Giant negative magnetoresistance effect in PbTe(Yb,Mn)

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We report on the observation of the giant negative magnetoresistance effect in PbTe doped simultaneously with Yb and Mn. In some impurity concentration range, the sample resistance at the liquid helium temperature drops by about three orders of magnitude when the magnetic field increases up to 5–6 T, with subsequent rise by about one order of magnitude as the field increases to 17.5 T. The effect is observed up to $T=35$ K. The possible origin of the effect is discussed.

Lead chalcogenides are well-known materials for the infrared optoelectronics. They are mainly used for the production of lasers and LEDs operating in the middle and far infrared.[1] Besides that, there is a considerable success in construction of photodiode infrared photodetecting arrays with a large number of elements matched to a silicon substrate.[2]

Doping of the lead telluride and some other narrow-gap IV-VI semiconductors with certain impurities results in appearance of a range of strong and unusual effects that are not characteristic for the undoped material.[3] In particular, doping of the lead telluride-based alloys with some of the group III impurities, such as In or Ga, leads to the Fermi-level pinning effect and to appearance of long-term nonequilibrium phenomena at low temperatures, for instance, the persistent photoconductivity effect. This effect is used for construction of extremely sensitive far-infrared photodetectors.[4] This comes as a result of formation of the *DX*–like impurity states in the group III-doped PbTe and related alloys.[5] Formation of analogous impurity states has been reported for the Yb-doped PbTe.[6–8] There is however some substantial difference of the Fermi-level pinning effect in PbTe(Yb) compared to the cases of In or Ga doping.

First of all, indium and gallium do not modify the host PbTe energy spectrum, but introduction of ytterbium results in increase of the energy gap with the rate of $\partial E_g/\partial x \simeq 33$ meV/mol % YbTe.[9] Consequently, the position of the pinned Fermi level does not depend on the amount of indium introduced in PbTe(In),[10] but it strongly depends on N_{Yb} in PbTe(Yb). For relatively low N_{Yb} the Fermi level is pinned at ~ 10 meV below the valence-band top. For higher N_{Yb} the chemical potential enters the gap providing semi-insulating behavior of the semiconductor at low temperatures.[6]

Secondly, the Fermi-level pinning effect in PbTe(In) results from the In^{+}-In^{3+} valence switching.[5,11] Electron paramagnetic resonance data show that in the case of Yb doping the Fermi-level pinning is provided by switching of the impurity valence by one: Yb^{2+}-Yb^{3+}.[8]

Finally, the impurity states are very well localized in PbTe(In) and PbTe(Ga), and there are no signs of conductivity via the impurity band even for $N_{In}\sim 1$ at %.[12] At the same time, the impurity level providing the Fermi-level pinning effect in PbTe(Yb) is considerably broadened, its half-width is ~ 7 meV.[7] On the other hand, this estimate of broadening of the Yb level has been done not for the pure PbTe(Yb), but for PbGeTe(Yb), in which introduction of Ge could lead to substantial modification of the effect. No sign of negative magnetoresistance has ever been observed in the Yb-doped lead telluride-based alloys.

Doping of PbTe with Mn gives rise to the bandgap with the rate $\partial E_g/\partial x \simeq 40$ meV/mol % MnTe, but does not provide appearance of local or quasilocal levels in the vicinity of the actual bands.[13] Local magnetic moments in the *d* shell of Mn atoms have strong exchange interaction with the free holes.[14] In some cases this interaction gives rise to small negative magnetoresistance effect.[15]

We report on the observation of a giant negative magnetoresistance effect in PbTe doped simultaneously with Yb and Mn. The effect amplitude reaches several orders of magnitude thus far exceeding the negative magnetoresistance effect observed in PbTe(Mn).

