ELECTRONIC STRUCTURE OF DILUTED MAGNETIC SEMICONDUCTORS $Pb_{1-x}Ge_xTe$:Cr

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Abstract

The galvanomagnetic effects (B≤0.1 T, 4.2≤T≤300 K) in the n-$Pb_{1-x}Ge_xTe$:Cr alloys under variation of alloy composition (0.02≤x≤0.10) and under hydrostatic compression up to 17 kbar have been investigated. The metal-insulator transition under the increase of germanium content in the alloys and insulator-metal transition, induced by hydrostatic compression in $Pb_{1-x}Ge_xTe$:Cr (x=0.10) alloy, were revealed. Using the experimental data in the frame of two-band Kane dispersion relation the composition and pressure dependences of the free electron concentration and the Fermi level position were calculated. The composition and pressure coefficients of the chromium deep level movement were obtained and the models of the electronic structure reconstruction were built.

1. Introduction

Doping with magnetic mixed-valence impurities (Eu, Gd, Yb, Ti, Cr …) induces an appearance of deep impurity states in the electronic structure of PbTe-based narrow-gap semiconductors and turns them into the diluted magnetic semiconductors [1, 2]. The specific feature of these materials is that the magnetic activity of impurity ions is directly connected with their charge activity [3-5]. For example, substituting the metal in the host semiconductor lattice, the Yb impurity atoms can contribute as either electrically neutral and non-magnetic Yb^{2+} ($4f^{14}$) ions or electrically and magnetically active Yb^{3+} ($4f^{13}$) ions. Under these conditions the magnetic properties of the PbTe-based alloys are determined not only by the concentration of impurity introduced but also by the occupancy of impurity deep levels and hence by the mutual arrangement of the deep impurity level, the allowed band edges and the Fermi level [4, 5].

In PbTe chromium impurity deep level E_{Cr} situates in the conduction band, stabilizing Fermi level approximately by 100 meV higher than its bottom [6-8]. We suppose that similar to the situation with ytterbium impurity level in PbTe-based alloys the energy position of chromium deep level relative to the allowed band edges should be very sensitive to the alloy composition and hydrostatic compression. However, the electronic structure of PbTe-based alloys doped with chromium is not yet investigated.

In the present work the galvanomagnetic properties of n-$Pb_{1-x}Ge_xTe$:Cr alloys were studied under variation of matrix composition (0.02≤x≤0.10) and under hydrostatic compression (P≤17 kbar). The main aims were to reveal deep impurity-induced states in the energy spectrum of the alloys and to obtain the diagrams of electronic structure reconstruction under variation of the germanium content in the alloys and under pressure.

2. Experimental details

Single crystals of *n*-$Pb_{1-x}Ge_xTe$:Cr ($0.02 \le x \le 0.10$, C_{Cr}=1.0 – 3.0 mol.%) were grown by the modified Bridgman method. The germanium ratio as well as impurity concentration in the doped samples were determined from the initial amount of substance in the furnace charge, taking into 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 [9] and controlled by the energy dispersive X-ray fluorescence analysis.

At the atmospheric pressure the temperature dependences of the resistivity ρ and the 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 helium temperature and atmospheric pressure. Then the alloys with the maximal germanium content (x=0.10) were chosen for the investigation under hydrostatic compression. Pressures up to 17 kbar were obtained in the beryllium bronze chamber with kerosene-oil-pentane pressure transmitting media and were determined at helium temperatures by measuring the superconducting transition temperature in pure tin as a function of pressure in the chamber.

