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Temperature dependences and isotherms of galoanomagnetic properties of Bi doped PbTe crystals and thin films

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The temperature dependences of galvanomagnetic properties (the Hall coefficient, electrical conductivity, charge carrier mobility) of $(PbTe)_{100-x}Bi_x$ (x = 0–1) alloys obtained by doping PbTe with elementary Bi and thin films prepared from these alloys were studied in the temperature range 80–300 K. On the basis of the temperature dependences, the isotherms of the properties were plotted. It was established that a non-monotonic behavior of the dependences of the properties on the Bi concentration, which had been observed earlier at room temperature, is preserved at lower temperatures. This confirms our earlier suggestion about the self-organization processes taking place in the defect subsystem of the crystal at certain Bi concentrations.

Исследованы температурные зависимости (80–300 K) гальваномагнитных свойств (коэффициента Холла, электропроводности, подвижности носителей заряда) сплавов $(PbTe)_{100-x}Bi_x$ (x = 0–1), полученных путем легирования PbTe элементарным Bi, и пленок, приготовленных из этих сплавов. На основе температурных зависимостей построены изотермы свойств. Установлено, что наблюдаемый ранее при комнатной температуре немонотонный характер зависимостей свойств от содержания Bi сохраняется при понижении температуры. Это подтверждает высказанное ранее предположение о процессах самоорганизации, идущих в дефектной подсистеме кристалла при определенных концентрациях Bi.

Bismuth is among the donor impurities of a great importance in PbTe semiconductor. Its introduction makes it possible to control the electron concentration in the lead telluride crystals and thin film structures, to optimize the parameters of thermoelectric energy converters, p-n junctions in laser diodes, etc. [1–3].

PbTe can be doped with bismuth either by introducing elementary bismuth (PbTe–Bi system) or by introducing simultaneously Bi and excess Te. In the latter case, cationic substitution (PbTe–BiTe system) [4, 5] or introduction of Bi_2Te_3 compound (PbTe–Bi_2Te_3 system) [6, 7]. In [8], we have studied the structure and properties of PbTe-based solid solutions in the $(PbTe)_{100-x}Bi_x$ system (i.e., at elementary Bi introduction) at room temperature. The PbTe properties have been found to depend on bismuth content nonmonotonously and this fact has been attributed to Bi dissolution mechanism variations due to the composition changes, to the self-organization processes in the impurity subsystem of the crystal as well as to the percolation effects. In [9], we measured the charge carrier concentrations (n) in thin films prepared from $(PbTe)_{100-x}Bi_x$ crystals of various compositions, and a pronounced correlation was found between the n value and the charge composition, although the n values in the films were lower than in the charge. It was of interest to elucidate whether the dependences of the crystal and thin film properties on Bi concentration re-

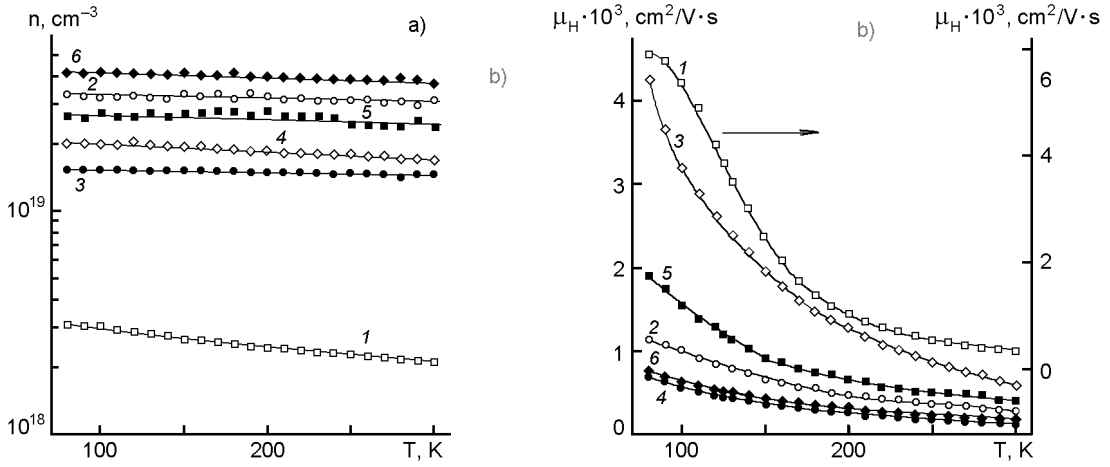

Fig. 1. Temperature dependences of charge carrier concentration n (a) and mobility μ_H (b) for $(PbTe)_{100-x}Bi_x$ crystals at x = 0 (PbTe) (*1*), 0.1 (*2*), 0.25 (*3*), 0.4 (*4*), 0.5 (*5*), 1.0 (*6*).