The PbTe(Yb,Mn) bulk crystal was grown by the Bridgman technique. Concentration of the dopants varies along the growth axis: whereas the N_{Mn} increases from the top to the end of the ingot, the concentration of Yb, instead, drops. Therefore the concentration of Yb that is enough to provide the Fermi-level pinning effect was reached only in a part of the ingot closer to its top. This part of the ingot was cut into slices perpendicular to the growth direction. We will refer in our paper to the slice number. The concentration of dopants in each slice is shown in the Table I. They were determined using energy dispersive x-ray fluorescence analysis. Distri-

TABLE I. Composition of the samples $Pb_{1-x-y}Mn_xYb_yTe$ measured. E_a is the impurity thermal activation energy at $H=0$ taken from our experiment.

Sample Number	x	y	E_a (meV)
1	0.0239	0.0054	17
6	0.0220	0.0073	21
9	0.0209	0.0089	32
12	0.0201	0.0103	22

bution of dopants in the slices was homogeneous within the method accuracy of several percent of impurity concentration. Samples of the size $5\times1\times1\ mm^3$ were cut from the slices 1, 6, 9, and 12. Platinum contacts to the samples were made by electric discharge. dc galvanomagnetic measurements have been done using the four-probe technique.

The magnetoresistance (MR) curves of sample 1 (see Table I) taken at different temperatures are shown in Fig. 1. The sample resistivity ρ at $T<9$ K could be measured correctly only in the fields $H>1$ T. The value of ρ in lower fields was at least higher than $10^6\ \Omega$ cm and could not be measured with the electronics available. For this range of ρ, first, the sample current could not be stabilized, and second, the input impedance of a voltmeter became comparable to the sample resistance. As the field increases up to 5–6 T, the resistivity measured at 4.2 K drops down to $2.5k\ \Omega$ cm. It means that the amplitude of the negative magnetoresistance effect is about three orders of magnitude. The sample resistance rises by about a factor of 10 with the further increase of magnetic field to 17.5 T . It should be noted that for $\rho<10^5\ \Omega$ cm the sample current used was low enough to provide the Ohmic regime of measurements. This could not be checked however for $10^5\ \Omega\ cm<\rho<10^6\ \Omega$ cm.

As the temperature increases, the amplitude of the negative MR effect drops. At $T=15$ K slight positive MR appears in low fields. It is followed by the negative MR in higher fields 1–10 T with the further transition again to the positive MR at $H>10$ T. With the further increase of the temperature the initial positive MR part becomes more pronounced, the amplitude of the negative MR drops, so that at $T=30$ K it is seen only as a saturation region in the $\rho(H)$ curve.

It can be seen from the Fig. 1 that the resistivity gradually rises with lowering temperature in the field intervals $H<3$ T and $H>7$ T . However, the sample resistance demonstrates metalliclike behavior at $T<9$ K in the field interval

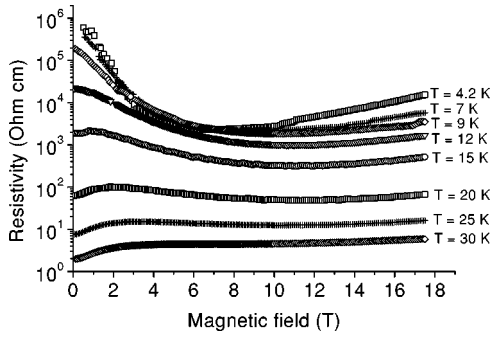

FIG. 1. Magnetoresistance of sample 1 taken at different temperatures.

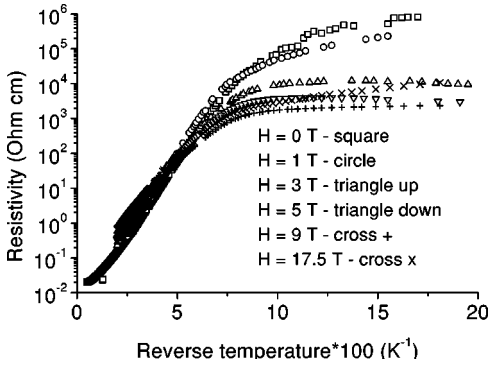

FIG. 2. Temperature dependence of resistivity of sample 1 taken in different magnetic fields.

