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THE BAND EDGE STRUCTURE OF THE IV-VI SEMICONDUCTORS

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Résumé. — Cet article résume les résultats de l'étude de l'effet Hall, de l'électroconductivité, du pouvoir thermoélectrique et de la thermoconductivité, dans le domaine de température de 77 °K à 1 200 °K, sur des échantillons mono ou polycristallins de PbTe, PbSe, PbS, SnTe, GeTe dont la concentration en porteurs va de $10^{13}$ à $10^{21}$ cm$^{-3}$. Des travaux sur des solutions solides, principalement PbTe-PbS et PbTe-SnTe sont aussi présentés. La dépendance des coefficients cinétiques et des paramètres de bandes en fonction de la température et de la concentration est analysée à l'aide d'un schéma de bandes non paraboliques. Le problème d'une structure multibande dans ces composés a été discuté en détail. Les paramètres de ce modèle compliqué à deux bandes, masses de densité d'états ou bord de bandes aux différents états, leur dépendance en fonction de la concentration, l'énergie des gaps etc... ont été définis quantitativement en se basant sur des travaux ne tenant pas compte de ces expériences.

Le changement de la disposition des bords de bande dans un large domaine de températures et de pressions (ainsi que de composition dans le cas de solutions solides) a été mis en lumière :

L'étude des paramètres de bandes permet de tirer quelques conclusions concernant les mécanismes de diffusion des porteurs dans les semiconducteurs considérés. En particulier, de nouveaux travaux prouvent que l'opinion répandue sur le rôle prédominant de la diffusion sur les modes acoustiques dans les composés IV-VI devrait être reconsidérée. Dans ce papier, les résultats expérimentaux ont été interprétés sur la base de mécanismes de diffusion mixtes, leur dépendance en fonction de la température et de la concentration ayant été définie. Parallèlement à ces résultats concernant la structure à deux bandes, nous avons étudié le rôle de la diffusion interbande.

Abstract. — The results of studying of the Hall effect — as well as transport phenomena in the absence of a magnetic field — electroconductivity, thermoelectric power and thermoconductivity in the temperature range from 77 to 1 200 °K in single and polycrystalline samples of PbTe, PbSe, PbS, SnTe, GeTe with a concentration of current carriers from $10^{13}$ to $10^{21}$ cm$^{-3}$ have been summarised. Data for some solid solutions based on the above compounds, namely PbTe-SnTe, are also presented.

Temperature and concentration dependences of the kinetic coefficients are analysed in terms of a non-parabolic dispersion law. The problem of the multiband structure in these compounds is discussed in detail. The parameters of the complicated two-band model — density of state masses at the band edges of different extrema, their concentration dependences, interband energy gaps, etc. — have been defined quantitatively from the joint analysis of the data irrespective of experiments. The change of band edge disposition in the wide range of temperatures and pressures (as well as compositions in the case of solid solutions) has been found.

Joint study of the kinetic coefficients allows one to make some conclusions concerning scattering mechanisms of current carriers in semiconductors considered. In particular, new data prove that present opinion about the predominant role of acoustical mode scattering in IV-VI compounds should be reconsidered. In the work reported, experimental results have been interpreted on the basis of complicated mixed scattering mechanisms, temperature and concentration dependences of that correlation have been defined. While working on the results concerning complicated doublet band edge structure the role of interband scattering has been estimated.

Introduction. — At present the interests of many researchers come to center on the problem of investigation of IV-VI compounds energy band structure in the energy region higher than the principal band edge. As a result of this extensive investigation, a very important step in the development of this field has been made. Studying heavily-doped materials throughout a wide temperature range is one of the most fruitful methods for obtaining new results concerning the band structure. The heavy doping of
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IV-VI semiconductors enables us to change the disposition of the Fermi-level, taken from the band edge, within the range of 0-0.4 eV, and so to trace the variation of energy band structure. The treatment of the kinetic coefficients can give the valuable information concerning this variation. In sec. I we deal with the two-band model of the valence band of lead chalcogenides. In sec. 2 the problem of the presence of the second conduction band edge at high energies is under discussion. The related problems, namely, the band non-parabolicity and the scattering mechanism are treated. In sec. 3 a brief review of the data connected with other IV-VI compounds such as GeTe, SnTe, and solid solutions PbTe-SnTe is given.

The author does not mean to give a complete review of the matter. His intention is to dwell especially upon results obtained by group of researchers working at the Institute of semiconductors of Academy of sciences of USSR.

