temperature on the content of scandium generally follows the same trend as the Hall coefficient (see Fig. 4*a*). The absolute values of the Hall mobility in the majority of samples are of the order of $10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, i.e. at least two orders of magnitude below the values typical of undoped crystals. Mobility is changing rapidly only in the neighborhood of the *p*-*n*-conversion point: in two samples it is close to the value of $10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and in other two samples it decreases sharply to $10^2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The dependences of galvanomagnetic parameters at T = 4.2 K on the tin content look very similar (see Fig. 4b), but all the changes in the parameters mentioned above occur with a decrease in the concentration of tin in the alloys. Besides, at the minimum tin concentrations (i.e. at the maximum scandium impurity concentrations), all the three parameters in Fig. 4b reach saturation and almost coincide with the values characteristic for the previously studied Pb1-vScvTe samples with the Fermi level stabilized by the resonant level of scandium [1] (points at *x* = 0 in Fig. 4b). This result is in good agreement with the general concept of increased spatial homogeneity of galvanomagnetic parameters and reproducibility of parameters of the energy spectrum in the case of stabilization of the Fermi level by the impurity level in lead telluride-based alloys doped with mixed-valence impurities [24]. Together with the effect of saturation of electron concentration with increasing concentration of scandium content, this indicates a pinning of the Fermi level by the impurity level in heavily doped Pb_{1-x-y}Sn_xSc_yTe allovs.

In general, it should be noted that a qualitatively similar behavior of galvanomagnetic parameters at the liquid-helium temperature (*p*-*n*-inversion of the conductivity type, decrease and saturation of the absolute

value of the Hall coefficient, ...) was observed earlier with an increase in the concentration of Sc in samples from the $Pb_{1-y}Sc_yTe$ (y = 0.01) ingot [1]. The main difference here is that in $Pb_{1-y}Sc_yTe$, all samples were *n*-type (i.e. *p*-*n*-conversion has already occurred even in the sample with the minimum concentration of Sc impurity), while in the $Pb_{1-x-y}Sn_xSc_yTe$ samples under study, the *p*-*n*-inversion of the conductivity type occurs only between samples 7 and 8. The most likely reason for this is the high concentration of tin in samples 2–7 from the end of the ingot, which leads to a significant increase in the concentration of intrinsic point defects of the acceptor type (vacancies in the metal sublattice) [25] and a shift of the *p*-*n*-conversion point almost to the middle of the ingot.

Now, if in Fig. 4a and b we start from the p-n-conversion point (from sample 8) and go towards the beginning of the ingot (to sample 24), just as in Pb1-vScvTe, the electron concentration increases and the values of ρ , $|R_H|$, $|\mu_H|$ decrease due to the increase of the concentration of the Sc donor impurity and the weakening of the Sn acceptor action up to the pinning the Fermi level by the Sc resonant level. In this case, the main role is played by a rapid increase in the concentration of Sc, since the concentration of Sn at the beginning of the ingot tends to saturation at the minimum value $x \approx 0.045$ (see Fig. 3). In contrast, if we go from the p-n-conversion point (from sample 7) towards the end of the ingot (to sample 2), the concentration of holes increases and the values of ρ , $|R_H|$, $|\mu_H|$ decrease due to the reduction of the Sc concentration and the increase of the acceptor action of Sn. Here the main role is played by a rapid increase in the concentration of Sn, since the concentration of Sc at the end of the ingot tends to saturation at the minimum level $\gamma \approx$ 0.004 (see Fig. 3).

In almost all the investigated samples, the temperature dependences of galvanomagnetic parameters have "metallic" character, typical of undoped Pb_{1-x}Sn_xTe and indicating the absence of localized states in the forbidden band of Pb_{1-x-y}Sn_xSc_yTe (Fig. 5). The resistivity decreases and eventually saturates upon cooling. The Hall coefficient remains almost constant at low temperatures and monotonically increases with temperature for T > 70 K. In contrast, the Hall mobility monotonically decreases with temperature in the whole explored temperature range. The power-law scaling of mobility with temperature ($\mu_{H} \propto T^{-\alpha}$, $\alpha \approx 2.1$) in the high-temperature range indicates scattering of charge carriers on acoustic phonons, whereas the saturation of mobility at low temperatures is obviously due to the scattering on the native point defects and impurity ions [25].