$3\ T<H<7$ T. This fact is most clearly seen in the temperature dependence of resistivity taken in different fields (Fig. 2). It is important to note that the resistivity temperature dependence consists of two activation parts at $H<3$ T . The activation energy corresponding to relatively high temperatures $T>20$ K slightly drops with H rising. At the same time the low-temperature activation energy decreases with field with the rate $\partial E_a/\partial H\simeq0.7$ meV/T going down to zero at $H\simeq3$ T. At $H>7$ T the resistivity temperature dependence in the low-temperature region can be much better fit with the relation assuming the hopping conductivity $\rho=\rho_0\exp\{(T_0/T)^{1/4}\}$. For the parameter T_0, it was found $T_0\sim(H-H_0)^{5/2}$, where $H_0=7$ T—the field corresponding to the onset of the hopping conductivity (see Fig. 3, open squares).

Data taken for sample 6 demonstrate the same trends. The only difference is that the sample has higher resistance, and reliable data at $T=4.2$ K were taken only in the fields $H>3$ T. For this sample the ''metallic-type'' behavior is not observed in any field. Nevertheless, the temperature dependence of resistance in different fields shows that the low-temperature activation behavior at $H<3$ T transforms to the hopping conductivity at $H>3$ T. For this sample, again, in the low-field range the low-temperature activation energy decreases with field with the rate of $\partial E_a/\partial H\simeq3$ meV/T and for the high-field range the parameter T_0 satisfies the same relation (2) with $H_0=3$ T (Fig. 3, full squares).

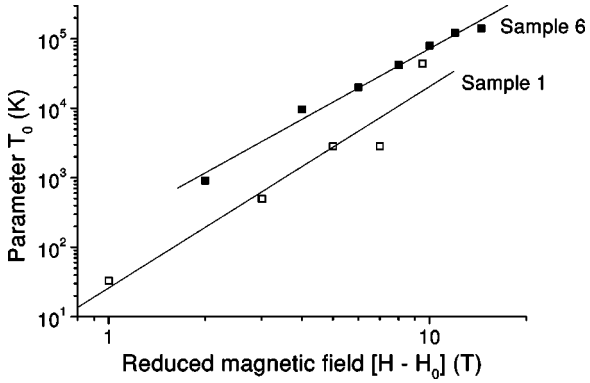

FIG. 3. Dependence of the parameter T_0 of the hopping conductivity on the reduced magnetic field H-H_0 for the samples 1 (open squares) and 6 (full squares). The solid lines give the mean-square fit for the respective dataset.

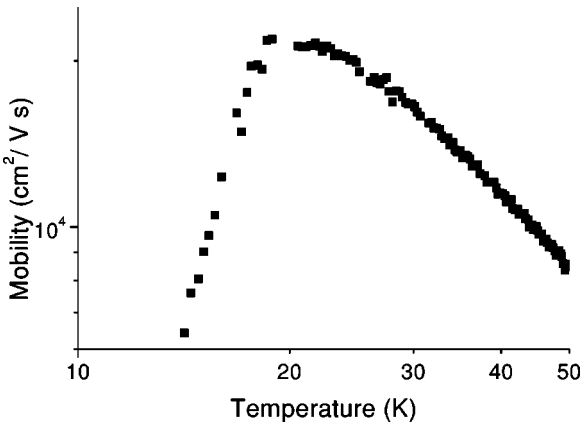

FIG. 4. The temperature dependence of the Hall mobility for the sample 6.

For samples 9 and 12 the data could be taken only at $T > 15\,\mathrm{K}$ and $T > 10\,\mathrm{K}$, respectively, since for the lower temperatures the resistivity could not be measured reliably in any field. However these high-temperature data show presence of the negative MR effect which is observed up to 25–30 K.

