DEEP GALLIUM-INDUCED DEFECT STATES IN $Pb_{1-x}Sn_xTe$

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The galvanomagnetic effects in $Pb_{1-x}Sn_xTe$: Ga under variation of alloy composition were investigated. It was found for samples with tin content $x \leq 0.06$ the temperature dependences of resistivity and the Hall coefficient have a low temperature activation range of impurity ionization, while for samples with $0.09 \leq x \leq 0.21$ they have a "metallic" character. The results were discussed assuming an appearance of two different deep impurity levels E_{Ga1} and E_{Ga} stabilizing the Fermi level in the energy spectrum. The activation energy for "insulating" samples as well as the Fermi level position for "metallic" samples were determined and used to build the energy level diagram.

1. Introduction

For a long time numerous studies of gallium impurity behavior in lead telluride based alloys did not yield any full unambiguous interpretation of its doping action due to a number of non-trivial effects observed [1, 2]. In particular it was incomprehensible how gallium-induced deep level revealed in the gap in PbTe: Ga changes its energy position in lead telluride based alloys. There was no reliable explanation of the mechanism of the Fermi level pinning by impurity level. It was also reported an existence of at least two ranges of the Fermi level pinning on the electron concentration versus gallium content dependence and drawn a hypothesis assuming the appearance of two different Ga-induced states in PbTe-based alloys [3-5]. Only recent studies performed on the $Pb_{1-x}Ge_xTe$: Ga alloys cleared up some of the peculiarities of the Fermi level pinning in gallium-doped materials [5, 6]. A model has been proposed according to which doping with gallium leads to the appearance of two different defect levels in the energy spectrum of alloys situated in the gap and on the background of the conduction band depending on the alloy composition and impurity concentration. At the same time we are still lacking of information about the energy position of these impurity levels in other PbTe based alloys.

In this article we report the results of our measurements of the galvanomagnetic effects in the $Pb_{1-x}Sn_xTe$: Ga alloys for various alloy composition. The main aims are to reveal gallium-induced defect states stabilizing the Fermi level in the energy spectrum of alloys and to construct the energy level diagram as a function of alloy composition. The variation of tin concentration over the wide range ($0 \leq x \leq 0.21$) was expected to alter the position of the impurity-induced levels relative to the principal band edges and to shift the Fermi level stabilization range from the energy gap to the conduction band.

2. Experimental Details

Single crystals of *n*-$Pb_{1-x}Sn_xTe$:Ga ($0 \le x \le 0.06$, C_{Ga}=0.3–0.7 mol. %) were synthesized from the vapor phase by sublimation and *n*-$Pb_{1-x}Sn_xTe$:Ga ($0.09 \le x \le 0.21$, C_{Ga}=0.2–2.2 mol. %) were grown by a modified Bridgman method. The tin ratio and impurity concentration in doped samples were determined from the initial amount of substance in the furnace charge, taking into

Table 1. Parameters of the *n*-$Pb_{1-x}Sn_xTe$:Ga samples used in this study at T=4.2 K.

Sample	x	C_{Ga} (mol%)	ρ (Ω·cm)	$\lvert R_H \rvert$ (cm^3/C)	μ_H (cm^2/V·s)	n (cm^{-3})
Sn-0-3	0	0.5	2.4×10^4	$<4.2 \times 10^3$	$<1.8 \times 10^{-1}$	$<1.5 \times 10^{15}$
Sn-0-4	0	0.7	5.7×10^5	$<1.0 \times 10^5$	$<1.8 \times 10^{-1}$	$<6.3 \times 10^{13}$
Sn-6	0.06	0.5	3.3×10^5	$<1.8 \times 10^5$	$<5.5 \times 10^{-1}$	$<3.5 \times 10^{13}$
Sn-9	0.09	0.2	1.3×10^{-4}	9.7×10^{-1}	7.8×10^3	6.5×10^{18}
Sn-10	0.10	0.3	1.4×10^{-4}	9.0×10^{-1}	6.5×10^3	7.0×10^{18}
Sn-11	0.11	0.9	1.4×10^{-4}	9.4×10^{-1}	6.8×10^3	6.9×10^{18}
Sn-14	0.14	0.5	1.6×10^{-4}	8.0×10^{-1}	5.1×10^3	7.9×10^{18}
Sn-16	0.16	0.3	2.7×10^{-4}	5.2×10^{-1}	4.3×10^3	1.2×10^{19}
Sn-18	0.18	0.7	1.1×10^{-4}	4.1×10^{-1}	3.9×10^3	1.6×10^{19}
Sn-21	0.21	2.2	1.5×10^{-4}	2.7×10^{-1}	1.7×10^3	2.3×10^{19}

account the distribution of impurity along the ingot during the growth process according to the exponential law of impurity distribution in A^4B^6 solid solutions established in [7] and controlled by the energy dispersive X-ray fluorescence analysis. For each sample the temperature dependences of the resistivity ρ and Hall coefficient R_H ($B \le 0.1$ T, $4.2 \le T \le 300$ K) were measured by four-probe technique. Table 1 summarizes the main parameters of the samples at T=4.2 K.