1. Two-band model of the valence band in lead chalcogenides. — As it is well-known Allgaier [1] was the first to surmise the presence of the second valence band edge with the energy separation from the principal one \( \Delta E = 0.15 \) eV [2]. This idea has arisen from analysis of the temperature dependence of the Hall-effect. This statement proposed by Allgaier was thereafter confirmed by the serial investigations [3, 4, 5, 6, 7, 8, 9, 10, 11]. We have referred to only some of the whole body of literature connected to this subject, namely, which are concerning the transport phenomena. In [3] the deviations in the behavior of the thermoelectric power \( \alpha \) and electroconductivity \( \sigma \) from that, which is typical for a single band model, have been reported. An enormously large increase of the effective mass with temperature, which was observed in [3], is accounted for by the influence of the second valence band, whose density of states is larger than that of the principal one. In [6, 7] the Hall-coefficient dependence on high pressure has been found. Such a dependence should only occur if redistribution of carriers is the case. The most pronounced influence of the second valence band manifests very distinctly in investigation of the Hall effect over a wide temperature range [4, 5, 10]. The temperature dependence of this effect is rather complicated. It is depicted by a slope with well-resolved maximum. The relative increase of the Hall coefficient \( R \) is 2-3 times at the point of extremum. (See, for example, Fig. 1.) This complexity of the Hall coefficient behavior can be interpreted uniquely only on the ground of the two overlapping valence bands model. The increase of \( R \) up to the maximum value as well as the following decrease of \( R \) in the extrinsic region is

(1) The decrease of \( R \) as the temperature is raised above the point corresponding to the maximal value of \( R \), cannot be regarded as the manifestation of intrinsic conductivity. It has been proved by investigation of the electron heat conductivity which is very sensitive to the presence of carriers of the opposite sign, and by quantitative estimate of density of intrinsic carriers. This statement is true for the temperature region of order of 100 °C higher than the point of the maximum value of \( R \).
connected to the redistribution of carriers over bands [4, 5, 10]. There were unsuccessful attempts to explain this dependence by a possible increase of the Hall factor, which is due to the band non-parabolicity. We don't discuss them.

1.1 The method of calculation of two-band model parameters from transport phenomena.
— The analysis of the temperature and carrier concentration dependences of the Hall effect, together with the data on the thermoelectric power and the conductance, enables us to determine the subset of two-band model parameters in a fairly unique way.

The carrier concentration in bands satisfies the condition:

\[ p_1 + p_2 - p_0 = n_i, \]  

(1)

where \( p_1 \) and \( p_2 \) are the hole concentrations in the first and second bands, respectively, \( p_0 \) is the extrinsic hole concentration, \( n_i \) is the electron concentration.

With the assumption concerning the band dispersion law the eq. (1) can be expressed in terms of microscopic parameters. We adopt the non-parabolic dispersion law in the form predicted by the generalized Kane model for the principal valence band. This model seems to be the possible one for description of the band non-parabolicity and it was considered by Dubrovskaya and Ravich [12]. It is the usual Kane model extended to the case of the many-valley band structure and anisotropic energy surfaces. The assumption is made that there is only one value of effective interaction gap which defines the energy dependence on wavevector \( k \) along all the main axes of energy ellipsoid. (See [13] for details.) It has been ascertained in [12] that the generalised Kane model may be used for the lead chalcogenides if we are not concerned with the anisotropic effects and we introduce the averaged mass value into our relations. Basing our treatment on the conclusions of [12] we employ the transport theory of Kolodziejchak and Žukotynsky [14] to investigate the semiconductors under test. The second valence band separated by \( \Delta E \) from the principal one was described by the simple parabolic law.

The eq. (1) contains the magnitudes of the density-of-states effective masses as parameters. Their values for the principal valence band edge and conduction band edge are available from the other experiments, at least, at low temperatures [12, 13, 15, 16, 17, 18]. The values of masses at high temperatures were calculated by means of extrapolation, it being supposed the temperature coefficient of the interaction gap to be equal to that of the forbidden energy gap. This assumption can be confirmed by the measurements of the density-of-states effective mass carried out by Kajdanov et al. [16] for \( n \)-PbTe at temperatures of 120-300 oK. Therefore the two parameters, which have to be adopted, are the density-of-states second valence band effective mass and the energy gap between two valence subbands (valence gap). These two quantities were chosen in such a way to achieve the best fit to the experimental data on \( R, \alpha, \sigma \).