Temperature dependence of the Hall mobility μ may give important information on the carrier scattering mechanisms. The curves $\mu(T)$ for sample 6, for which the R_{Hall} value was measured in the field $H = 1$ T, are shown in the Fig. 4. It can be seen that at high temperatures $T > 20 - 25\,\mathrm{K}$ the value of μ is proportional to $T^{-1.5}$ which is characteristic for the acoustic phonon scattering. For the lower temperatures the mobility reaches maximum and then drops very fast. For this region $\mu \sim T^4$. This kind of temperature dependence of mobility is normally observed in the disordered systems, or in the situations when the conductivity is defined by percolation.[16] The Hall signal could be measured on the background of noise only at $T > 14\,\mathrm{K}$. The absolute value of mobility taken at 14 K is $6000\,\mathrm{cm^2/V\,s}$ that is much lower than the normally measured free hole mobility $\sim 10^4\,\mathrm{cm^2/V\,s}$ in PbTe in this temperature range. At lower temperatures the Hall signal becomes too small compared to noise in all fields $H < 17.5\,\mathrm{T}$. The respective Hall mobility is at least lower than $100\,\mathrm{cm^2/V\,s}$. Such a low absolute value of μ is also characteristic for disordered systems and percolative transport.

The giant negative magnetoresistance effect has been observed earlier in the semimagnetic II–VI semiconductors.[17,18] The low-temperature conductivity in these materials is defined by thermal activation of holes from a shallow acceptor level. The activation energy drops with increasing magnetic field providing fast increase of the free hole concentration and, consequently, the negative magnetoresistance effect. This mechanism however is not applicable to PbTe(Yb,Mn).

Doping of the lead telluride with ytterbium results in the Fermi-level pinning in the proximity of the valence-band top. Exact position of the pinned Fermi level depends on the amount of Yb introduced into the crystal. Doping with Mn further increases the gap, so in PbTe(Yb,Mn) the chemical potential is pinned within the gap. Thus the high-temperature activation in the $\rho(T)$ curves is due to the thermal excitation of free holes from the Yb-induced impurity level to the valence band. High mobilities of the carriers in this temperature range support that the conductivity is defined by the activation to the valence band. The respective activation energy at $H = 0$ is given in the Table I. It depends only slightly on magnetic field, and the magnetoresistance is positive. It means that the free holes may give contribution to the positive magnetoresistance in the low fields at elevated temperatures, but not to the negative magnetoresistance. This aspect makes substantial difference from the case of II–VI semiconductors.

The activation energy corresponding to the process observed at the low temperatures and in the low fields is much smaller than the distance between the impurity level that pins the chemical potential and the valence band. Besides that, the Hall data suggest that the charge carriers responsible for this activation have much lower mobility. It is natural to assume therefore that the mechanism of this low-temperature activation is the following. Contrary to the indium impurity case, for which the respective impurity states are very well localized, and the width of the respective level is very small < 1 meV,[12] in the case of Yb-doped PbTe there may exist a considerable widening of the impurity level, as it has been suggested in Ref. 7. In certain cases this widening may lead to the possibility of percolative transport as long as the Fermi level is inside the middle part of the respective density of states profile. If it stays in the ''tails'' of this profile, the conductivity is defined by the thermal activation from the Fermi level to the mobility edge. Apparently the Fermi level shifts in magnetic field with respect to the mobility edge in PbTe(Yb,Mn)

Since the effect is not observed in the other lead telluride-based alloys doped with Yb, it is natural to assume that it results from the interaction of Yb and Mn impurities. The possible mechanism of the effect is the following. There is a strong exchange interaction between magnetic moments localized on the *d* shell of Mn atoms and free holes in the valence band of PbTe. The Yb impurity level lies rather close to the valence band top, so it is likely that there is a hybridization of the impurity state and the valence band wave functions. Thus the *d* states of Mn may affect Yb impurity states. Modification of this interaction in magnetic field may result in changes in the profile of the density of states in the impurity band. Consequently, position of the Fermi level may shift with respect to the mobility edge.

Another possibility is the following. Application of magnetic filed may result in noticeable splitting of impurity states with different spin directions. Under these conditions the overall filling of the band does not change, but filling of each of the spin-polarized impurity subbands may change and result, in turn, in a shift of the Fermi level with respect to the mobility edge in each subband. However, the presented schemes of the processes involved are quite speculative, and further research is needed to clarify the origin of the effect.