main the same or not as the temperature varies. The aim of this work is to study the temperature dependences of galvanomagnetic properties for $(PbTe)_{100-x}Bi_x$ system crystals and thin films within the range of 80 to 300 K and to establish the variation character of those properties as functions of Bi content (x) at various temperatures.

The galvanomagnetic properties were measured within the 80 to 300 K temperature range using polycrystalline samples of $(PbTe)_{100-x}Bi_x$ system (x varying from 0 to 1) as well as thin films prepared from those alloys. The bulk crystals for the work were synthesized by fusing together the high-purity (at least 99.999 %) Pb, Bi, and Te in evacuated (about 0.1 Pa) quartz ampoules under vibrational mixing, then annealed at 820 K for 200 h and cooled down with the furnace. The alloy compositions correspond to x values of 0; 0.25; 0.5; 0.75; and 1.0. According to microstructure studies [8], the concentration range (x = 0 to x = 1.0) corresponds to the single-phase solid solution area, the segregation of another phase being observed first at $x \approx 2$. The homogeneity examination by microhardness and micro-thermal e.m.f. methods has shown that the scattering of those parameters over the sample did not exceed the measurement errors. The thin films were obtained by thermal evaporation of various $(PbTe)_{100-x}Bi_x$ charges onto mica substrates. The procedures of thin film preparation, the electrical conductivity σ and Hall coefficient R_H measurements and the charge carrier concentration $n(p)$ and Hall mobility μ_H calculations have been described in [9].

In Fig. 1, the temperature dependences of the charge carrier concentration and mobility for $(PbTe)_{100-x}Bi_x$ crystals of various compositions, including undoped PbTe are shown. As the latter, the stoichiometric PbTe was used possessing the hole conductivity, that is in agreement with literature data and is explained by a slight shift of the fusibility curve maximum in the PbTe homogeneity region of Pb–Te system towards Te excess (to about 50.01 at. % Te) [10].

It is seen from Fig. 1 that the charge carrier (electron) concentration n remains essentially constant for all the doped alloys studied, while μ_H drops monotonously as the temperature rises, that being typical of degenerate semiconductors [11]. A slight reduction of the hole concentration p at temperature decreasing as observed in the initial p-PbTe is a known fact and is attributed usually to the complex structure of p-PbTe valence band consisting of two overlapping subbands with different state densities [12]. In the deeper "heavy" subband, the carriers are less mobile and the contribution of that subband to kinetic effects increases with the temperature growth. The increasing contribution from the heavy holes, R_H increases and thus n drops.

Basing on $\mu_H(T)$ and $\sigma(T)$ dependences, the charge carrier mobility $\mu_H(x)$ and electrical conductivity $\sigma(x)$ isotherms were constructed; these are presented in Fig. 2a. For room temperature, these dependences coincide essentially with those presented in [8]. As the temperature drops down to 80 K, the $\mu_H(x)$ and $\sigma(x)$ remain unchanged quali-