The relations for \( R, \alpha, \sigma \) contain, besides the values of \( p_1/p_2 \) ratio and of Fermi-level both obtained from eq. (1), also the ratio of the carrier mobilities in two valence bands \( b = \frac{<M_1>}{<M_2>} \). Here the notation \(<\>\) stands for

\[
< A > = \int_0^\infty \left( - \frac{df}{d\varepsilon} \right) A(\varepsilon) \left[ \frac{\varepsilon}{\varepsilon^*_g} \right]^{3/2} d\varepsilon
\]

\[
= \int_0^\infty \left( - \frac{df}{d\varepsilon} \right) \left[ \frac{\varepsilon}{\varepsilon^*_g} \right]^{3/2} d\varepsilon,
\]

\[ E_g^* \] is the effective interaction gap.

As the first order approximation we take the \( \frac{<M_{1,2}>}{<M_{1,2}>} \) (quantities being involved in formula for the Hall coefficient in the case of the presence of two types of carriers) to be equal. Then the \( \langle b \rangle \) can be derived from the relative maximum increase of the Hall coefficient. (See the elementary theory in [5],) When comparing solution of eq. (1) with experimental data, using such a way \( \langle b \rangle \) we can compute \( \frac{<M_{1,2}>}{<M_{1,2}>} \) and \( \frac{<M_{1,2}>}{<M_{1,2}>} \) and so can specify the value of \( \langle b \rangle \). Though the procedure can be repeated, the results of calculations prove these new corrections to be negligible.

When calculating we assume the energy dependence of the relaxation time in the form [14]:

\[
\tau = \tau_0 \left[ \varepsilon \left( 1 + \frac{\varepsilon}{\varepsilon^*_g} \right) \right]^{r/2} \left( 1 + 2 \frac{r}{\varepsilon^*_g} \right)^{-1},
\]

(3)

where \( r = -1, +1 \) for the acoustical and optical \( (T > \theta_d) \) scattering respectively.

In accordance with [16, 18] the best fit to the measured transport coefficients corresponds to \( r = 0 \) in lead chalcogenides. It is the value that we have chosen in our calculation. We shall dwell on the problem of the mixed scattering in lead chalcogenides in section 2.

1.2 Some experimental data and two-band model parameters in lead chalcogenides. — Experimental results on the transport coefficients dependence on temperature, concentration and pressure for
p-PbTe have been reported in [2-7, 10, 11]. So there is no evident need to include this information into the paper. Two-band model parameters obtained from the analysis are collected in table I.

The main conclusion resulting from the investigation of p-PbTe is the ascertainement of the inversion of the valence band edges at temperatures of about 450 °K [4, 9]. This statement is confirmed by investigation of the temperature dependence of the energy gap [19, 9]. The picture of band edges shift for PbTe is presented in figure 4.

Figure 1 shows the fractional change in the Hall coefficient versus temperature for PbSe. The dashed curve in figure 1 is referred to p-PbTe and is given for comparison. One can observe the similar behavior of these dependences. This result leads us to the conclusion about the similarity of the valence band structure in these compounds. As it is also seen in figure 1 the «two-band Hall» slope for PbSe is extended over the temperature range which is larger than that for PbTe. One can think that the carrier redistributions over bands proceeds more slowly in PbSe. It can occur if the energy gap between valence subbands is larger or the temperature coefficient of the gap is less. The data on the temperature dependence of the energy gap in PbSe [20] show the «$E_g$» to be practically independent of $T$ at the temperatures higher than 760-800 °K. If

Table I

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band parameters</th>
<th>$m_{don}/m_0$</th>
<th>$E_g$ (eV) $T=0^\circ K$</th>
<th>$E_g$ (eV) $T=0^\circ K$</th>
<th>$\Delta E_g$ $dE_g/dT$ (eV/°K)</th>
<th>$\Delta E_g$ $dE_g/dP$ (eV/bar)</th>
<th>$\Delta E_g$ $dE_g/dT$ (eV/°K)</th>
<th>$\Delta E_g$ $dE_g/dP$ (eV/bar)</th>
<th>$\Delta E_g$ $dE_g/dT$ (eV/°K)</th>
<th>$\Delta E_g$ $dE_g/dP$ (eV/bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe</td>
<td></td>
<td>[16]</td>
<td>[13]</td>
<td>[19, 9]</td>
<td>[7]</td>
<td>1.3-1.5</td>
<td>[4]</td>
<td>[4, 5]</td>
<td>[4, 9]</td>
<td>7 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.13</td>
<td>0.13</td>
<td>0.19</td>
<td>(−8 ± 0.5)</td>
<td>300 °K</td>
<td>0.17-0.18</td>
<td>0°</td>
<td>4 ± 0.5</td>
<td>700°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>0.23</td>
<td>0.23</td>
<td>0°</td>
<td>$\approx 0$</td>
<td>$\approx 0$</td>
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<td>120°</td>
<td>120°</td>
<td>120°</td>
<td>120°</td>
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<tr>
<td>PbTe</td>
<td></td>
<td>[18]</td>
<td>[18]</td>
<td>[21]</td>
<td>[20]</td>
<td>[22]</td>
<td>[22]</td>
<td>[22]</td>
<td>[22]</td>
<td>[22]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.11</td>
<td>0.11</td>
<td>0.16</td>
<td>(3-4)</td>
<td>−7.5 ± 0.5</td>
<td>0.6-1.0</td>
<td>0.25-0.35</td>
<td>0°</td>
<td>4 ± 0.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.21</td>
<td>0.23</td>
<td>0.23</td>
<td>0°</td>
<td>$\approx 0.35$</td>
<td>$\approx 0.35$</td>
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<tr>
<td>SnTe</td>
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<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
|              | $m_{don}$, $m_{don}$, $m_{don}$ — the density-of-states effective mass values at the conduction, principal valence and second valence subband bottom, respectively; $E_g$ — the principal energy gap.