Only two samples on either side of the p-n-conversion point show



Fig. 5. Temperature dependences of the resistivity ρ (*a*), the Hall coefficient R_H (*b*) and the Hall mobility μ_H (*c*) in *n*-type (samples 24–8) and *p*-type (samples 7–2) Pb_{1-x-y}Sn_xSc_yTe alloys.

noticeable deviations from this behavior. These samples feature nonmonotonic dependences $\rho(T)$ (see curves 7 and 8 in Fig. 5*a*), the maximum resistivity, the maximum absolute value of the Hall coefficient, and the minimum mobility at low temperatures, as well as an increase in the Hall mobility and inversion of the sign of Hall coefficient and of the Hall mobility with increasing temperature (see curves 7 and 8 in Figs. 5*b*, 5*c*). All these features can be associated with the proximity of the *p*-*n*-conversion point and with changes in the concentration and mobility of electrons and holes along the samples and with increasing temperature due to the movement of the band edges and thermal activation of electrons from the heavy valence band to the light valence band [25].

In addition, the temperature dependences of the Hall coefficient in all weakly doped *p*-type samples (especially in the sample 7) also look abnormal (see curves 2–7 in Fig. 5*b*). In these samples, the value of R_H increases significantly (by a factor from 2 to 7.5) with temperature. A similar effect was observed recently in Pb_{1-y}Fe_yTe and Pb_{1-x-y}Sn_xFe_yTe *p*-type alloys [10,19,26] and was attributed to the reduction of hole concentration due to the pinning of the Fermi level by the resonant impurity level of iron and the flow of electrons from the level to the valence band. However, in iron-doped alloys, the Fe resonant level is located in the valence band, while the Sc resonant level should be located in the conduction band, well above its bottom.

Therefore, the most reasonable explanation of this anomaly is the reduction of the concentration of free holes in the light valence band in *L*-extremes of the Brillouin zone due to the thermal activation of electrons from the heavy-hole Σ -band, i.e. the redistribution of holes between *L*- and Σ -extremes of the valence band with increasing temperature. Since the mobility of heavy holes is much lower than that of light holes, this redistribution should lead to an increase in the Hall coefficient with temperature. This effect has long been investigated both experimentally and theoretically in the *p*-type PbTe [25,27–29]. It was shown that in samples with hole concentrations up to 10^{20} cm⁻³, the Hall coefficient increases by several times upon heating to 400–450 K, passes through a maximum and then decreases. Fitting of these dependences by theory allowed for obtaining information about the existence of a heavy-hole Σ -band and for determining its main parameters.

3.3. Compositional dependences of the free charge carrier concentration and of the Fermi energy

To detect the resonant scandium level and to determine its energy and nature of its movement with respect to the band edges upon variations of the composition of the matrix (the content of tin in the alloy), we plot the dependences of the concentration of free charge carriers (holes *p* and electrons *n*) and of the Fermi energy E_F at T = 4.2 K on the concentrations of scandium and tin in $Pb_{1-x-y}Sn_xSc_yTe$ (Fig. 6). Given that at the liquid-helium temperatures all our samples are degenerate, the concentrations of free charge carriers were determined by the absolute value of the Hall coefficient: n, $p = 1/dR_H$. Then, using the ellipsoidal approximation of the six-band Dimmock dispersion relation [25,30] with parameters determined in [31,32] for $Pb_{1-x}Sn_xTe$ ($x \le$ 0.30) alloys, the Fermi energy position with respect to band edges was calculated from the charge carrier concentrations for each sample (the calculation was described in detail in Ref. [1]). The dependences thus obtained are shown in Fig. 7.

It is convenient to analyze these dependences by comparing them with the results obtained previously for $Pb_{1,y}Sc_yTe$ alloys in [1]. First of all, we note that despite the fact that the concentration of scandium impurity in the ingot studied here is twice higher than in [1], the dependences of the electron concentration and of the Fermi energy on the scandium content look similar to those obtained in [1] (see Figs. 6*a* and 7 *a*). In both cases, the electron concentration and the Fermi energy increase monotonically along the ingot. The concentration tends to saturate at $n_{sat} \approx 1.0 \times 10^{20} \text{ cm}^{-3}$. However, all the samples of Pb₁.



