Transport and Magnetic Properties of $Pb_{1-x}Mn_xTe$ Doped with Cr and Mo

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Transport and magnetic properties of $Pb_{1-x}Mn_xTe$ ($x < 0.18$) semiconductor alloys doped with Cr or Mo are investigated in a broad range of temperatures and magnetic fields. In PbMnTe(Cr) alloys the Fermi level may be pinned either in the conduction band or in the energy gap, depending on Mn concentration. In PbMnTe(Mo) alloys the pinning of the Fermi level is observed in the valence band as well as in the energy gap. In the latter case persistent photoconductivity is observed at low temperatures. The analysis of the temperature dependence of magnetic susceptibility shows that PbMnTe alloys doped with Cr or Mo are Curie–Weiss paramagnets revealing weak antiferromagnetic interactions between magnetic ions.

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1. Introduction

Lead telluride (PbTe) is a member of the family of IV–VI semiconductor compounds and alloys well-known for infrared laser and detector optoelectronic applications. PbTe is a narrow-gap semiconductor compound with its direct energy gap of 190 meV (at $T = 0$ K) located at the L-point of the Brillouin zone. IV–VI semiconductors are known to crystallize with a high deviation from the stoichiometric composition. It results in a high concentration ($10^{18}-10^{19}$ cm^{-3})

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of electrically active native defects (vacancies and interstitial atoms). Conducting carrier concentration can be also controlled via doping of PbTe with the elements of group I, III, V, and VII. In particular, doping of PbTe-based IV–VI alloys with In or Ga leads to the Fermi level pinning effect and to the appearance of long-term relaxation phenomena and persistent photoconductivity at low temperatures. In a certain range of indium concentration the Fermi level can be pinned within the gap leading to the appearance of a semi-insulating state at low temperatures [1]. This is explained by a model of the In dopant as a multi-charge defect center in In^+, In^{2+}, and In^{3+} charge states, acting both as donor and acceptor centers [2].

Doping of IV–VI semiconductors with transition metal and rare earth impurities is of a special interest since the position of the respective impurity levels may be, in principle, tuned by the magnetic field. In PbTe(Yb) and PbTe(Cr) the Fermi level is pinned in the valence and conduction band, respectively [3, 4]. In contrast to the In dopant the valence of these magnetic impurities is changed only by one: $Yb^{2+} \rightarrow Yb^{3+}$, $Cr^{2+} \rightarrow Cr^{3+}$. In this case persistent photoconductivity and other long-term non-equilibrium processes are not observed. However, these effects appear in PbTe-based semiconductor alloys (e.g., in $Pb_{1-x}Mn_xTe$) doped with Yb. In PbMnTe solid solution the incorporation of Mn ions increases the band gap at the rate of 30–40 meV/mol.%Mn [5] but does not provide local or quasilocal levels in the energy gap or close to the conduction and valence band edges. Hence, if the Fermi level is pinned by doping with other impurities in one of the allowed bands, the variation of the Mn concentration may lead to a shift of the Fermi level into the gap and to the appearance of a semi-insulating state at low temperatures. In this case persistent photoconductivity and other long term non-equilibrium processes can be observed.

In this paper, we report on transport and magnetic properties of $Pb_{1-x}Mn_xTe$ alloys doped with Cr and Mo. Previously, in *p*-type $Pb_{1-x}Mn_xTe$(Yb) alloys giant negative magnetoresistance and persistent photo-conductivity effects have been observed at low temperatures [6]. The Cr impurity is known to form in PbTe a state resonant with the conduction band, whereas Yb forms a state resonant with the valence band. We will examine whether the negative magnetoresistance and persistent photoconductivity effects are observed also in *n*-type $Pb_{1-x}Mn_xTe$(Cr) and $Pb_{1-x}Mn_xTe$(Mo). In the latter case, our work provides the first experimental data on the transport and magnetic properties of PbMnTe doped with a $4d$ transition metal (Mo) ion possessing electronic configuration of the outer shell similar to Cr.

2. Samples

Bulk crystals of PbMnTe(Cr) and PbMnTe(Mo) were grown by the Bridgman technique. The concentration of Mn as well as Cr and Mo dopants in the ingot was determined by the energy dispersive X-ray fluorescence analysis for chromium

doped samples and by the emission spectral analysis for samples doped with molybdenum. It was found that along the ingot the concentration of Mn increased from the top to the end of the ingot whereas the concentration of both Cr and Mo decreased. Samples of the dimensions $1 \times 1 \times 5$ mm^3 were prepared from slices cut perpendicularly to the growth direction of the ingot. Electrical contacts to the n-type samples were soldered with indium and to the p-type samples were made by welding platinum wires. Galvanomagnetic, photoelectrical, and magnetic susceptibility measurements were performed in the temperature range of 4.2–300 K under magnetic fields up to 17.5 T.

