Magnetic and electric properties of impurity states in $Pb_{1-x}Ge_xTe$ doped with ytterbium.

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ABSTRACT

We study temperature dependence of the Hall constant, resistivity and magnetic susceptibility of $Pb_{1-x-y}Ge_xYb_yTe$. We have found that Yb forms impurity states in the vicinity of the valence band edge, the position of the states depends strongly upon Ge and Yb content. The alloys reveal paramagnetic susceptibility at low temperatures due to the presence of magnetic Yb^{3+} ions. The Yb^{3+} concentration found from the Curie constant is by about an order less than total ytterbium content, that indicates co-existence of magnetic Yb^{3+} and non-magnetic Yb^{2+} ions in the alloys. Using the magnetization data, the model of charge carriers energy spectrum has been proposed and dependence of Yb impurity band position upon the Yb content has been determined.

INTRODUCTION

IV-VI alloys containing magnetic ions (Mn^{2+}, Eu^{2+}, Cr^{3+}, Gd^{3+}, Yb^{3+}, Ce^{3+}) form an important group of diluted magnetic semiconductors, attracting much attention due to the effects arising from influence of electronic properties on their magnetic behavior [1-3]. These are, for example, carrier concentration induced magnetic phase transitions in alloys containing Mn, or resonant enhancement of *f-f* exchange in Gd doped alloys with high carrier concentration. The crucial role in these effects is played by the mutual arrangement of the allowed band edges, the Fermi energy and the deep impurity level positions.

Lead telluride based alloys doped with ytterbium are novel members of this family. It has been known, that ytterbium induces formation of localized deep states in a vicinity of the valence band top, either in the energy gap or within the valence band, depending upon the alloy composition, temperature, pressure [4, 5]. The localized states form a significantly widened impurity band, which pins the Fermi level due to a large amount (about 10^{20} cm^{-3}) of empty and filled with electrons impurity states. The density of states in the band can be approximated by the Gauss function.

Magnetization measurements performed for p-$Pb_{1-x-y}Ge_xYb_yTe$ revealed paramagnetic behavior of the alloys due to presence of the magnetically active $Yb^{3+}(4f^{13})$ ions [4, 6]. Estimated concentration of Yb^{3+} appeared to be significantly smaller, than a total Yb content in the alloys. The selfsame samples, annealed to n-type conductivity were diamagnetic, that indicates a transfer of all the Yb ions to the non-magnetic $Yb^{2+}(4f^{14})$ charge state. Thus, one can suppose, that a position of the Fermi level with respect to the impurity band determines charge state of Yb impurity: when the Fermi level is within the impurity band, Yb^{2+} and Yb^{3+} ions coexist, when it is above the impurity band, and all the impurity states are filled with electrons, the ytterbium exists in Yb^{2+} charge state only.

One can conclude, that complex investigation of galvanomagnetic and magnetic properties of $Pb_{1-x-y}Ge_xYb_yTe$ is a powerful tool for determining parameters of the impurity states (i.e.,

energy position, width, and capacity of the impurity band). In order to determine main parameters of Yb-induced impurity band as well as fraction of magnetic ions and electron population of the impurity band in lead telluride based alloys doped with Yb, we investigate the magnetic susceptibility and galvanomagnetic properties of $Pb_{1-x-y}Ge_xYb_yTe$ ($0 \le x \le 0.02$, $0.005 \le y \le 0.065$) alloys. We suppose that variation of Ge content would allow us to change energy position of the impurity band, while Yb content would influence both the energy and the total capacity of the band.

2. EXPERIMENTAL DETAILS

$Pb_{1-y}Yb_yTe$ single crystal boule with nominal y-value of 0.015 and $Pb_{1-x-y}Ge_xYb_yTe$ (x=0.1, y=0.005) boule were grown by a modified Bridgman method [7]. Ytterbium and germanium concentrations along the boules were checked by the energy dispersive X-ray fluorescence analysis, the obtained results are summarized in Table 1. Samples were cut in shape of bars with typical dimensions of 3×5×8 mm. In each sample the temperature and magnetic field dependences of magnetization were studied using vibrating sample magnetometer equipped by gas-flow cryostat over the temperature range $5 \le T \le 300$ K in magnetic field up to 0.5 T. From these samples, the smaller ones (1×1×5 mm) were cut, for which the temperature dependence of resistivity ρ and the Hall constant R_H ($4.2 \le T \le 300$ K, $B \le 0.1$ T) were measured. Temperature was controlled by Cu-CuFe thermocouple and magnetic field was determined by the Hall probes.

