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RESONANT STATE OF $4f^{14/13}$ Yb ION IN $Pb_{1-x}Ge_xTe$*

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The study of transport and of magnetic properties of $Pb_{1-x}Ge_xTe$:Yb mixed crystals ($0 \leq x \leq 0.04$) is reported. It is shown that Yb forms a donor state resonant with the PbTe valence band. The donor state position may be tuned (shifted relative to the energy gap) by admixture of Ge. The properties of the Yb ion in the $Pb_{1-x}Ge_xTe$ matrix makes the system unique from the point of view of magnetic properties. It is demonstrated that the change of the conductivity type from p to n induces transitions from the paramagnetic state to the diamagnetic one.

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Rare earth elements are often used as constituents of alloys with IV–VI compounds when the wider energy gap is needed for application purposes. The first investigation of $Pb_{1-x}Yb_xTe$ mixed crystals, which showed that single phase material with considerably increased band gap might be grown, was done in late 70's by Suryanarayanan and Paparoditis [1]. Further investigations performed by Partin [2] confirmed that result. Nevertheless, some data suggested that ytterbium was unstable in 2+ valence state and could undergo the transition $Yb^{2+} \rightarrow Yb^{3+} + e_{band}$. Then, it was postulated that ytterbium introduced a deep donor state into the band gap in the vicinity of the valence band edge. That explained why it was impossible to produce heavy doped p-type $Pb_{1-x}Yb_xTe$ alloys. New EPR

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experiments [3] directly evidenced the presence of $Yb^{3+}4f^{13}$ ions in $Pb_{1-x}Yb_xTe$ crystals.

Recently a successful growth of $Pb_{1-x}Ge_xTe$:Yb mixed crystals has been reported [4]. On the basis of transport investigations it has been concluded that in PbTe the Yb level is degenerated with the valence band and in mixed crystals its position may be shifted upwards into the energy gap by adding Ge to the matrix.

The aim of our paper was to verify previous conclusions.

Crystals of $Pb_{1-x}Ge_xTe$, in the composition range $0 \leq x \leq 0.04$, were doped with Yb up to 0.8 at.%. The composition of the crystals was checked by the energy dispersive X-ray fluorescence analysis. The values of Ge content x detected by this method were smaller than those nominally added to technological charges.

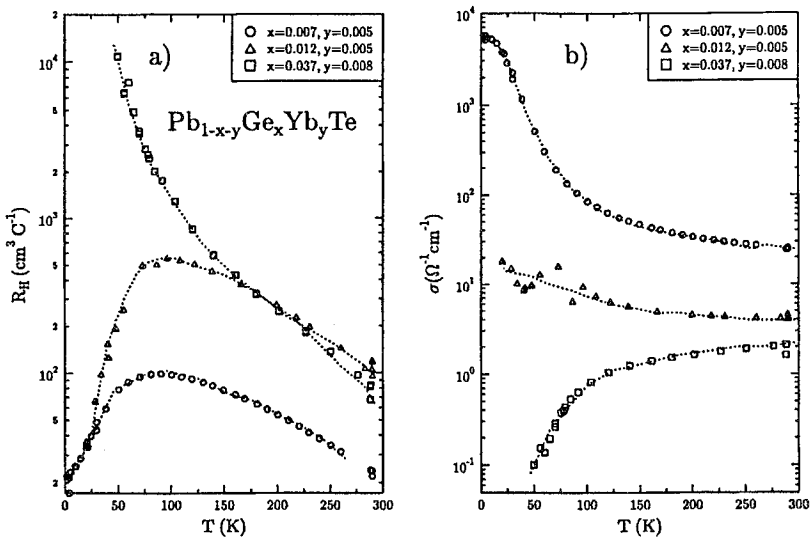

Fig. 1. The dependence of the Hall coefficient (a) and the hole conductivity (b) in $Pb_{1-x-y}Ge_xYb_yTe$.

The Hall coefficient and the carrier conductivity were measured in temperatures ranging from 2 to 300 K in a continuous flow cryostat. The Hall voltage was measured at the magnetic field 1 T. Figure 1a shows the Hall coefficient vs. temperature for three samples of $Pb_{1-x}Ge_xTe$. It may be noted that the character of the curves changes as the quantity x of germanium increases. In samples containing about 1% Ge the Hall coefficient depends on the temperature rather weakly, the hole concentration does not seem to depend on the temperature crucially. Different behavior is observed in samples containing 3.7% germanium as a constituent. With decreasing temperature the Hall coefficient dramatically increases and hence the obtained hole concentration decreases. Figure 1b shows the dependence of the hole conductivity on the temperature. The differences between samples of $Pb_{1-x}Ge_xTe$, $x \approx 0.01$, and samples with the higher Ge content are even more substantial than they were observed in the Hall coefficient. In the first

set of samples the value of the conductivity sharply increases with the decreasing temperature, especially below 100 K, and reflects the vanishing role of the phonon scattering. For the samples with the higher Ge content the tendency is opposite. The conductivity diminishes at low temperatures. The crystal approaches to the insulating state.