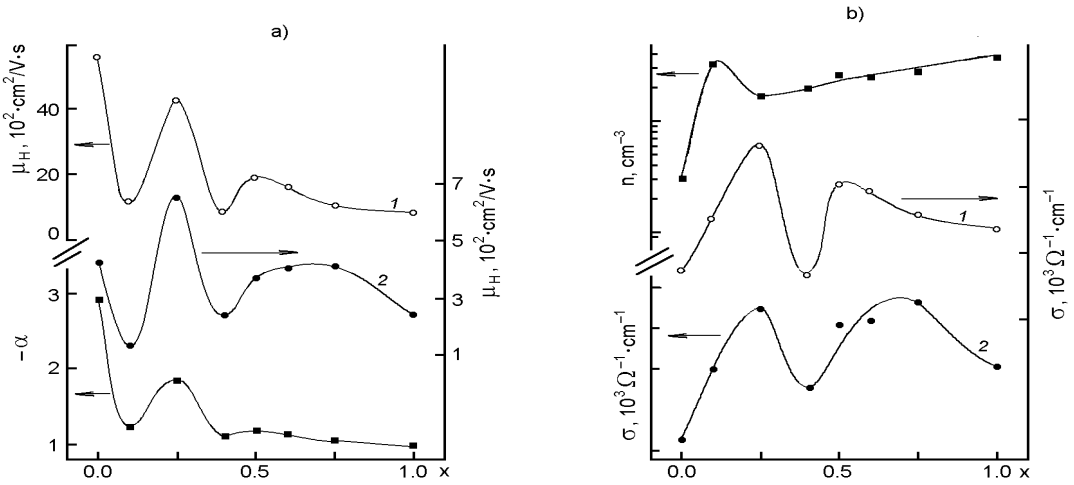

Fig. 2. Dependences of charge carrier mobility μ (a), exponent α in temperature dependence of μ_H (a), charge carrier concentration n (b) and electrical conductivity σ (b) on Bi content for $(PbTe)_{100-x}Bi_x$ crystals at 80 K (*1*) and 300 K (*2*).

tatively although the absolute μ_H and σ values increase.

The non-monotonous character of $\mu_H(x)$ curve evidences complex defect formation processes occurring in the PbTe crystal lattice as Bi is introduced thereto. The $\mu_H(x)$ curve sections where the charge carrier mobility is decreased are obvious to be associated with the increased defectness of the crystal lattice due to increasing Bi content and thus with the increased contribution from the impurity-induced scattering. However, the presence of a pronounced maximum in the $\mu_H(x)$ curve near to $x \sim 0.25$ and a less noticeable one at $x \sim 0.5$ to 0.6 combined with minima at the same compositions observed in the microhardness dependence on the Bi content in PbTe [8] suggests that at certain critical Bi concentrations, self-organization processes take place in the impurity subsystem of the crystal. These processes result in a reduced scattering on the defects. Before, we have found anomalies in composition-property dependences for several solid solutions of IV–VI compounds [see e.g. [13–15]). The anomalies have been attributed to critical phenomena accompanying the transition from the impurity-discontinuum to the "impurity-containing condensate" [16]. It has been noted that the formation of percolation channels at the impurity concentration increasing may stimulate the cooperative self-organization processes in the impurity defect subsystem. The processes can be reduced to the redistribution of impurity atoms over the crystal lattice sites (long-range or short-range ordering), to the qualitative change in the localization of the impurity atoms, etc. Perhaps a similar situation takes place in the $(PbTe)_{100-x}Bi_x$ system, so the anomalous (from the standpoint of usual solid solutions) increase in μ_H at Bi content increase within certain concentration ranges ($x = 0.1$ to 0.25 and $x = 0.4$ to 0.75) is due to a great extent to changes in the charge carrier scattering mechanisms resulting from changes in the crystal defect subsystem.

To date, it is established reliably enough [12] that it is just the scattering on acoustic phonons that is the main mechanism of the charge carrier scattering in lead chalcogenides, including PbTe. At that scattering, the exponent α in the temperature dependence of the charge carrier mobility $\mu_H \sim T^{-\alpha}$ takes the values of $\alpha = 3/2$ and $\alpha = 1$ for non-degenerate and degenerate semiconductors, respectively. The higher exponent values observed in PbTe ($\alpha \sim 5/2$) are attributed today to the temperature dependence of effective mass [11], since it is believed to be established that the main mechanism of the charge carrier scattering in PbTe at moderate and high temperatures is the scattering on acoustic phonons.

