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## Features of Energy Spectrum of $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ Doped with V

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Recently new effects that are not characteristic of undoped lead telluride, such as the Fermi level pinning, giant negative magnetoresistance, were observed in  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  alloys doped with transition and rare earth elements — Cr, Mo, Yb. We have studied transport and magnetic properties of  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  doped with another transition element — vanadium. A series of  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}(\text{V})$  samples of different composition and degree of doping was investigated. It was observed that the resistivity demonstrates activation behavior at low temperatures for the samples with considerable amount of vanadium as well as for the samples without vanadium. The activation energy is proportional to the Mn content. In some of the samples, photoconductivity was observed at low temperatures. The results are discussed in terms of a model assuming formation of the impurity level by the vanadium impurity and the effect of the Fermi level pinning by this level.

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### 1. Introduction

Lead chalcogenides are well-known materials for the infrared optoelectronics. Lead telluride is a semiconductor with the direct gap of 190 meV at the zero temperature. The gap increases with the rate of 0.4 meV/K with the temperature rise. Lead telluride-based solid solutions grow with high deviation from stoichiometry.

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All native defects are electrically active, so high concentration of vacancies and interstitial atoms results in high free carrier concentration of about  $10^{19} \text{ cm}^{-3}$ . This value can be controlled via doping the initial PbTe with elements of several groups of the periodic table (e.g. I, V, VII group elements). On the other hand, doping of the lead telluride and some other narrow-gap IV–VI semiconductors with certain other impurities results in appearance of a range of strong and unusual effects (such as the Fermi level pinning and persistent photoconductivity) that are not characteristic of the undoped material [1]. In particular, doping of the lead telluride-based alloys with In or Ga leads to the Fermi level pinning and to appearance of long-term relaxation phenomena at low temperatures. In a certain range of indium concentration, the Fermi level can be pinned within the gap providing appearance of the semi-insulating state at low temperatures. This is explained in terms of a model assuming mixed valence of an impurity center with  $\text{In}^+$ ,  $\text{In}^{2+}$ , and  $\text{In}^{3+}$  charge states [2]. The neutral with respect to the lattice  $\text{In}^{2+}$  charge state appears to be unstable and decays to a donor–acceptor couple:  $2\text{In}^{2+} \rightarrow \text{In}^+ + \text{In}^{3+}$ .

The transition metal and rare earth impurities are of a special interest since the position of the respective impurity levels may be, in principle, tuned by magnetic field. In PbTe(Yb) and PbTe(Cr), the Fermi level is pinned in one of the allowed bands [3, 4]. In contrary to the case of an In impurity, the valence of an impurity atom is changing by one:  $\text{Yb}^{2+} \rightarrow \text{Yb}^{3+}$ ,  $\text{Cr}^{2+} \rightarrow \text{Cr}^{3+}$ . In this case, the persistent photoconductivity and other long-term non-equilibrium processes are not observed. They appear only in the case of ternary alloys, for instance, in Cr- or Yb-doped  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ , when the Fermi level is pinned in the gap. Indeed, the increase in Mn content in  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  gives rise to the band gap with the rate of  $40 \text{ meV/mol.\%MnTe}$  [5], but does not provide appearance of local or quasilocal levels in the vicinity of the actual bands. Therefore if the Fermi level is pinned in one of the allowed bands by doping with other impurities, variation of the Mn concentration may allow to shift the Fermi level into the gap providing appearance of a semi-insulating state at low temperatures.

In this paper, we report on transport and magnetic properties of  $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$  alloys doped with vanadium. Impurity states formed by some of the transition elements — Cr and Mo — in PbTe have been studied recently [6]. Impurity states formed by other transition metals of the same group, for instance, vanadium, have not been investigated previously.