The analysis of our transport data confirms the conclusions of the earlier works [2,4]. As grown PbTe crystals are always *p*-type with the hole concentration about 10^{18} cm^{-3} at 300 K, in Yb doped samples the carrier concentration decreases significantly achieving 5×10^{16} cm^{-3} at the same temperature. The temperature dependence of the Hall coefficient, may be understood assuming that in PbTe the Yb level is located in the vicinity of the top of the valence band and that its energetic position shifts up relative to the band edges with the growing Ge content. The self-ionization process of Yb ions $4f^{14} \rightarrow 4f^{13} + e_{band}$ leads to a decrease in the hole concentration as the Yb concentration increases. At 4.2 K, for $x > 0.01$, the Yb level crosses the valence band edge and enters the band gap. Alloys from this composition range, at a sufficiently high doping level, approach to the *semi-insulating* state.

The crucial test of the model presented above was performed by magnetization measurements. Magnetic properties were investigated by means of a SQUID magnetometer in the temperature range 1.3–50 K and magnetic fields up to 5 T. We found, in accordance with our expectations, that the as-grown *p*-type samples of $Pb_{1-x}Ge_xTe$:Yb are paramagnetic (see Fig. 2a). In these samples, due to the self-ionization process, Yb ions are in the electrically and magnetically active

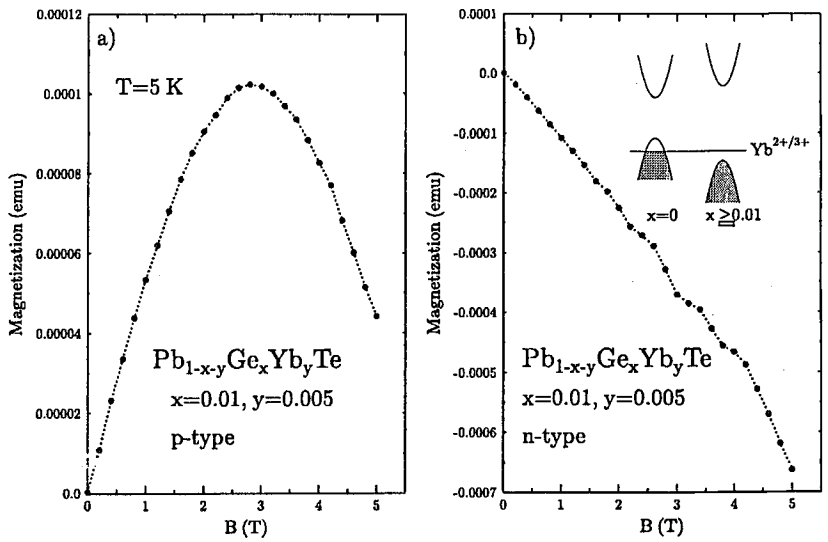

Fig. 2. The magnetization of $Pb_{1-x-y}Ge_xYb_yTe$ mixed crystals, (a) *p*-type sample, (b) the same sample after annealing to *n*-type. The inset shows the scheme of the band structure of $Pb_{1-x-y}Ge_xYb_yTe$.

Yb^{3+} charge state ($4f^{13}$, $S = 1/2$). The magnetization curve (after the correction due to the diamagnetism of PbTe lattice) is described by the appropriate Brillouin function. The low values of magnetization are a result of the low number of magnetically active centers, approximately 10^{18} cm^{-3}. The same samples when annealed to the *n*-type show a *diamagnetic* behavior (see Fig. 2b). In such situation the Fermi level is located above the $Yb^{3+/+2}$ level and all Yb ions are in the Yb^{2+} ($4f^{14}$ — a complete atomic shell) nonmagnetic state. It results in the *diamagnetic* response of these samples.

We can conclude that our results are fully consistent with the results of earlier investigations. Moreover, we show for the first time that in $Pb_{1-x-y}Ge_xYb_yTe$ system it is possible to induce the paramagnet–diamagnet transition driven by the change of the conductivity type.

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