RESULTS AND DISCUSSION

Magnetic properties of $Pb_{1-x-y}Ge_xYb_yTe$

From the temperature dependence of the magnetic susceptibility we have found that at the room temperature all the alloys are diamagnetic (Fig.1). The obtained value of magnetic susceptibility for PbTe is in a good agreement with previously known data [8]. Increase of either Ge or Yb content in alloys leads to a reduction of high temperature diamagnetic response χ_0. As the temperature decreases, a diminishing of the diamagnetic share and a rapid Curie-like

Table I. Parameters of $Pb_{1-x-y}Ge_xYb_yTe$ alloys.

Sample	x	y	N_{Yb3+} (cm^{-3})	N_{Yb} (cm^{-3})	N_{Yb3+}/N_{Yb}	E_F-E_v, $^*\Delta E_{Yb}$ (meV)
1	0	0.005	1.1×10^{19}	8.0×10^{19}	0.14	-5.5
2	0	0.008	1.5×10^{19}	1.2×10^{20}	0.12	-2.3
3	0	0.015	2.4×10^{19}	2.2×10^{20}	0.11	-1.4
4	0	0.030	6.6×10^{19}	4.6×10^{20}	0.14	-0.6
5	0	0.065	9.6×10^{19}	9.6×10^{20}	0.10	18.9*
6	0.02	0.007	9.7×10^{18}	1.0×10^{20}	0.09	12.7*
7	0.02	0.010	2.4×10^{19}	1.5×10^{20}	0.16	-
8	0.02	0.014	3.6×10^{19}	2.1×10^{20}	0.18	16.7*
9	0.02	0.019	7.6×10^{19}	2.8×10^{20}	0.27	-

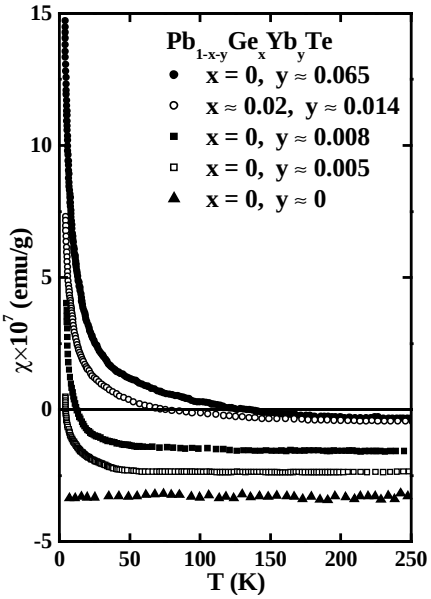

Fig.1. Temperature dependence of magnetic susceptibility for the alloys with various Ge and Yb contents.

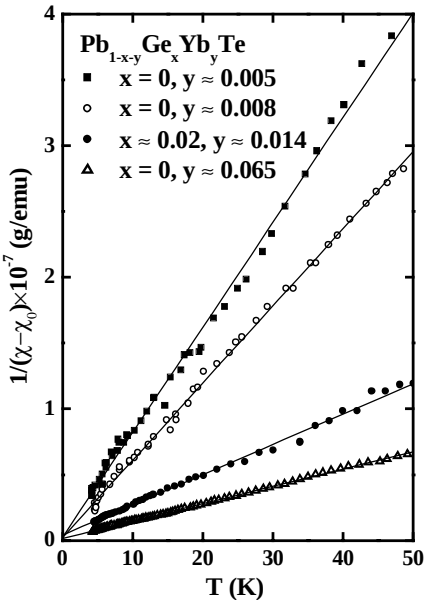

Fig.2. Temperature dependence of inverse magnetic susceptibility, corrected due to diamagnetic share.

growth of the paramagnetic susceptibility occurs. The magnetic field dependence of magnetization, measured at liquid helium temperature, is linear, in accordance with known for the paramagnets linear magnetization at low fields.

In order to determine the Curie constants for the alloys of various Yb and Ge content we present the temperature dependence of inverse magnetic susceptibility, corrected due to the diamagnetic share (Fig.2), in accordance with the Curie-Weiss law:

$$\chi = \chi_0 + \frac{C}{T - \Theta} \qquad (1)$$

where C and Θ are the Curie constant and temperature.

As it was expected, the obtained dependence is satisfactory described by straight line, which intersect the abscissa at slightly negative temperature. It indicates rather weak antiferromagnetic exchange between the magnetic centers. We refrain from a further discussion of this interaction as the value of Θ is of about the accuracy of our measurements.

The values of C were used to estimated the concentration of Yb^{3+} (N_{Yb3+}) single ions:

$$N_{Yb^{3+}} = \frac{3k_B C}{g^2 \mu_B^2 S(S+1)} \qquad (2)$$

where k_B is the Boltzmann constant, μ_B is the Bohr magneton. The values of g-factor g=2.52 and effective spin S=1/2 for Yb^{3+} in lead telluride we used, were experimentally determined from electron paramagnetic resonance in [8].