3. Experimental results

3.1. Transport measurements

In several samples of PbMnTe doped with Cr the temperature dependence of the resistivity, ρ, revealed an activation part at temperatures $T > 30$ K followed by saturation at lower temperatures. In these samples the persistent photoconductivity effect was observed at $T < T_{\mathrm{PC}} = 35$ K (Fig. 1a). It is interesting to note that the activation energy, E_{a}, calculated from the linear part of the plot, $\ln \rho = \mathrm{const} + E_{\mathrm{a}}/(2k_{\mathrm{B}}T)$, decreases with the increase in Mn concentration (see Table I). In some PbMnTe(Cr) samples a metallic-type temperature dependence of the resistivity was also observed.
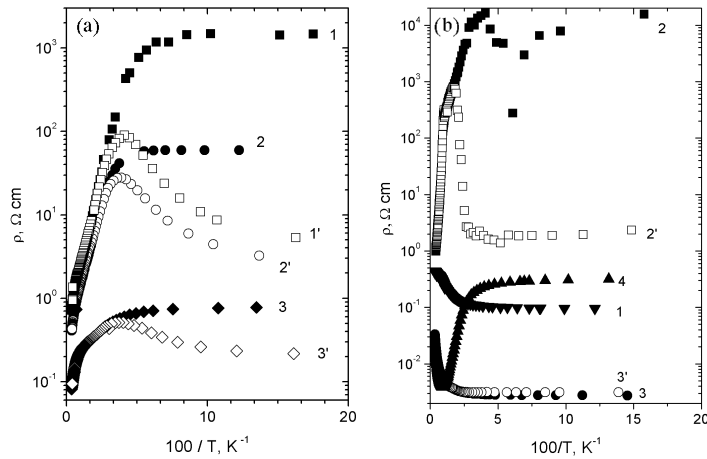

Fig. 1. (a) Temperature dependences of the resistivity of $Pb_{1-x}Mn_xTe$(Cr) taken in darkness (1–3) and under infra-red illumination ($1'–3'$). Mn concentration, mol.%: $1, 1'$ — 11.2; $2, 2'$ — 14.2; $3, 3'$ — 18.2. (b) Typical temperature dependences of the resistivity of four groups of $Pb_{1-x}Mn_xTe$(Mo) samples in darkness (solid symbols) and under infra-red illumination (open symbols). 1 — $N_{\mathrm{Mn}} = 9.5$ mol.%, $N_{\mathrm{Mo}} = 0.015$ at.%; $2, 2'$ — 3.56 mol.%, 0.025 at.%; $3, 3'$ — 7 mol.%, 0.025 at.%; 4 — 19.94 mol.%, 0.84 at.%.

Activation energy and the characteristic temperature of the appearance of the photoconductivity for $Pb_{1-x}Mn_xTe(Cr)$.

Manganese concentration N_{Mn} [mol.%]	Chromium concentration N_{Cr} [at.%]	Activation energy E_a [meV]	Photoconductivity temperature T_{PC} [K]
18.2	< 0.5	5.4	38.6
14.2	< 0.5	21.7	35.9
11.2	< 0.5	25.2	38.9

The samples of molybdenum doped $Pb_{1-x}Mn_xTe$ are divided into four groups revealing distinctly different temperature dependences of the resistivity (Fig. 1b). Samples with low Mo concentration ($N_{Mo} < 0.018$ at.%) belong to the first group, which is characterized by a metallic type of conductivity. The second group consists of samples with $0.018 < N_{Mo} < 0.038$ at.%. The temperature dependence of the resistivity measured in PbMnTe(Mo) samples from this group reveals an activation part at temperatures higher than 50 K and saturation at lower temperatures. Infrared illumination of these samples leads to the appearance of considerable persistent photoconductivity at $T < 50$ K. The amplitude of this effect decreases with increasing Mo concentration. Samples with the concentration of molybdenum between 0.04 and 0.4 at.% constitute the third group, characterized by a metallic-type temperature dependence of the resistivity and a resistance drop of more than one order of magnitude at high temperatures. In some of these samples a weak negative photoconductivity was observed at temperatures $T < 50$ K. The fourth group is formed by the samples with $N_{Mo} > 0.4$ at.%. Here, the activation-type temperature dependence of the resistance with saturation at low temperatures was observed. The values of the resistance for this group of samples are by three to four orders of magnitude smaller than for the second group. Photoconductivity has not been detected in these samples.