Fig. 6. Dependences of the free charge carrier concentration at the liquid-helium temperature on the scandium impurity concentration (*a*) and on the tin content (*b*) in $Pb_{1-x-y}Sn_xSc_yTe$ (x = 0.08, y = 0.02) (1) and $Pb_{1-y}Sc_yTe$ (y = 0.01) studied earlier [1] (2).

 $_{y}Sc_{y}Te$ were characterized by the *n*-type conductivity, while weakly doped samples 2–7 of Pb_{1-x-y}Sn_xSc_yTe are *p*-type and along the ingot, the concentration of charge carriers and the Fermi energy vary even more widely (see Figs. 6 and 7). Given that with decreasing impurity content in the samples at the end of Pb_{1-x-y}Sn_xSc_yTe ingot, the concentration of tin in the alloys increases rapidly up to $x \approx 0.175$, this is probably due to the increase in the concentration of free holes as a result of rising concentration of intrinsic point defects of acceptor type (vacancies in the metal sublattice) upon increasing the tin content in Pb_{1-x}Sn_xTe alloys – an effect known from the literature [25,33,34].

The most important finding here is that the maximum concentration of electrons in heavily doped samples of $Pb_{1-x-y}Sn_xSc_yTe$ remains almost the same (only ~10 % higher) as in the ingot of $Pb_{1-y}Sc_yTe$ (see Fig. 6). This fact, on the one hand, can be considered as a direct confirmation of the existence of the pinning effect of the Fermi level in scandium-doped PbTe-based alloys, since the saturation of the n(y) dependence is observed at almost the same value at an impurity concentration which is twice as high. On the other hand, it indicates a weak sensitivity of the position of the scandium level, which stabilizes the Fermi level in the region of heavy doping, to changes in the composition of the matrix.

The increase of the maximum Fermi energy in Pb_{1-x-y}Sn_xSc_yTe alloys is most noticeable in the dependence of the Fermi energy counted from the bottom of the conduction band $E_F - E_c$ on the tin concentration (see Fig. 7). It seems that the scandium level, which stabilizes the Fermi level, significantly shifts up in energy as the tin concentration increases from x = 0 to $x \approx 0.045$. However, this is mainly due to the fact that with increasing tin content in alloys, the effective electron mass and the density of states in the conduction band gradually decrease, which leads to an increase in the Fermi energy with respect to the bottom of conduction band even at a constant electron concentration in the sample. More adequate information about the possible nature of the movement of the scandium level with respect to band edges with an increase in the concentration of tin can be obtained with the help of the diagram of the electronic structure of Pb_{1-x-y}Sn_xSc_yTe alloys (Fig. 8). Now it is clearly





Fig. 7. Dependences of the Fermi energy measured with respect to the band edges at the liquid-helium temperature on the scandium impurity concentration (*a*) and on the tin content (*b*) in $Pb_{1-x-y}Sn_xSc_yTe$ (x = 0.08, y = 0.02) (1) and $Pb_{1-y}Sc_yTe$ (y = 0.01) studied earlier [1] (2), calculated in the framework of the six-band Dimmock dispersion relation.



Fig. 8. Diagram for the rearrangement of the electronic structure in $Pb_{1-x-y}Sn_xSc_yTe$ at the liquid-helium temperature with increasing tin content in the alloy [25]. The points (1) for $Pb_{1-x-y}Sn_xSc_yTe$ (x = 0.08, y = 0.02) and point (2) for $Pb_{1-y}Sc_yTe$ (y = 0.01) studied earlier [1] show the Fermi level obtained in the framework of the six-band Dimmock dispersion relation.

seen that there are no noticeable changes in the position of the scandium level E_{sc} with respect to the middle of the gap E_i and that with the increase in the concentration of tin in the alloy, the scandium level is likely to move almost parallel to the middle of the gap.

This result contradicts the previously obtained data on the nature of the movement of levels of other impurities of 3*d* transition metals (Cr, V and Fe) in Pb_{1-x}Sn_xTe alloys [7,8,10,35]. In all these cases, deep impurity levels were moving almost parallel to each other downwards from the middle of the gap with an average rate $d(E_{TM}-E_i)/dx = -(4.5-5.0)$ meV/mol %. To resolve this contradiction and determine the compositional coefficient of the scandium level movement with respect to the band edges more accurately, it is necessary to study Pb_{1-x-y}Sn_xSc_yTe alloys with a stabilized Fermi level in a wider range of tin concentrations.