The results are summarized in Table I, where the last but one column represents fraction of Yb^{3+} ions, i.e., the ratio of Yb^{3+} concentration obtained from the Curie constant to the total Yb concentration found from the y-value. One can see that a fraction of Yb^{3+} ions in all the alloys is rather low. In $Pb_{1-y}Yb_yTe$ concentration of magnetic ions accounts for 10 – 15% of ytterbium content, independently on its overall concentration. Different situation is observed in Ge doped alloys, where increase of Yb content leads to a pronounced growth of magnetic Yb^{3+} fraction.

Galvanomagnetic properties and energy spectrum of $Pb_{1-x-y}Ge_xYb_yTe$

The investigation of the galvanomagnetic effects in $Pb_{1-x-y}Ge_xYb_yTe$ alloys shows strong dependence of its properties upon the alloy composition. Temperature dependence of the Hall constant and resistivity for $Pb_{1-y}Yb_yTe$ ($y \leq 0.03$) reveals metal-like behavior, the values of R_H at 4.2 K monotonously increase with enhancement of Yb content (Fig.3). The $\rho(100/T)$ and $R_H(100/T)$ curves for $Pb_{1-y}Yb_yTe$($y \approx 0.065$) are completely different from those mentioned above, as the distinctive low-temperature activation region is observed, indicating appearance of localized states in the energy gap. All the alloys containing Ge reveal activation behavior of $\rho(100/T)$ and $R_H(100/T)$ curves (Fig. 4).

The obtained results were used to determine the Fermi energy E_F in metal-like alloys and the activation energy of the Yb-induced states ΔE_{Yb} for the alloys with activation behavior of resistivity. E_F was determined from the values of free hole concentration, obtained from R_H at 4.2 K, while the activation energy was found from the slope of the activation region on $\rho(100/T)$ curves. The obtained results are summarized in the last column of Table 1. In $Pb_{1-y}Yb_yTe$ ($y \approx 0.005$) the Fermi level appears about 5.5 meV below the valence band edge. As Yb content rises, the Fermi level gradually approaches the valence band top and almost attains it at $y \approx 0.03$. Then it shifts into the energy gap and appears 19 meV higher the valence band top at $y \approx 0.065$. In $Pb_{1-x-y}Ge_xYb_yTe$($x \approx 0.02$) alloys the impurity level is about 15 meV above the valence band edge.

We explain the results obtained by the formation of Yb-induced impurity level, which is situated in the valence band in $Pb_{1-y}Yb_yTe$ with low ytterbium content. Increase of Ge content in $Pb_{1-x-y}Ge_xYb_yTe$ enhances energy gap in the alloys. Thus, with increase of its concentration, the impurity states shift from the valence to the forbidden gap. This result is in a good agreement with earlier data on Yb-induced level in $Pb_{1-x}Ge_xTe$. Doping with Yb also increases energy gap of $Pb_{1-y}Yb_yTe$, the impurity deep level approaches the top of the valence band, intersects it and enters into forbidden gap upon rising Yb content.

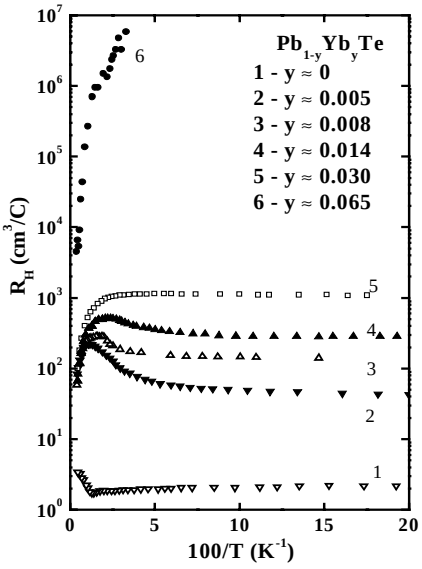

Fig.3. Temperature dependence of the Hall constant in $Pb_{1-y}Yb_yTe$ with various Yb content.