$\Delta E_g$ The mobility ratio depends on the carrier concentration: the higher values are to be referred to the concentration of $(1-2) \times 10^{20}$ cm$^{-3}$, while the lower values to the $(1-2) \times 10^{19}$ cm$^{-3}$.
band model in p-PbS were not estimated quantitatively.

1.3 On localization of additional band extrema in Brillouin-zone. — If the relative placement of the band extrema in PbTe along energy axis can be considered to be well stated, the problem of localization of additional band extrema in k-space remains unanswered. The above experimental data are not sensitive to the disposition of the band extrema in the Brillouin zone, therefore the only source of assumptions on this subject is the theoretical considerations. The theoretical picture of the PbTe band structure produced by Lin and Kleinman [23] shows the presence of some band extrema with the energy near to that of the principal extrema. These additional extrema are placed in directions <110> and <111> while the principal ones as it will be useful to repeat here are located at L-points. It is likely, that the extrema in these directions are, namely, those which are detected.

1.4 Interband scattering for two-band model. — In the presence of two overlapping bands we encounter the interband scattering besides the intraband scattering. If relaxation time of the former mechanism is comparable to that of the latter one, the total relaxation time can be changed. The change in the magnitude of the relaxation time affects all the transport coefficients. Assuming the interband relaxation time to be inversely proportional to the squared matrix element for these transitions and to the density of states in the second band, we can estimate the total relaxation time, and, further, can write down all the transport coefficients with the aid of general kinetic relations. This kind of interband scattering theory with assumption of acoustical scattering and parabolic energy law was developed in [24, 25]. The fit parameter of the theory is the ratio of matrix elements of intra- and interband transitions.

The first attempts of taking care of the interband scattering in the transport phenomena for IV-VI compounds were undertaken by Kaidanov et al. [26, 25] and by Smirnov et al. [11]. It was shown in [26, 25, 11] that it is the interband scattering which is capable to explain the anomalously low value of the thermoelectric power in SnTe and PbTe which are observed at such carrier concentration when Fermi-level is near the second heavy-hole band edge. As it was pointed out by Kaidanov, this low thermoelectric power value can be qualitatively regarded as decrease of the light-hole energy in the flux. The behavior of the electron heat conductivity also reveals very characteristic features of the picture when the interband scattering occurs. The Lorentz ratio takes on the anomalous large values and its concentration dependence becomes rather complicated [27, 11].

Estimations point out that the influence of the interband scattering on the Hall effect mainly reveals in the decrease of the carrier mobility in the light-hole band and therefore as a result of it in the decrease of the ratio of mobilities. For the time being one cannot evaluate this effect quantitatively, since the part of interband transitions and the temperature
dependence of this effect are unknown. All the above results are obtained by neglecting the interband scattering. However, it is worth to remark that the more adequate explanation of the experimental data demands us to decrease artificially the mobility ratio \( \frac{\mu}{b} \) at the temperatures above the point of the valence band inversion. The above qualitative consideration allows to suppose that this decrease of \( \frac{\mu}{b} \) is possible due to neglect of the effect of the interband scattering.