The onset of the variable range hopping conductivity is clearly observed in the high fields. The fact that in different samples the field dependence of the parameter T_0 is analogous suggests some universal mechanism of localization in high magnetic fields. However, the physical meaning of the parameter H_0 remains unclear.

In sample 1 the hopping conductivity onset occurs well after the chemical potential crosses the mobility edge in

magnetic field providing rather extended range of fields 3–7 T in which the metallic behavior of conductivity is observed at low temperatures. In sample 6 the crossover and the hopping conductivity onset take place practically in the same field. Apparently these two processes depend on the density of states profile in the impurity band, and further investigations are needed to determine whether they are linked to each other or not.

In summary, we have observed the giant negative magnetoresistance effect with the amplitude of about 10^3 in PbTe(Yb,Mn). The effect is most likely to come from the shift of the chemical potential with respect to the mobility edge in the impurity band in magnetic field. Positive magnetoresistance observed in high fields results from the variable range hopping conductivity onset observed at $H>H_0$, the parameter T_0 of the hopping conductivity being proportional to $(H-H_0)^{5/2}$.

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[1] A. Lambrecht *et al.*, Semicond. Sci. Technol. **8**, S334 (1993).
[2] H. Zogg *et al.*, Semicond. Sci. Technol. **6**, C36 (1991).
[3] B. A. Akimov *et al.*, Phys. Status Solidi A **137**, 9 (1993).
[4] S. N. Chesnokov *et al.*, Infrared Phys. **35**, 23 (1994).
[5] D. R. Khokhlov and B. A. Volkov, in *Proceedings of the 23rd International Conference on Physics of Semiconductors, Berlin, Germany, 1996* (World Scientific, Singapore, 1996), Vol. 4, p. 2941.
[6] I. I. Ivanchik *et al.*, in *Proceedings of the 24th International Conference on Physics of Semiconductors, Jerusalem, Israel, 1998* (World Scientific, Singapore, 1998), Pt. VIII B, paper 8.
[7] E. P. Skipetrov *et al.*, Phys. Status Solidi B **210**, 299 (1998).
[8] I. Isber *et al.*, Cryst. Res. Technol. **31**, 701 (1996).
[9] D. L. Partin, J. Appl. Phys. **57**, 1997 (1985).
[10] V. I. Kaidanov, R. B. Mel'nik, and I. A. Chernik, Fiz. Tekh. Poluprovodn. **7**, 759 (1973) [Sov. Phys. Semicond. **7**, 522 (1973)].
[11] I. A. Drabkin and B.Ya. Moizhes, Fiz. Tekh. Poluprovodn. **17**, 969 (1983) [Sov. Phys. Semicond. **17**, 611 (1983)].
[12] B. A. Akimov *et al.*, Fiz. Tekh. Poluprovodn. **13**, 752 (1979) [Sov. Phys. Semicond. **13**, 441 (1979)].
[13] J. Niewodniczańska-Zawadzka *et al.*, Physica B & C **117**, 458 (1983).
[14] G. Bauer, H. Pascher, and W. Zawadzki, Semicond. Sci. Technol. **7**, 703 (1992).
[15] A. V. Brodovoi *et al.*, Fiz. Tekh. Poluprovodn. **18**, 1547 (1984) [Sov. Phys. Semicond. **18**, 970 (1984)].
[16] M. K. Sheinkman and A.Ya. Shik, Fiz. Tekh. Poluprovodn. **10**, 209 (1976) [Sov. Phys. Semicond. **10**, 128 (1976)].
[17] A. Mycielsky and J. Mysielski, J. Phys. Soc. Jpn. **49A**, 807 (1980).
[18] A. V. Germanenko *et al.*, Fiz. Tverd. Tela **26**, 1754 (1984) [Sov. Phys. Solid State **26**, 1062 (1984)].