In chromium doped $Pb_{1-x}Mn_xTe$ negative magnetoresistance was observed at temperatures less than 15 K (Fig. 2a). The amplitude of the effect is much lower than in the case of $Pb_{1-x}Mn_xTe(Yb)$ [6] but is still about 30%, that is, much higher than the negative magnetoresistance normally observed in disordered systems. The drop of the resistance in magnetic field decreases with increasing temperature and disappears above 15 K. It can be seen from Fig. 2 that the resistance gradually rises with lowering temperature in the field intervals $H < 5$ T and $H > 8$ T at temperatures below 15 K. However, the sample resistance almost saturates at temperatures less than 10 K in the field interval 5 T $< H < 8$ T. It is important to note that the temperature dependence of the resistance consists of two activation parts at $H < 5$ T. The activation energy corresponding to the relatively high temperatures ($T > 15$ K) is about 5–6 meV and slightly rises with
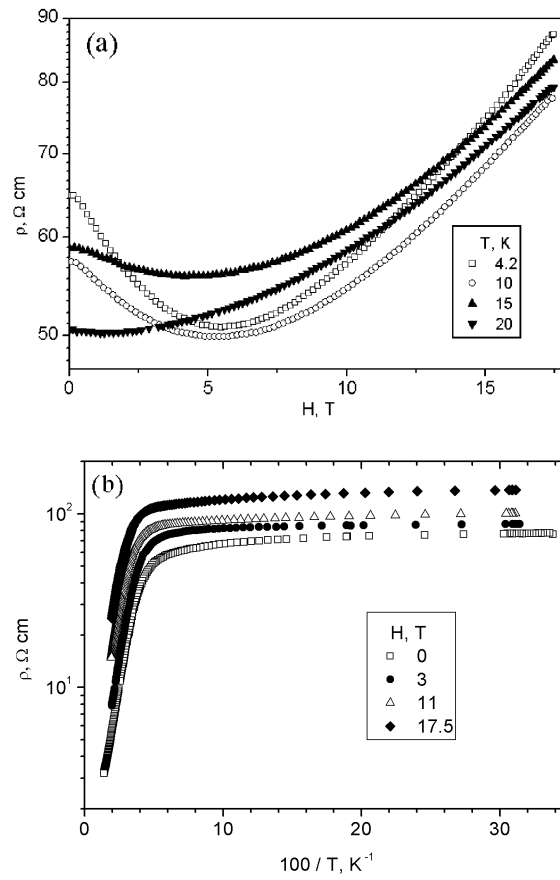
Fig. 2. Magnetic field (a) and temperature (b) dependences of the $Pb_{1-x}Mn_xTe(Cr)$ resistivity for $N_{Mn} = 14.2$ mol.%.
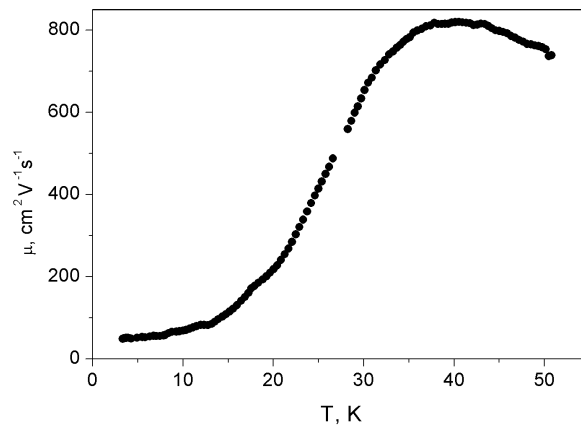

Fig. 3. Typical temperature dependence of the mobility of $Pb_{1-x}Mn_xTe(Cr)$, $x = 0.182$.

increasing magnetic field. At the same time the low-temperature activation energy decreases with increasing magnetic field and goes down to zero at H $\sim$ 5 T. At $H > 8$ T the conductivity rises again with decreasing temperature below 15 K. The Hall mobility rises with decreasing temperature, reaches a maximum at $T \approx 35$ K and then quickly drops (Fig. 3). Such a drop in the temperature dependence of the mobility is normally observed in disordered systems or in the situation when the conductivity is defined by the percolation mechanism. The maximal value of the mobility, $\mu \sim 10^3$ cm^2/(V s), is typical of the conduction band electrons in this temperature range. Data taken for other Pb$_{1-x}$Mn$_x$Te(Cr) samples demonstrate the same trends.