2. On interpretation of some anomalous behavior of transport coefficients in n-type lead telluride. — In accordance with investigations \([12, 16, 17, 18]\) the non-parabolic single band model is applicable to n-type lead chalcogenides at least over the energy range about 0.2-0.3 eV, taken from the band edge. However, a certain increase of the band density of states was revealed at energies above 0.3 eV \([12]\). The Hall effect measurements upon the heavy-doped samples of \( n\text{-}\text{PbTe} \) \( (n \approx 2.0 \times 10^{20} \text{ cm}^{-3}) \) also indicate a sudden large rise of the Hall coefficient with increasing temperature. In these samples increase of the Hall effect is more than 1.5 times within the temperature range 77-700 °K. Such a behavior of the Hall coefficient can not be explained within the frame of the simple non-parabolic model as result removal of the strong degeneracy condition and following enlargement of the Hall-factor. There are some other anomalies in the behavior of the heavy-doped samples of \( n\text{-}\text{PbTe} \). For example, the temperature dependence of the mobility within the temperature range 700-1 100 °K is described by the law \( T^{-1/2} \). The data on the thermoelectric power for \( n \gtrsim 1.1 \times 10^{20} \text{ cm}^{-3} \) cannot be understood from the point of view of the simple non-parabolic model \([28]\).

The above mentioned features of n-type lead telluride behavior can result from various reasons. For instance, the presence of the second band edge or intensifying of the non-parabolicity effect can give rise to this result. In order to extract the role of these factors we have analyzed the temperature and carrier concentration dependence of the Hall-factor in n-type PbTe basing on the generalized Kane non-parabolic model and taking care of new considerations of scattering mechanism in lead chalcogenides developed by Ravich \([13]\).

Ravich had calculated the mobilities in PbTe when the scattering by polar optical oscillations in the liquid nitrogen temperature region occurs. His evaluation was made in terms of microscopic consideration of the problem and did not require any fit parameters. The non-elastic character of scattering, the Debye screening effect on matrix element and the band non-parabolicity were taken into account. The calculations have shown that the scattering by the longitudinal optical phonons is essential and becomes more significant as the degeneracy of the electron gas removes. To take into account the scattering by acoustical as well as by optical phonons one can explain the concentration dependence of carrier mobility which is observed.

When calculating the transport coefficients with the assumption of mixed scattering at \( T > \theta_D \) \((\theta_D = 160 \text{ °K for PbTe})\) we can use the relaxation time approximation for scattering by optical oscillations. The energy dependence of the relaxation time in the case of scattering by acoustical or optical phonons was chosen according to \((3)\) (See Sec. 1). Adding up the inverse relaxation times we have got the expression for \( \tau_{\text{mix}} \) as a function of \( \tau_{\text{ac}} \) and \( \tau_{\text{op}} \) which are the values of \( \tau_0 \) for acoustical and optical scattering, respectively. In the case of the mixed scattering we have obtained the formula for the Hall-factor \((*)\), thermoelectric power, as well as for relative mobility change as a function of the ratio \( \tau_{\text{ac}}/\tau_{\text{op}} \). The following task was to calculate the ratio \( \tau_{\text{ac}}/\tau_{\text{op}} \) under condition of the correspondence between the theoretical and experimental values of \( R \), \( \alpha \) and relative mobility change within a large temperature and concentration range. The value of the Fermi-level necessary for this calculation was computed from the usual expression for the concentration in the case of non-parabolic band \([14]\). As regards the density-of-states effective mass and the interaction energy gap we have taken the same assumptions as those discussed in sec. 1 in connection with the calculation method of the two-band model parameters.

The adequate description of the data obtained from the three independent experiments has been reached with the \( \tau_{\text{ac}}/\tau_{\text{op}} \) of 0.2 eV at 300 °K being practically independent of the temperature. The calculated concentration dependence of the thermoelectric power fits rather well to experimental dependence with the density-of-states effective mass at the band bottom \( m_{\text{e}} \) being equal to 0.17 \( m_0 \) at 300 °K which is in good agreement with the result of \([16]\), obtained by the method independent of assumptions about the scattering mechanism. Assuming the mixed scattering the