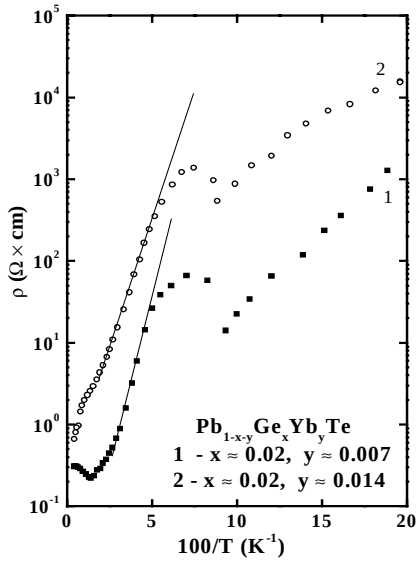

Fig.4. Temperature dependence of resistivity in $Pb_{1-x-y}Ge_xYb_yTe$ with various Yb content.

In order to determine the dependence of the Yb impurity band energy position upon the ytterbium content, we used the model of $Pb_{1-x}Ge_xTe<Yb>$ energy spectrum, supposing that impurity band is significantly widened and partially filled with electrons [5]. For the alloys with impurity level situated in the forbidden band, we consider the energy of the impurity band with respect to the valence band edge equal to the activation energy of Yb impurity level ΔE_{Yb}.

In the metal-like alloys the Fermi level is pinned within the impurity band, which partially overlaps with the valence band. So the position of the impurity band middle E_{Yb} was calculated from the equation:

$$p_{Yb} = \int_{E_F}^{\infty} g_{Yb}(E)dE \qquad (3)$$

Here p_{Yb} is the concentration of empty states in the impurity band and g_{Yb} is the density of states function.

Following the earlier data on Yb-induced level in $Pb_{1-x}Ge_xTe<Yb>$, we suppose, that density of states in impurity band can be approximated by the Gaussian distribution with $\sigma \approx 7$ meV [5]:

$$g_{Yb}(E) = \frac{N_{Yb}}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E - E_{Yb})^2}{2\sigma^2}\right] \qquad (4)$$

where N_{Yb} is the capacity and σ - the width of the impurity band.

We set N_{Yb} equal to the total ytterbium concentration in alloy, assuming that every impurity atom takes part in the formation of impurity states and accounts for one electronic state in the impurity band. In order to determine electron population of the band we suppose, that Yb^{2+} ions give filled states, Yb^{3+} ions – empty ones. Thus, number of empty states in the impurity band p_{Yb} is equal to Yb^{3+} concentration N_{Yb3+}, determined from the magnetic measurements:

$$p_{Yb} = N_{Yb^{3+}} \qquad (5)$$

The obtained results are presented in Fig.5. One can see, that the dependence of the impurity band position upon the Yb content is non-linear. At low Yb content there is a pronounced shift of the impurity band toward the valence band edge. Then in a wide range of higher Yb concentrations the shift is insignificant and the impurity band still stays within the valence band. And finally in alloy with the highest Yb content the impurity band surprisingly jumps into the energy gap.

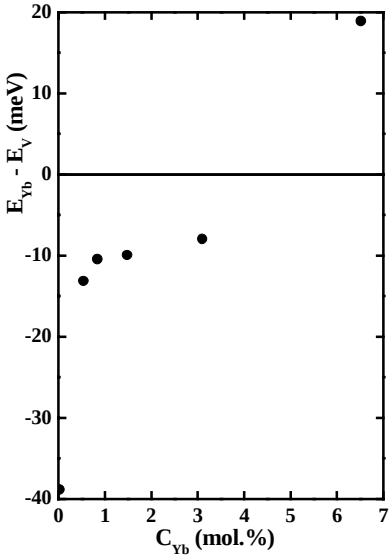

Fig.5. Position of the impurity band middle upon Yb content in $Pb_{1-y}Yb_yTe$.

CONCLUSIONS

The magnetic susceptibility of $Pb_{1-x-y}Ge_xYb_yTe$ contains two shares: the diamagnetic, prevailing at high temperature, and the Curie-Weiss paramagnetic, growing as the temperature decreases. In terms of the Curie-Weiss law concentration of magnetically active Yb^{3+} ions and the Curie temperature in the investigated alloys have been determined. It is shown that concentration of magnetic ions is by about an order less, than total ytterbium concentration in the alloys.

Ytterbium forms impurity band in the energy spectrum of $Pb_{1-x-y}Ge_xYb_yTe$, the position of which depends upon Ge and Yb content. Growth of Ge and Yb concentration results in shift of the impurity band from the valence to the forbidden band. The impurity band is significantly widened and more than half-filled with electrons, so that the Fermi level is situated above the band middle. The model is introduced for determining energy position of Yb impurity band in lead telluride based alloys. According to this model, in $Pb_{1-y}Yb_yTe(y\leq 0.03)$ the impurity band is resonant with the valence band states. With growth of Yb content it gradually approaches the valence band edge and stays there in a wide range of Yb content. At the highest value of Yb content, the impurity level jumps into forbidden gap.

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