3. Galvanomagnetic Effects

The measurements performed for the samples with low tin content ($x \le 0.06$) have shown that the temperature dependences of the resistivity ρ (Fig. 1a) and the Hall coefficient R_H have a low temperature activation range of the impurity ionization, indicating an existence of the deep gallium-induced level E_{Ga1}, which stabilizes the Fermi level in the forbidden band of the alloys. The temperature dependences of ρ (Fig. 1b) and R_H for the samples with tin content $0.09 \le x \le 0.21$ have a "metallic" character. However, the Hall coefficient is changed in anomalous manner: an absolute value of R_H increases by more than two times with increasing temperature. This behavior is thought to be associated with an existence of gallium-induced resonant level E_{Ga}, stabilizing the Fermi level on the background of the conduction band. The similar character of the R_H variation with temperature has been observed earlier for indium-doped PbTe alloys when the indium level was resonant with the conduction band [1, 8]. As the tin concentration in the alloys increases activation energy of deep gallium level ΔE_{Ga1} for the "insulating" samples decreases and free electron concentration for the "metallic" samples monotonously increases.

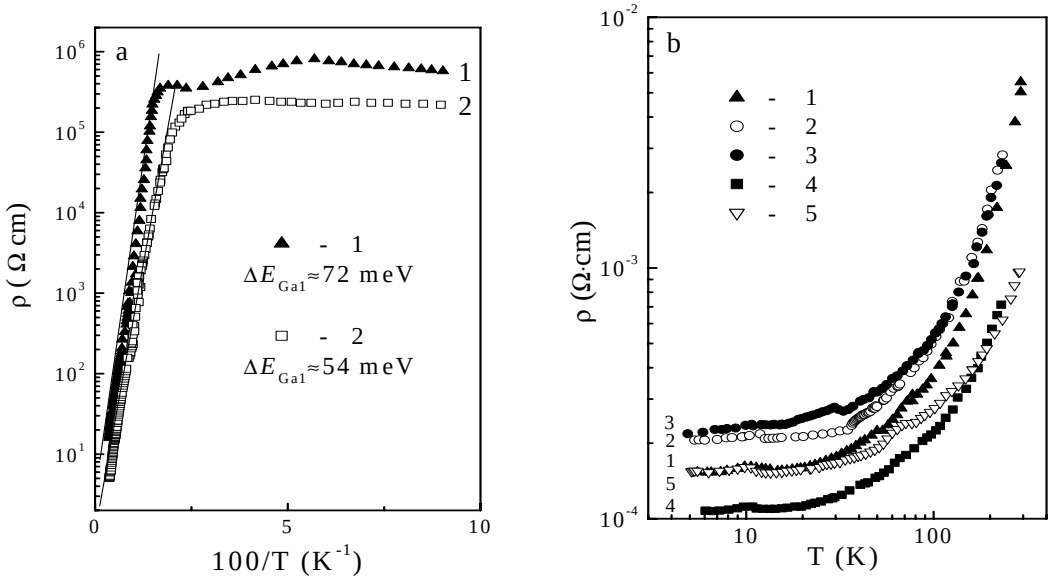

Fig. 1. Temperature dependences of the resistivity in the $Pb_{1-x}Sn_xTe$: Ga alloys upon varying tin content x: (a) 1 - 0; 2 - 0.06; (b) 1 - 0.10; 2 - 0.11; 3 - 0.14; 4 - 0.18; 5 - 0.21.

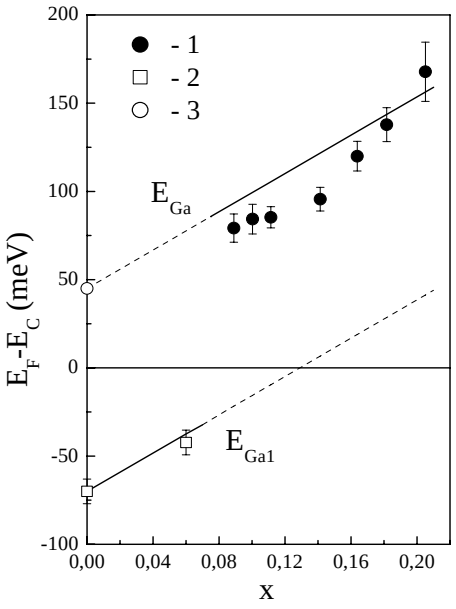

Fig. 2. Dependence of the Fermi level position in $Pb_{1-x}Sn_xTe$:Ga on the alloy composition.
1, 2 – results of the present work,
3 – an extrapolation of the data obtained for $Pb_{1-x}Ge_xTe$:Ga [5].