## 2. Samples

The  $\text{Pb}_{1-x}\text{Mn}_x\text{Te(V)}$  bulk crystals were grown by the Bridgman technique. In the case of growing by this method, the alloy composition and the dopant concentration usually vary along the growth axis. Therefore the content of manganese increased from the top to the end of the ingot, the concentration of V, instead, dropped. The ingot was cut into slices perpendicular to the growth direction. The

concentration of dopants in each slice was determined using two methods: the mass spectroscopy and the X-ray diffraction. Samples of the size  $1 \times 1.5 \times 4 \text{ mm}^3$  were cut from the slices. Contacts to the samples with the  $n$ -type conductivity were soldered with indium. The contacts to the  $p$ -type samples were made by welding platinum wires. Photoelectrical and magnetic susceptibility measurements have been performed in the temperature range  $4.2 \div 300 \text{ K}$ .

### 3. Experimental results

#### 3.1. Transport measurements

The resistance temperature dependence was measured for all samples. The resistance temperature dependence of all samples has an activation part at temperatures  $T > 70 \text{ K}$  followed by saturation at low temperatures. For some of the samples, the dependence has two activation parts with different activation energy. The photoconductivity effect was observed in some of the samples at  $T < 50 \text{ K}$  (Fig. 1). The activation energy calculated using the formula  $\varrho = \varrho_0 \exp(E_a/kT)$  drops with the increase in Mn content  $N_{Mn}$  for the  $n$ -type samples (Table).

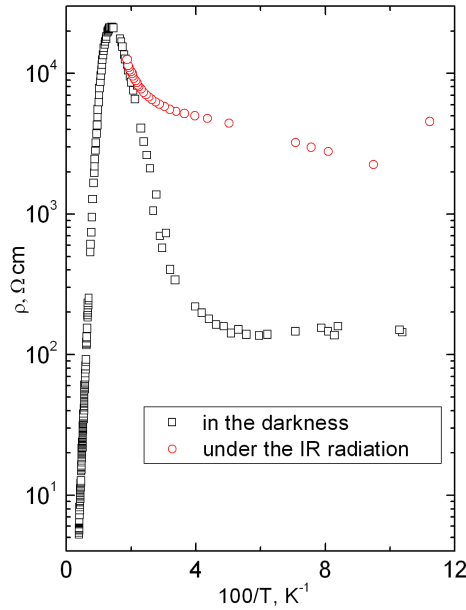


Fig. 1. The temperature dependence of the resistivity of the samples of  $Pb_{1-x}Mn_xTe(V)$ .

#### 3.2. Magnetic measurements

Measurements of the magnetic susceptibility at the temperatures from  $4.2 \text{ K}$  to  $120 \text{ K}$  were carried out for two samples of  $Pb_{1-x}Mn_xTe(V)$ . The magnetic susceptibility temperature dependence demonstrates the Curie–Weiss behavior.

TABLE

Composition and resistivity activation energy of the investigated samples.

Vanadium concentration $N_V$ [mol.%]	Mn content (mass spectroscopy) $N_{Mn}$ [mol.%]	Mn content (X-ray) $N_{Mn}$ [mol.%]	Magnetic ion concentration $N$ [mol.%]	Activation energy $E_a$ [meV]	Conductivity type
0	$3.71 \pm 0.01$			56	$p$
				142	$n$
0.48	$6.20 \pm 0.02$			129	$n$
0.52	$5.74 \pm 0.02$	$4.9 \pm 0.3$	$6.3 \pm 0.6$	103	$n$
				111	$n$
0.46	$4.99 \pm 0.01$	$5.1 \pm 1.2$		74	$p$
				32	$p$
0.05	$8.77 \pm 0.06$	$5.8 \pm 0.4$	$9.4 \pm 0.9$	43; 150	$n$
				70	$p$
				86	$p$
				143	$p$

The curves were fitted using the formula  $\chi = C/(T - \Theta_C)$ . The magnetic ion concentration  $N$  was estimated using the expression

$$C = \frac{1}{3k_B} NS(S+1)(g\mu_B)^2,$$

where  $C$  is a coefficient in the Curie–Weiss law. These estimates for the  $N$  value are presented in Table along with the data of mass spectroscopy and X-ray diffraction.