Finally, it should be noticed that variations of the concentration of free charge carriers and of the position of the Fermi level with respect to the band edges along the ingot are very strong: about 1.3 \times $10^{20}\,cm^{-3}$ and 430 meV, respectively. At the beginning of the ingot, the Fermi level tends to saturate due to its pinning by the resonant scandium level, while at the end of the ingot, as the concentration of tin in the alloy increases, the Fermi level moves deep into the light valence band L_6^+ , approaches the top of the heavy-hole Σ -band, and then moves almost parallel to it. However, as the temperature increases, the edges of the light and heavy valence bands should rapidly converge [25], the Fermi level should enter inside the Σ -band, and the density of states at the Fermi level should sharply increase. In general, this means that heavily- and weakly-scandium-doped alloys featuring high tin concentration can be used to fabricate, respectively, n- and p-branches of advanced thermoelectric devices. An increase in thermoelectric efficiency can be expected due to the resonant level of scandium in the conduction band in *n*-type materials and as a result of the convergence of the valence bands of light and heavy holes upon increasing temperature [36,37] in p-type materials.

4. Conclusions

Studies of the phase and of the elemental composition of a singlecrystal ingot Pb_{1-x-y}Sn_xSc_yTe (x = 0.08, y = 0.02) synthesized by the vertical Bridgman–Stockbarger method show that all samples are single-phase. No microscopic inclusions of the second phase are detected. The tin content monotonically increases from the beginning to the end of the ingot from $x \approx 0.045$ to $x \approx 0.175$ as in alloys doped with Cr, V or Fe. In contrast, the concentration of Sc impurity *y* increases from the end to the beginning of the ingot, which is opposite to the dependence found for all other previously studied impurities. The solubility of Sc is abnormally high, exceeding 3 mol %.

Galvanomagnetic measurements show a monotonic decrease in the concentration of holes, *p*-*n*-inversion of the conductivity type, and a subsequent increase in the concentration of free electrons with increasing concentration of Sc impurity along the ingot. In heavily doped alloys (y > 0.015), the free electron concentration at the liquid-helium temperature tends to saturate at $n \approx 1.0 \times 10^{20}$ cm⁻³, indicating the donor nature of the scandium impurity and the pinning of the Fermi level by the scandium resonant level located well above the bottom of the conduction band. In weakly doped *p*-type alloys with a high tin content (x = 0.075–0.175), anomalous temperature dependences of the Hall coefficient were found. These are most likely associated with a decrease in the concentration of light holes due to redistribution of holes between the *L*- and Σ -extremes of the valence band upon increasing temperature.

The dependences of the concentration of free charge carriers and of the position of the Fermi level with respect to band edges in the *L*-points of the Brillouin zone at T = 4.2 K on the concentrations of scandium and tin were obtained from experimental data using the six-band Dimmock dispersion relation. A comparison of these dependences with earlier data for Pb_{1-y}Sc_yTe allowed us to confirm the existence of the resonant impurity level of scandium in the conduction band of the alloys ($E_{Sc} \approx E_c + 280$ meV at $x \approx 0.045$). In contrast to the previously studied levels of Cr, V and Fe, the resonant level of Sc moves almost parallel to the middle of the gap E_i upon increasing tin content in the alloys.

We believe that both heavily and weakly doped $Pb_{1-x-y}Sn_xSc_yTe$ alloys with a high tin content may be promising thermoelectric materials for advanced thermoelectric devices due to the presence of the resonant level of scandium in the conduction band in *n*-type alloys and the convergence of the valence bands of light and heavy holes with increasing temperature in *p*-type alloys.

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CRediT authorship contribution statement

E.P. Skipetrov: Conceptualization, Methodology, Writing - review & editing, Project administration. **A.V. Khvorostin:** Investigation, Formal analysis, Visualization. **A.V. Knotko:** Investigation, Data curation. **V.E. Slynko:** Writing - original draft.

Declaration of Competing Interest

There are no conflicts of interest.

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