3.2. Magnetic measurements

Measurements of the ac magnetic susceptibility at temperatures from 4.2 K to 120 K were carried out for several samples of Pb$_{1-x}$Mn$_x$Te(Cr) (Fig. 4a) and
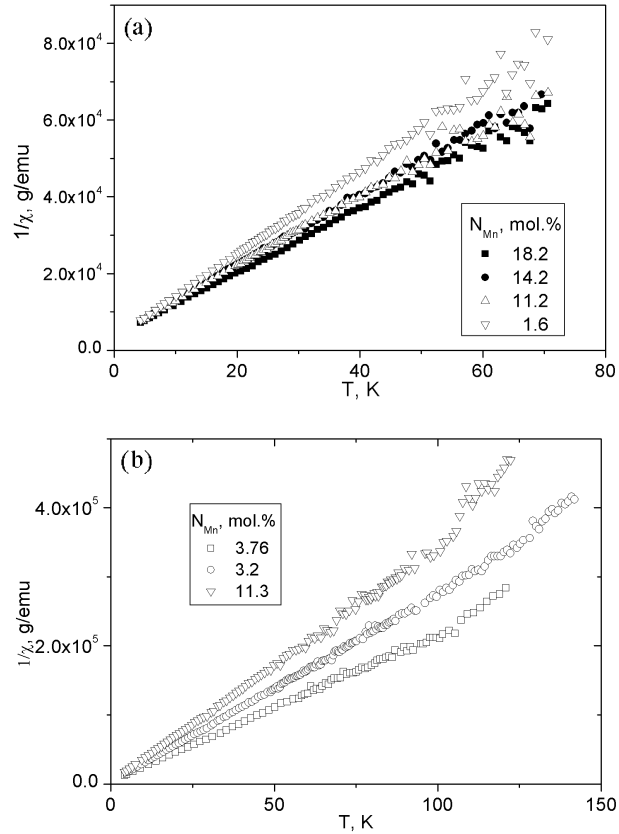

Fig. 4. Temperature dependences of inverse magnetic susceptibility of Pb$_{1-x}$Mn$_x$Te(Cr) (a) and Pb$_{1-x}$Mn$_x$Te(Mo) (b).

TABLE II

The results of magnetic measurements.

Chromium concentration N_{Cr} [at.%]	Molybdenum concentration N_{Mo} [at.%]	Manganese concentration N_{Mn} [mol.%]	Magnetic ion concentration N [mol.%]	Curie–Weiss temperature Θ [K]
0	0.019	3.76	3.8	–1.7
0	0.036	3.2	2.98	–1.4
0	0.052	2.62	2.32	–1.1
0	0.45	11.2	2.2	–1.0
0	0.847	19.94	2.56	–0.9
< 0.5	0	18.2	18.5	–4.4
< 0.5	0	14.2	16.88	–4.3
< 0.5	0	11.2	16.96	–4.4
< 0.5	0	1.6	14.18	–3.70
0.56	0	8.7	9	–0.15
0.2	0	6.6	8.82	–0.82
0.5	0	9.8	11.46	–0.6
0.25	0	8.1	9.94	–1.7

$Pb_{1-x}Mn_xTe$(Mo) (Fig. 4b) revealing the standard Curie–Weiss behavior. The Curie–Weiss temperature Θ for all measured samples is shown in Table II. The magnetic ion concentration, N, was determined using the following expression:

$$C = NS(S + 1)(g\mu_{\mathrm{B}})^2/(3\mathrm{k}_{\mathrm{B}}),$$

where C is the Curie constant from the Curie–Weiss formula: $\chi = C/(T - \Theta)$, S is the spin of the magnetic ion, g is the Lande g-factor, k_{B} is the Boltzmann constant, μ_{B} is the Bohr magneton, and χ is the magnetic susceptibility.

Changes in the slope of the temperature dependence of the inverse of the magnetic susceptibility have been found for some of the molybdenum doped samples at about $T \sim 100$ K. The apparent Curie–Weiss temperature estimated from the high temperature part of these curves is about 40 K.