From the temperature dependences of mobility, the exponents have been determined in the $\mu \sim T^{-\alpha}$ dependence for various alloys. It is seen (Fig. 2) that as the Bi concentration increases, the exponent tends to drop (that is in agreement with the increasing degeneration degree of charge carriers

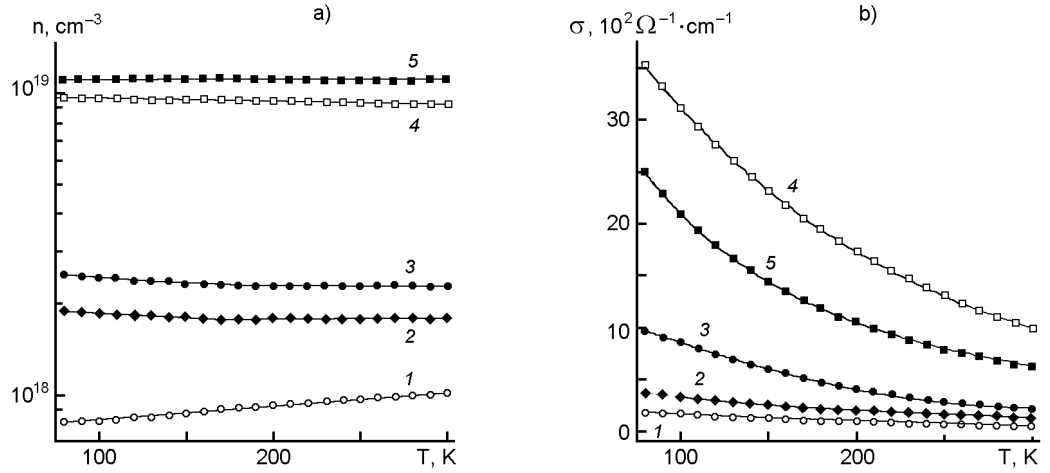

Fig. 3. Temperature dependences of charge carrier concentration n (a) and mobility μ_H (b) for $(PbTe)_{100-x}Bi_x$ films at x = 0 (PbTe) (*1*), 0.25 (*2*), 0.5 (*3*), 0.75 (*4*), 1.0 (*5*).

resulting from increasing n). However, a pronounced maximum is observed in $\alpha(x)$ dependence as well as in $\mu_H(x)$ and $\sigma(x)$ ones that evidences, in its turn, a reduction of the impurity scattering contribution.

Fig. 3 presents the temperature dependences of charge carrier concentrations and electrical conductivity for thin films obtained from $(PbTe)_{100-x}Bi_x$ charge of various compositions. As in the case of bulk crystals, the σ value for all the alloys drops monotonously as temperature rises, while the carrier concentration remains essentially constant as is typical of degenerate semiconductors.

Basing on the temperature dependences of galvanomagnetic properties, $n(x)$, $\sigma(x)$, $\mu_H(x$ and $\alpha(x)$ isotherms have been constructed for thin films of various compositions (Fig. 4). As for the crystals, the dependences are non-monotonous but do not coincide with those for crystals (cf. Fig. 2). A single maximum is observed at $x\approx0.75$ in $\sigma(x)$ and at $x\approx0.6$ in $\mu_H(x)$ and $\alpha(x)$ isotherms. The difference in the isotherm character for the crystals and thin films is associated with the fact that the charge composition is not reproduced in the film, although there is a rather good correlation between the charge composition and properties [9].

It follows from the data presented that the complex character of PbTe galvanomagnetic properties as functions of Bi content observed before in the crystals and films at room temperature [8, 9] is retained within the temperature range of 80 to 300 K. Both for the $(PbTe)_{100-x}Bi_x$ crystals and thin films, a correlation between the $n(x)$, $\sigma(x)$, $\mu_H(x)$ and $\alpha(x)$ dependences is observed within the whole temperature range studied.

The results obtained evidencing the complex variation character of the galvanomagnetic properties resulting from elemental Bi introduction into PbTe are to be taken into account when interpreting and predicting properties of the crystals and thin films of Bi-doped PbTe as well as when predicting the property variation character in PbTe/Bi heterostructures resulting from the Bi–PbTe interaction at the interface.