\((*)\) It should be noted that under the Hall-factor calculation we adopt the value of the factor being due to energy band anisotropy to be equal to 1. It is reasonable because the evaluation of this factor, based on the known data on the anisotropy coefficient at 300 °K, gives the value of 0.9, with this value tending to 1 at higher temperatures in accordance with the tendency of the anisotropy energy coefficient variation.
The temperature dependence of the mobility for the lightly doped samples \( (n \approx 2.0 \times 10^{19} \text{ cm}^{-3}) \) is described by the law \( T^{-2.5} \). For the more high-doped this law is rather less and described by \( T^{-1.6} \). This result also correlates with experimental data. The estimations of the mobility magnitude have been performed for the optical scattering in the case of high degeneracy with a rather good agreement being obtained with the theoretical value calculated according to Ravich’s formula (taking into account screening effect and band non-parabolicity). It is to remark that the partial mobility (calculated with correction on taking down of degeneracy), due to scattering by acoustical phonons, is described by the Bardeen-Shockley formula with the deformation potential constant value being equal approximately to 16 eV. This value is more close to that extracted from the experiment on piezoresistance. As to Hall-factor calculations, they are represented in figure 3. The experimental temperature dependence of the Hall coefficient and its concentration dependence at 473 °K are given in figure 3, too. An additional plot of figure 3 represents the calculated curves for the acoustical and optical scattering, separately. To compare the calculated curves with experimental ones, it is easily seen that the concentration dependence for the acoustical scattering is in strong contradiction with the experiment. The mixed mechanism describes satisfactorily the temperature and concentration dependences except the region of extremely heavy-doping (about \( 2.0 \times 10^{20} \text{ cm}^{-3} \)). As to this region of the doping we have to make the conclusion that the Hall effect increase is left outside of interpretation in the frame of the simple non-parabolic model. It should be reminded that the deviation in the thermoelectric power behavior from the simple theory description for carrier concentration of \( 2.0 \times 10^{20} \text{ cm}^{-3} \) is also observed.

It is evident that either the second band edge or the non-parabolicity of higher order is to be taken into account. We find it difficult at the present stage to separate these factors with reasonable arguments. From our point of view the first variant is more preferable because all not correspondent with theory experimental facts may be interpreted more easily in terms of the two-band model. Keeping to this point of view we have tentatively introduced the additional band edge into the picture of the band edges displacement of PbTe. From estimation this additional

![FIG. 3. — Fractional change in the Hall coefficient \( R/R_{77\text{°K}} \) for n-type PbTe versus temperature: 1, 2, 3, 4 — experimental curves for the samples with carrier concentration \( n = \frac{1}{eR_{77\text{°K}}} \cdots \) 2.0 \times 10^{20}, 7.0 \times 10^{19}, 1.5 \times 10^{18}, 6.3 \times 10^{18} \text{ cm}^{-3} \); dashed curve is theoretical one corresponding to the sample with carrier concentration \( 7.0 \times 10^{19} \text{ cm}^{-3} \); this curve is calculated in assumption of the mixed scattering by acoustical and optical phonons. Additional plot: Concentration dependences of the Hall-factor \( r = \frac{\tau^2/m^2}{\tau/m^2} \) for the various scattering mechanisms: single curves are calculated for the scattering by acoustical, optical and acoustical and optical phonons together at the temperature 473 °K; dot-dashed curve is experimental one.](image-url)
band edge is separated from the principal one by the gap no less than 0.3 eV (See Fig. 4). The theoretical model developed by Lin and Kleiman [23] admits the presence of the second edge in the conduction band, with the extrema of the second band edge being placed at the <110> directions and having an energy close enough to that of the principal ones.

We have carried out the measurements of the $R$, $\alpha$, $\sigma$ for n-type PbS. We have also performed the calculations analogous to that of n-PbTe. The experimental relations are described satisfactorily for all temperatures and carrier concentrations. Thus, there are no indications as to the presence of the second band edge in conduction band of PbS at attainable energies up to 0.3 eV, taken from the principal band edge.

3. Band structure of GeTe, SnTe and Solid Solutions PbTe-SnTe. — Both GeTe and SnTe are crystallized with departure from stoichiometric composition with excess of tellurium. The surplus tellurium behaves as an acceptor which is responsible for the observed p-type conductivity. In both semiconductors the sign of conductivity is not changed even at high temperatures up to the melting point. Therefore the general information derived from investigation of the transport coefficients relates to the valence band structure.

3.1 Germanium Telluride. — The transport coefficients, mainly, $\alpha$, $\sigma$, and thermoconductivity were the object of extensive investigation carried out by Kolomoyetz et al. [21, 30, 31]. Their papers contain a body of observed relationships, which to explain Kolomoyetz proposed the model of two overlapping valence bands with the different density of states.

The measurements of the Hall effect for GeTe over a wide temperature range upon the specimens with various carrier concentration were carried out in [32]. The temperature dependence of the Hall effect does not reveal anomalies being due to processes of the carrier redistribution between the subbands which is the feature of the two-band model (See Fig. 5).

![Figure 4: Displacement of the band edges for PbTe against temperature.](image)

**Figure 4.** Displacement of the band edges for PbTe against temperature.

![Figure 5: Temperature dependences of the Hall coefficient for GeTe.](image)

**Figure 5.** Temperature dependences of the Hall coefficient for GeTe: 1.3 — the polycrystalline samples, 2.4 — the single crystal ones. Additional plot: Temperature dependence of conductivity for sample with carrier concentration $6.2 \times 10^{20}$ cm$^{-3}$. 