#### 4. Discussion

Several interesting experimental observations must be mentioned. The first one is the drop of the resistivity activation energy with the increase in Mn content in  $Pb_{1-x}Mn_xTe(V)$ . In the case when the Fermi level is pinned in the conduction band in  $PbTe(V)$  and is linked to the middle of the gap as it is in  $PbTe(Cr)$  [3], the increase in the Mn content that gives rise to the band gap should provide a shift of the pinned Fermi level below the conduction band bottom and further in the gap. However, it is known that manganese normally does not distribute uniformly in the lattice, but, instead, tends to form clusters and inclusions of different phases. Therefore it is important to find out if all of the manganese had built up into the lattice, or not. The manganese content was determined by several methods. The mass spectroscopy provides integral data on all manganese atoms present in a sample: clustered as well as built into the lattice. The X-ray diffraction gives a lattice constant which is related to Mn content incorporated to the lattice of  $Pb_{1-x}Mn_xTe$  through the Vegard law:  $a = 6.460 - 0.632x$  Å.

The magnetic susceptibility measurements give the concentration of magnetic ions. Since the vanadium concentration is by more than an order of magnitude lower than concentration of manganese, and the magnetic moment of V ( $\frac{3}{2}\mu_B$  as a maximum) is lower than the magnetic moment of Mn ( $\frac{5}{2}\mu_B$ ), manganese gives the most considerable contribution to the magnetic susceptibility. Possible inclusions of other phases, such as MnTe and MnTe<sub>2</sub> or the Mn clusters, are either ferromagnetic or antiferromagnetic at the temperatures of the investigation, so they cannot provide any significant temperature dependence of the magnetic susceptibility. Therefore the magnetic ion concentration may be considered as the concentration of manganese that has built up into the lattice.

The results of the three methods mentioned above are in a good agreement (Table). Therefore it is possible to conclude that all of the manganese has built up into the lattice relatively uniformly. Consequently, it is possible to calculate the band gap using the relation  $\delta E_g/\partial x = 48 \text{ meV}/\%MnTe$ . Then the position of the level that provides the activation process can be found using the following procedure: the activation process corresponds to electron transitions from the level to the conduction band for the *n*-type samples, and from the top of the valence band to the level for the *p*-type samples. As a result, it is possible to plot the position of the vanadium impurity level as a function of Mn content (Fig. 2). One can see that all points related to *n*-type samples are on a horizontal line which is about 120 meV higher than the middle of the gap. The points corresponding to the *p*-type samples form another line near the bottom of the valence band. Moreover, the point corresponding to the sample cut out from the ingot of  $Pb_{1-x}Mn_xTe$  without vanadium falls on the same line (the ultimate left point in Fig. 2).

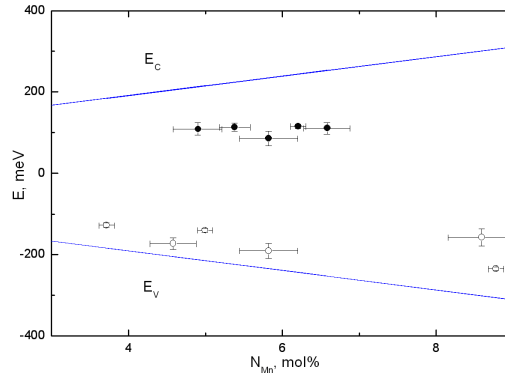


Fig. 2. Reconstruction of the energy spectrum as a function of manganese content in  $Pb_{1-x}Mn_xTe(V)$  alloys.

It is natural to assume that the first line corresponds to the impurity level of vanadium. If the extrapolation is correct, the vanadium impurity level must lie at about 25 meV above the conduction band bottom in  $PbTe(V)$ . The amount of

vanadium in the  $p$ -type samples is lower than in the  $n$ -type samples, so the amount of intrinsic defects may be higher than amount of vanadium in these samples. Therefore the second level may be related to the states of intrinsic defects such as Pb vacancies or interstitial Te. The fact that the point corresponding to the sample without vanadium lies on the same line supports this statement.

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