Thus, temperature dependences of electrical conductivity σ, Hall coefficient R_H, the charge carrier concentration n and mobility μ_H have been studied for $(PbTe)_{100-x}Bi_x$ polycrystals and thin films obtained by thermal evaporation of the $(PbTe)_{100-x}Bi_x$ charge onto mica substrates. Basing on those dependences, isotherms for the properties have been constructed. The non-monotonous character of $n(x)$, $\sigma(x)$, and $\mu_H(x)$ dependences observed before in the crystals and thin films at room temperature has been found to be retained in the 80–300 K range. It has been found that not only $\sigma(x)$ and $\mu_H(x)$ dependences are non-monotonous in the $(PbTe)_{100-x}Bi_x$ crystals and thin films but also that of the exponent α in the temperature dependence of charge carrier mobility $\mu_H \sim T^{-\alpha}$. The decrease of α at increasing x is associated with the increasing degeneration degree of the charge carriers and the non-monotonous character, with changes in the crystal impurity subsystem. The results obtained confirm once again the

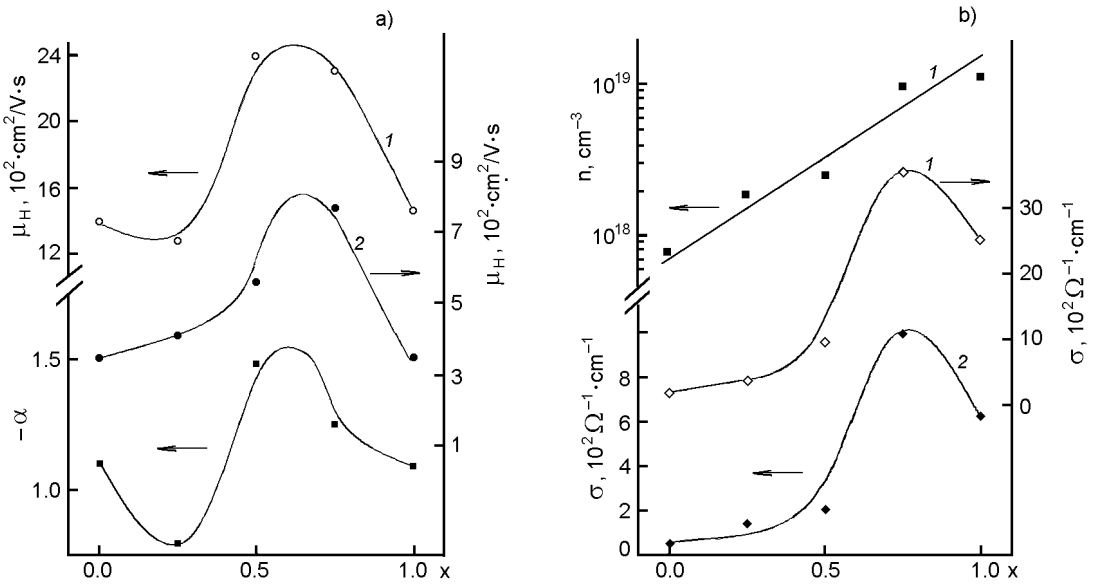

Fig. 4. Dependences of charge carrier mobility μ (a), exponent α in temperature dependence of μ_H (a), charge carrier concentration *n* (b) and electrical conductivity σ (b) on Bi content for $(PbTe)_{100-x}Bi_x$ thin films at 80 K (*1*) and 300 K (*2*).

validity of our assumption concerning the self-organization processes in the PbTe impurity subsystem as certain Bi concentrations are attained. Those processes define the non-monotonous character of the property dependences on Bi content.

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Температурні залежності та ізотерми гальваномагнітних властивостей кристалів та тонких плівок PbTe, легованого Bi

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Досліджено температурні залежності (80–300 К) гальваномагнітних властивостей (коефіцієнта Холла, електропровідності, рухливості носіїв заряду) сплавів $(PbTe)_{100-x}Bi_x$ (x = 0–1), які одержані шляхом легування PbTe елементарним Bi, та плівок, що виготовлені з цих сплавів. На основі температурних залежностей побудовано ізотерми властивостей. Встановлено, що немонотонний характер залежностей властивостей від вмісту Bi, що спостерігався раніше при кімнатній температурі, зберігається при зниженні температури. Це підтверджує припущення, що висловлювалося раніше, про процеси самоорганізації, що йдуть у дефектній підсистемі кристала при певних концентраціях Bi.