The rapid decrease of $R$ in the temperature range of 600-700 OK can result from either the phase transition for the given semiconductor or the intrinsic conductivity effect. Let us note, however, that under certain conditions, namely, the mobility ratio to be close to 1, $\frac{d\Delta E}{dT} \approx 0$, the strong interband scattering, the carrier redistribution influence on the Hall effect can vanish. Thus we conclude the band parameters values in [30] should be accurately accounted for temperature dependence of the Hall effect.

3.2 Tin Telluride and Solid Solutions PbTe-SnTe. — The $R$, $\alpha$, $\sigma$-measurements in SnTe [33, 34, 26, 25] as well as the Nernst-Ettingshausen coefficient [26, 25] and thermoconductivity [27] measurements have pointed out that the two-valence band model is to be employed for interpretation of the data. The band parameters for the parabolic law approximation were obtained in [26, 25]. In particular, one of the results is the energy gap between subbands $\Delta E$ to be equal about 0.3 eV at 0 OK, with the temperature coefficient of this gap being $(2-3) \times 10^{-4}$ eV/OK. We have measured the Hall effect in SnTe over a wide temperature range. The experimental results are plotted in figure 6. It is easily seen the similarity between the gap to be $(2-3) \times 10^{-4}$ eV/OK and value of gap to be 0.3 eV we have achieved the satisfactory description of the experimental picture. Let us remark, however, that all the calculations for this bad researched semiconductor performed under certain assumptions and simplifications are to be regarded as tentative ones which are rather a possible variant of explanation.

The investigations of the properties of solid solutions PbTe-SnTe enable us to trace the modification of the complicated two-band structure of the valence band from PbTe to SnTe. In figure 7 the concentration dependences of the thermoelectric power for the some compositions of solid solution system are given. The featured minimum at the given curves $\alpha(n)$ is due to double band structure [35]. The Hall effect temperature dependence for all compositions also reveals a complicated behavior being typical for the carrier redistribution process in the case of the two-band model. Thus, the qualitative conclusion about conservation of the complicated structure of the valence band in the solution system can be made.

The correct calculations of the two-band model parameters require the principal energy gap and its temperature dependence to be known. It is well known the problem of energy gap change for the PbTe-

![Figure 6](https://example.com/figure6.png)

**Fig. 6.** — Fractional change in the Hall coefficient $R/R_{770}$ for SnTe versus the temperature:

1, 2, 3, 4 — the samples with carrier concentration $p = \frac{1}{eR_{770}} = 1.8 \times 10^{20}, 7.5 \times 10^{19}, 10.0 \times 10^{20}, 1.3 \times 10^{21}$ cm$^{-3}$, respectively.

data for SnTe and lead chalcogenides. According with this analogy as well as with the other experimental results we have handled our data on the ground of the two-band model. With the temperature coefficient of SnTe solutions to be extensively researched at now At the present stage the scheme of the band displacement advanced by Dimmock et al. [36] is generally accepted. According to this consideration for a cer-
tain composition of the solution system must occur the inversion of the states $L_{\text{I}}$ and $L_{\text{II}}$ which combine the valence and conduction bands in the compounds involved. The energy gap is equal to zero at the inversion point. The inversion is also accompanied by the reversal of the sign of the band displacement temperature coefficient. So, for SnTe in contrast to the PbTe the energy gap has to diminish when increasing temperature. In the case of the approaching and crossing at the certain temperature bands the strong band non-parabolicity must occur when the energy gap vanishes. This can lead to a significant influence on the transport coefficients, in particular, on the Hall-factor.

If we even adopt the model of the crossing bands one remains unclear how we can take care of the strong non-parabolicity effect in a more or less accurate way because the band parameters, namely, the density-of-states effective masses and the interaction gap are badly determined. For that reason we have undertaken no attempts to calculate any transport coefficients for the mixed crystals. So we emphasize that our above estimations for SnTe are of purely tentative kind.

We also treated the intrinsic conductivity in the PbTe-SnTe solid solutions. The general law is a displacement of the temperature range, in which the intrinsic conductivity is observed, to the higher temperatures as the molar content in SnTe increases. This fact is very reasonably illustrated by figure 8, which depicts the values of the thermoelectric power corresponding to the intrinsic region edge $\alpha_{\text{max}}$ for the different compositions and carrier concentrations at appropriate temperatures. In the frame of scheme of the crossing bands this result along with the decrease of the magnitude of $\alpha_{\text{max}}$ can be interpreted only as the consequence of increasing carriers degeneracy degree. Increase of the degeneracy, from our

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**FIG. 7.** - Thermoelectric power for the Pb$_{1-x}$Sn$_x$Te solid solution system versus the hole concentration at the temperature of 300 °K.