4. Discussion

In PbTe(Cr) the Fermi level is pinned high in the conduction band by the electronic state formed by the Cr impurity, which provides a certain reference energy level [3]. Therefore, it is expected that the increase in Mn content in the PbMnTe(Cr) alloys rapidly increases the energy band gap and shifts up the bottom of the conduction band. It should result in a shift of the pinned Fermi level below the bottom of the conduction band and further into the energy gap.

Unexpectedly, the main effect observed experimentally is only a decrease in the impurity activation energy with increasing Mn content (see Table I). The physical origin of such behavior is at present not fully understood.

In Cr doped $Pb_{1-x}Mn_xTe$ the thermally activated behavior of the resistivity observed at $T > 15$ K corresponds to the thermal activation of free electrons from the pinned Fermi level to the conduction band as suggested by the high value of electron mobility. It means that the free conduction band electrons contribute to the positive magnetoresistance observed at low fields and elevated temperatures, but they do not contribute to the negative magnetoresistance effect. The activation energy of the process observed at the low temperatures and low fields is much smaller than the distance between the impurity level that pins the chemical potential and the conduction band. Moreover, the Hall effect data suggest that the charge carriers responsible for this activation have much lower mobility. Therefore, it is natural to assume that the mechanism of this low-temperature activation energy is related to electron transport in a relatively broad Cr impurity band. The widening of the impurity band expected for relatively high Cr concentrations results in the metallic-like impurity-band transport as long as the Fermi level is located in the middle part of the respective density of states distribution. This type of transport is observed in the intermediate range of magnetic fields 5 T $< H < 8$ T. If the Fermi level stays in the "tail" of the impurity density of states profile, the conductivity requires thermal activation from the Fermi level to the mobility edge in the impurity band. Apparently, this situation takes place in the low $H < 5$ T and high $H > 8$ T range of magnetic fields. The question arises: why does the Fermi level shift with respect to the impurity band under magnetic field? One of the explanations is that the application of a magnetic field may result in the splitting of impurity states with different spin orientations. Under these conditions the overall filling of the band does not change but the filling of each of the spin-polarized impurity subbands may change and result in a shift of the Fermi level with respect to the mobility edge in each subband. In any case, it is clear that the effect is defined by peculiarities of the magnetotransport via the impurity band and not by the conduction band electrons, as in the case of II–VI semiconductors [7].

The division of the samples of PbMnTe(Mo) into four groups (see Sec. 3.1) with different transport properties may be explained in a following model. For the first group of samples it is likely that the Mo concentration is not high enough to compensate free carriers introduced by native defects, so that the Fermi level is not pinned in these samples. For the second group the most characteristic feature is the appearance of the photoconductivity effect at low temperatures. Since this effect has not been observed in undoped $Pb_{1-x}Mn_xTe$ solid solutions, the photoconductivity has to be related to the presence of molybdenum and to the formation of an impurity level which pins the Fermi level within the energy gap.

In the third group of samples the resistance drops by more than an order of magnitude with lowering temperature from 300 K to 4.2 K. However, in undoped PbTe this drop is only about one order of magnitude. This effect is a signature of the Fermi level pinning in the valence band since in this case the resistance drops with decreasing temperature not only due to the increase in mobility, but also because of the increase in the free hole concentration. The negative photoconductivity effect observed in this group of samples may be a result of the photoexcitation of electrons from the Mo resonant level to the valence band, which results in a decrease in the free hole concentration. In the fourth group of the Mo doped $Pb_{1-x}Mn_x$Te samples the Fermi level is pinned by the Mo level within the energy gap. The saturation of resistance at low temperatures is likely to be related to the carrier transport via the Mo impurity band.

The Curie–Weiss temperatures in all samples of PbMnTe(Cr) and PbMnTe(Mo) are negative which indicates antiferromagnetic exchange interaction between magnetic ions. The manganese concentration estimated from the Curie–Weiss formula appears to be equal to the concentration determined by the emission spectral analysis and by the X-ray fluorescence analysis. Therefore, the magnetic properties of PbMnTe(Cr) and PbMnTe(Mo) are determined by Mn ions only, with Cr and Mo contributions being negligible because of their small concentrations. The origin of the change in the slope of the temperature dependence of the inverse magnetic susceptibility found in the PbMnTe(Mo) sample with the Mn content of 11.3 mol.% is not clear yet. It may come up as a result of a structural phase transition but this assumption needs further examination.

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