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

Sample	*x*	C_{Cr}, mol.%	ρ, 10^{-4} Ω·cm	$-R_H$, cm^3/C	μ_H, 10^3 $cm^2/V{\cdot}s$	*n*, 10^{18} cm^{-3}
1	0.02	1.0	0.42	0.66	16	9.5
2	0.03	1.0	0.44	0.65	15	9.5
3	0.04	1.5	0.58	0.77	13	8.1
4	0.05	2.0	0.82	0.92	11	6.8
5	0.06	2.0	1.6	1.25	7.9	5.0
6	0.07	2.5	4.1	2.00	4.9	3.1
7	0.10	3.0	120	6.08	0.51	-

3. Galvanomagnetic effects in $Pb_{1-x}Ge_xTe$:Cr alloys

It was shown that in $Pb_{1-x}Ge_xTe$:Cr samples with low germanium content ($x \le 0.07$) the resistivity ρ and the Hall coefficient R_H reveal metal-like behavior (Fig. 1). However, the absolute value of R_H is changed in specific manner: an absolute value of the Hall coefficient increases by more than two times with increasing temperature that corresponded to the pinning of the Fermi level by the resonant impurity-induced level, situated in the conduction band. The concentration of free electrons, calculated from the values of R_H at helium temperature, monotonously decreases with the increase of germanium content in the alloys and tends to zero at x=0.09 – 0.10. In the sample with x=0.10 temperature dependences of resistivity ρ(1/*T*) and Hall coefficient $R_H(1/T)$ have an activation character in the temperature region 50-150 K (curve 6 in Fig. 1), associated obviously with the appearance of deep chromium-induced localized states under the conduction band bottom. The activation energy of chromium level, determined from the slope of the ρ(1/*T*) and $R_H(1/T)$ dependences, is ΔE_{Cr}= E_c-E_{Cr}=5 – 9 meV.

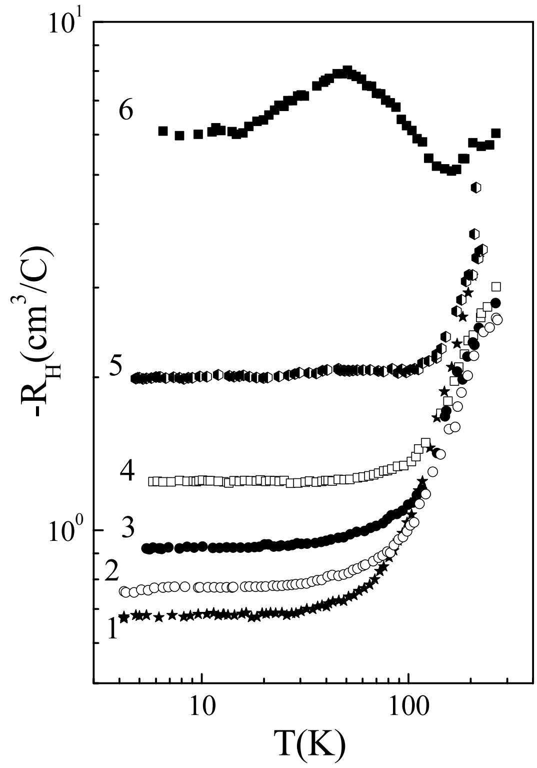


Fig. 1. Temperature dependences of the Hall coefficient in $Pb_{1-x}Ge_xTe$:Cr (x: 1 – 0.02, 2 – 0.04, 3 – 0.05, 4 – 0.06, 5 – 0.07, 6 – 0.10).