**FIG. 8.** - Displacement of the thermoelectric power maximum value versus the temperature and the value of $\alpha_{\text{max}}$ (in the relation Pb$_{1-x}$Sn$_x$Te) for the samples with the various hole concentration: $1 - x = 0.03$, $2 - x = 0.10$, $3 - x = 0.20$, $4 - x = 0.40$, $5 - x = 0.90$, $6 - x = 0.70$, $7 - x = 0.80$, $8 - x = 0.90$, $9 - x = 1.0$. The general law is a displacement of the temperature range, in which the intrinsic conductivity is observed, to the higher temperatures as the molar content in SnTe increases.
point of view, is possible due to the strong band non-parabolicity at small values of the energy gap.

From measurements of the conductivity in the region of the intrinsic conductivity for the compositions of Pb$_3$Sn$_{1-x}$Te with the value $x \approx 1$ within the range 1-0.7 we have estimated the value of the gap between the conduction band edge and the second valence band edge. It is the gap which is calculated from the data on the intrinsic region conductivity due to the inversion of the valence subbands edges at high temperatures. According to the correct calculation this gap is equal to 0.3-0.35 eV for the composition Pb$_{0.3}$Sn$_{0.7}$Te. This result is in no agreement with conclusion of the work [37].

As a final word, the author thanks Prof. I. S. Styl'bans and Dr. B. A. Efimova for the instructive discussions of the present paper and many useful comments; L. V. Prokof'eva for placing at his disposal some results of her new work; Dr. Yu. I. Ravich, Dr. I. A. Smirnov, Dr. V. I. Kaidanov and I. A. Chernik for stimulating discussions on various other aspects of the work.

References


DISCUSSION

HOWARD W. E. — On one of your slides you showed a mass for the second valence band of SnTe of 1.5-5.0 m$_0$. How was this obtained?

In view of the small mass seen for the second valence band by Shubnikov-de Haas measurements at low temperatures, isn't possible that one requires a third valence band?

ANDREEV, A. A. — I would like to say that the temperature and carrier concentration dependences...
of a number of the kinetic coefficients such as the Hall coefficient, the Nernst-Ettingshausen coefficient, as well as thermoelectric power and thermoconductivity coefficients can be satisfactorily explained if you employ the value of the density of states effective mass of holes in the second band of order 1.5-3.0 $m_0$.

The result of Shubnikov-de Haas effect measurement is well known, however, it is very difficult now to make any convincing conclusions as to the reason of a contradiction between the data from experiments in the weak or zero and the strong magnetic field. It is possible that you are right in assuming the presence of a third valence band. One can believe that the influence of this band is more remarkable at the higher temperatures.

ROGERS, L. M. — What is the highest concentration of holes you have obtained in PbTe and what was the dopant?

$$\left[ p^* = \frac{1}{R_{\gamma\gamma} e} \right]_{\text{max}} = 2 \times 10^{20} \text{ cm}^{-3}$$

Dopant : Na

ANDREEV, A. A. — The maximum value of the concentration \(p = \frac{1}{e R_{\gamma\gamma} e}\) in our samples of p-type PbTe is equal to \((3-3.5) \times 10^{20} \text{ cm}^{-3}\). The doping by Na has been applied to obtain such a high value of the concentration.

ALBANY, H. J. — Did you observe any Hall ratio kink as a function of hole concentration in the materials investigated? May I know which values you obtained for thermal energy gaps in Pb-rich alloys?

ANDREEV, A. A. — It seems that there are no kinks in the concentration dependences of the Hall effect; however, if any kinks take place, they are small and they are within the limits of the accuracy of the measurements. The accuracy is of the order of 5-10 %.

From the data on the intrinsic conductivity we have obtained the value of the gap between the conduction band edge and the second valence band edge. This value turns out to be equal to 0.3-0.35 eV for Pb_{0.8}Sn_{0.2}Te.

A k.p BAND MODEL FOR GeTe AND SnTe (1)

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Résumé. — En utilisant un modèle de bandes k.p, basé sur un fort couplage transverse à travers de faibles bandes interdites au point L, on trouve un accord assez correct avec de nombreux résultats expérimentaux pour GeTe et SnTe.

Abstract. — The use of a k.p band model based on strong transverse coupling across small energy gaps at the L-point gives fairly consistent agreement with a variety of experimental results for GeTe and SnTe.