4. Determination of Activation Energy and Fermi Level Position

From the slope of the activation range on the ρ(1/T) dependences in accordance with relation $\rho \propto \exp(\Delta E_{Ga1}/kT)$ we have determined an activation energy of gallium-induced level ΔE_{Ga1} for the alloys being in insulating state ($x \leq 0.06$). It was found that with increasing tin content in the alloys the activation energy of impurity level decreases. Its rate estimated from the slope of the $\Delta E_{Ga1}(x)$ dependence practically coincides with an average rate of the energy gap decreasing in the alloys under study [9] and is $d\Delta E_{Ga1}/dx \approx -5$ meV/mol.%, that means that the gallium level E_{Ga1} moves almost parallel to the valence band top.

Using the values of the Hall coefficient at helium temperature for the samples with higher tin content (in metallic phase) we have calculated the dependences of the free electron concentration and the Fermi level position E_F upon alloy composition in the frame of two-band dispersion law for A^4B^6 semiconductors [10, 11]:

$$\left(\frac{E_g}{2}-E\right)\cdot\left(-\frac{E_g}{2}-E\right)=E_{\perp}\cdot\frac{p_{\perp}^2}{2m_0}+E_{\parallel}\cdot\frac{p_{\parallel}^2}{2m_0} \quad (1)$$

where E_g is the energy gap, $p_{\perp}$ and $p_{||}$ are transversal and longitudinal components of the quasi-impulse relative to the <111> axis, respectively, $E_{\perp}$ and $E_{||}$ are the parameters characterizing an interaction between the valence and conduction bands ($E_{\perp} \approx 7.65$ eV and $E_{||} \approx 0.73$ eV for $Pb_{1-x}Sn_xTe$(x≈0.2) [12]).

The concentration of the free electrons n was calculated using the following expressions:

$$n = 2\cdot 4\cdot V_{el}/(2\pi\hbar)^3 \quad (2)$$

$$V_{el}=\frac{4}{3}\pi p_{\perp}^2(E_F)p_{\parallel}(E_F) \quad (3)$$

where V_{el} is a volume of the Fermi surface ellipsoid in the p-space.

Then the Fermi energy was determined from the dispersion law (1):

$$E_F=\sqrt{\left(\frac{3}{4}\cdot\frac{n\pi^2\hbar^3E_{\perp}\sqrt{E_{\parallel}}}{(2m_0)^{3/2}}\right)^{2/3}+\frac{E_g^2}{4}} \quad (4)$$

The Fermi level movement relative to the conduction band edge at the L-point of the Brillouin zone under variation of tin content in the alloys, calculated according to (4), is presented in Fig. 2. The Fermi energy value increases almost linearly with increasing tin concentration in the alloys. Solid lines in this figure represent the theoretical curves corresponding to the parallel movement of impurity levels E_{Ga} and E_{Ga1} relative to the valence band top L_6^+. One can see that the experimental dependences of the Fermi level position on tin content are in a good agreement with theoretical lines showing the impurity level movement on the energy scale.

5. Conclusion

The results obtained allow us to conclude that like in $Pb_{1-x}Ge_xTe$: Ga earlier investigated [5,6], doping of $Pb_{1-x}Sn_xTe$ with gallium leads to an appearance of two different impurity levels in the energy spectrum of the alloys: level E_{Ga1}, responsible for the Fermi level pinning in the gap for alloys in the insulating state, and resonant level E_{Ga}, stabilizing the Fermi level in the conduction band for alloys in the metallic state. The energy level diagram for $Pb_{1-x}Sn_xTe$: Ga alloys as a function of matrix composition was proposed and revealed that with increasing tin content in the alloy both levels move relative to the bottom of conduction band L_6^- with the rate approximately 5 meV/mol.%, while the energy position of the gallium levels relative to the valence band top L_6^+ remains practically unchanged.

This research was carried out under financial support from the Russian Federation President Program (Grant No SS 1786.2003.2) and Universities of Russia Program (No 01.03.068).

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