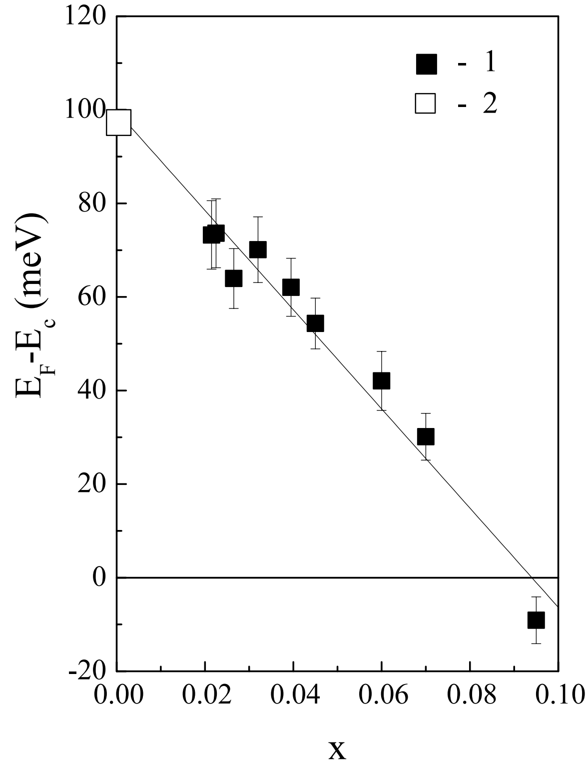
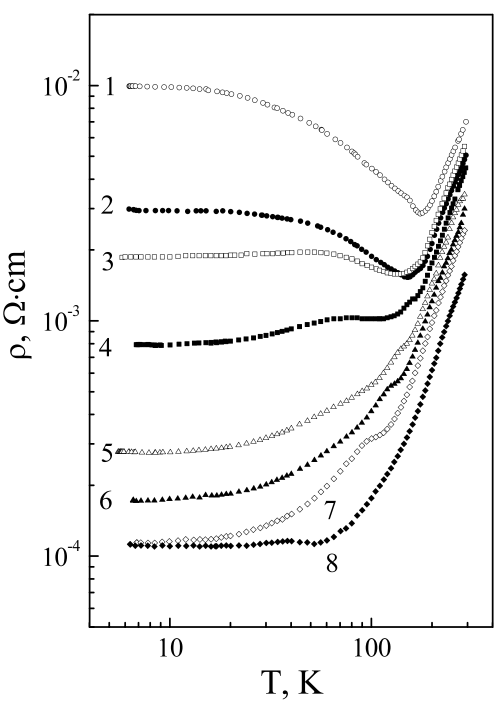


Fig. 2. Composition dependence of the Fermi energy in $Pb_{1-x}Ge_xTe$:Cr (1 – our experimental data, 2 – previously known data [6-8]).

Using the values of the free electron concentration for the samples in the metallic phase (x=0.02 – 0.07) we have calculated the Fermi energy versus alloy composition dependence in the frame of two-band Kane dispersion relation for A^4B^6 semiconductors [10, 11] (Fig. 2). Assuming the stabilization of the Fermi level in the investigated alloys by the chromium deep level, one can conclude that under the increase of germanium content chromium level moves almost linearly with the rate $d(E_{Cr}-E_c)/dx \approx -10$ meV/mol.%, while its position relative to the middle of the gap remains practically unchanged. So an increase of the germanium content in the alloys results in the shift of the level from the conduction band to the gap, flowing of electrons from the band to the localized states and transition from the metallic to the insulating phase at x≈0.10.

4. The insulator-metal transition, induced by pressure in $Pb_{1-x}Ge_xTe$:Cr (x=0.1)

Under hydrostatic compression the resistivity and absolute value of the Hall coefficient in $Pb_{1-x}Ge_xTe$:Cr (x=0.1) at helium temperatures decrease by two and almost one order of magnitude accordingly and the activation character of their temperature dependences changes for the "metallic" one at the critical pressure $P^* \approx 2$ kbar (Fig. 3). Obviously such a character of the galvanomagnetic properties changing is indicative of a transition of the alloy from the insulating to the metallic state under pressure. In the metallic phase ($P>2$ kbar) temperature dependences of the Hall coefficient become typical for the lead telluride-based alloys with the resonant impurity level, stabilizing the Fermi level in the conduction band. The following increase of pressure leads to the monotonous increase in the free electron concentration up to $n \approx 6\times10^{18}$ cm^{-3}.



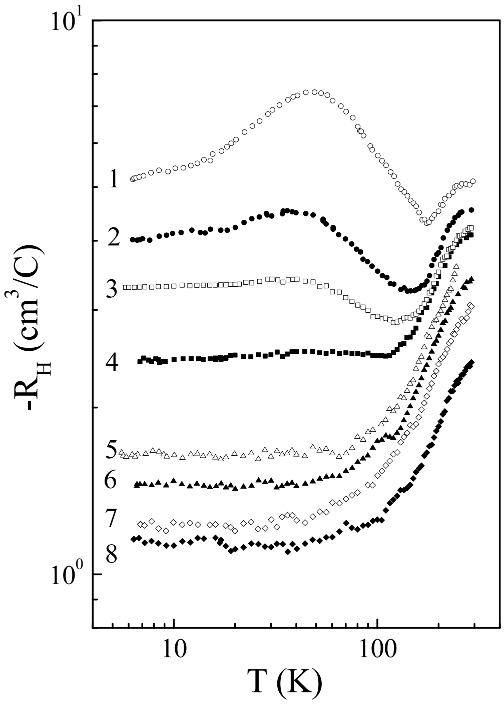


Fig. 3. Temperature dependences of resistivity and Hall coefficient in $Pb_{1-x}Ge_xTe$:Cr (x=0.10) alloy under pressure. P (kbar): 1 – 0, 2 – 0.5, 3 – 1.2, 4 – 2.2, 5 – 4.4, 6 – 6.3, 7 – 9.1, 8 – 16.4.

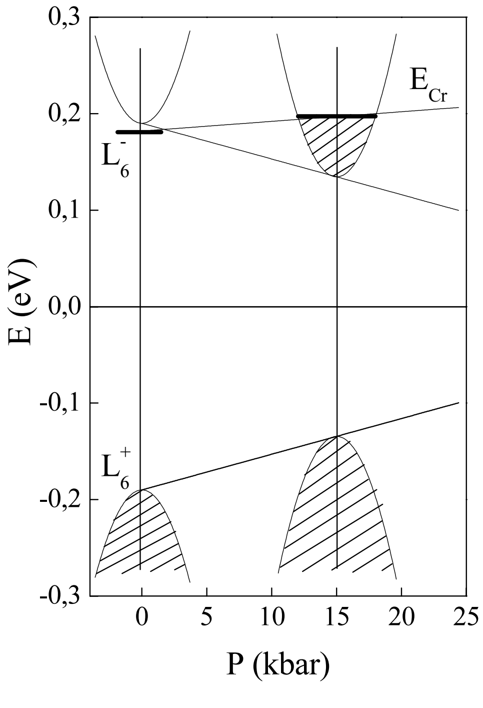


Fig. 4. Reconstruction of electronic structure in $Pb_{1-x}Ge_xTe$:Cr (x=0.10) alloy under pressure.

From the slope of the activation range on the $\rho(1/T)$ dependences in accordance with the relation $\rho\propto\exp(\Delta E_{Cr}/kT)$ we have determined an activation energy of the chromium-induced level ΔE_{Cr} in the insulating phase ($P\leq2$ kbar). It was found that with the increase of pressure the activation energy of impurity level decreases with the rate $d(\Delta E_{Cr})/dP\approx-3.5$ meV/kbar, that practically coincides with the half of the energy gap decreasing rate in the PbTe-based alloys under pressure [10]. This circumstance means that the chromium level E_{Cr} moves almost parallel to the middle of the gap, slightly shifting upward under pressure (Fig. 4). Thus under pressure the chromium deep level enters the conduction band, inducing the insulator-metal transition due to the flowing of electrons from the impurity level to the conduction band.

Using the experimental pressure dependence of the Hall coefficient at T=4.2 K in the frame of two-band Kane dispersion relation we have calculated the pressure dependences of the Fermi level and the electron concentration in the alloy. It was shown that theoretical dependences obtained in this way are in a satisfactory agreement with the experimental data over the entire investigated pressure range.

5. Conclusion

In the present work chromium-induced impurity states situated in the conduction band or in the gap in $Pb_{1-x}Ge_xTe$:Cr ($0.02 \leq x \leq 0.10$) alloys were revealed. The galvanomagnetic properties of investigated alloys were explained taking into account stabilization of the Fermi energy by the chromium level, the shift of the level relative to the bottom of conduction band and redistribution of electrons between the conduction band and the chromium level under variation of matrix composition and pressure. In the frame of the two-band Kane dispersion relation the composition and pressure dependences of electron concentration and Fermi energy in the alloys were obtained. It was shown that energy position of the chromium impurity level relative to the middle of the gap is practically independent of germanium content in the alloy and of pressure.

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