TRANSPORT AND MAGNETIC PROPERTIES OF PbTe:Cr AND PbSnTe:Cr*

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We present the results of the experimental studies of the low temperature transport and magnetic properties of PbTe, $Pb_{1-x}Sn_xTe$ ($x \leq 0.3$) and SnTe crystals doped with 0.5 at.% of chromium. Cr was found to be a resonant donor in PbTe and PbSnTe. Magnetic susceptibility measurements revealed that PbTe:Cr and $Pb_{1-x}Sn_xTe$:Cr ($x \leq 0.2$) are Curie paramagnets whereas SnTe:Cr exhibits van Vleck paramagnetism.
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In this communication we present the results of the experimental studies of the crystals of PbTe:Cr, $Pb_{1-x}Sn_xTe$:Cr and SnTe:Cr. Our interest in these new semimagnetic semiconductors (SMSC) is threefold. Firstly, this can be an important extension of the family of IV–VI SMSC to the systems with nonzero orbital magnetic moment of transition metal impurities. Secondly, it is an interesting resonant donor (acceptor) system with matrix composition controlled energetic location of the impurity level. Finally, the doping with Cr offers new possibilities in controlling the electric properties of IV–VI semiconductors.

All the studied samples were grown by the Bridgman method. We investigated the set of samples of $Pb_{1-x}Sn_xTe$ covering the composition range $x \leq 0.3$ with a typical concentration of Cr 0.5 at.% (i.e. $N_{Cr} = 7.5 \times 10^{19}$ cm^{-3}). We also studied the samples of $Pb_{1-y}Cr_yTe$ ($0 \leq y \leq 0.01$) and $Sn_{1-y}Cr_yTe$ ($y = 0.005$ and 0.02). The chemical composition of our samples was checked by X-ray fluorescent analysis revealing a rather strong effect of distribution of chromium ions along an ingot. The crystals of PbTe:Cr and SnTe:Cr were also investigated by X-ray Debye powder method. They were found free of second phase inclusions with the cubic lattice constants $a_0 = 6.449$ Å and $a_0 = 6.314$ Å for $Pb_{0.99}Cr_{0.01}Te$ and $Sn_{0.995}Cr_{0.005}Te$, respectively.

We investigated experimentally the transport properties (Hall effect and conductivity) in the temperature range $T = (4 - 300)$ K and the low temperature, $T = (1.6 - 4.2)$ K, ac magnetic susceptibility. The results of our transport measurements of PbTe:Cr agree well with the available literature data [1, 2] and can

be summarized as follows. The samples with small concentration of Cr are p-type. The n-type conductivity is observed only for crystals with $N_{Cr} \geq 1.5 \times 10^{19}$ cm^{-3}. The increase of the chromium concentration above $N_{Cr} \cong 3 \times 10^{19}$ cm^{-3} does not change the electron concentration $n \cong 1.3 \times 10^{19}$ cm^{-3}. It corresponds to Fermi energy $E_F \cong 100$ meV. It was suggested [1–4] that this behavior results from the process of the selfionization of Cr^{2+} ions generating the conducting electrons (Cr$^{2+} \Rightarrow$ Cr^{3+} + e). The electron concentration saturates when the Fermi level reaches the energy level of Cr^{2+} and the selfionization process stops. It is essentially the same mechanism as the one observed e.g. in HgSe:Fe [3] and PbTe:In [4]. The change of the type of conductivity with increasing Cr concentration is the result of an interplay between the concentration of Cr^{2+} (donor centers) and the concentration of metal vacancies (present in stoichiometrically grown IV–VI crystals and responsible for the p-type conductivity). The electrons generated in the process of selfionization of Cr^{2+} ions have first to fill the empty electron states in the valence band (generated by metal vacancies) and only then the electron states in the conduction band. Our PbTe:Cr samples have very high mobilities $\mu \cong 10^5 \div 10^6$ cm^2/(V s). With an increasing tin content in the Pb$_{1-x}$Sn$_x$Te:0.5 at. % Cr alloy one observes a decrease of the electron concentration. For approximately $x \geq 0.1$ the as-grown crystals are p-type. It is probably caused by the lack of chromium to fill all the empty states in the valence band. The number of these states is directly measured by the concentration of conducting holes in the PbSnTe matrix and is known to increase rather fast with increasing tin content. For SnTe:Cr crystals one observes usual p-type conductivity with very high concentration of carriers $p \cong 10^{21}$ cm^{-3} and very low mobility $\mu \cong 100$ cm^2/(V s).

The typical temperature dependence of the magnetic susceptibility of PbTe:Cr and Pb$_{1-x}$Sn$_x$Te ($x \leq 0.2$) is presented in Fig. 1. The magnetic susceptibility follows the simple Curie law ($\chi \propto 1/T$) indicating the presence in the crystal of the localized magnetic moments. The natural candidates for these moments are $3d^3$ Cr^{3+} ions which are expected to be $S = 3/2$ spins in the octahedral crystal field of PbTe lattice. A different behavior is observed in SnTe:Cr (see Fig. 2). There is practically no temperature dependence of the magnetic susceptibility of this sample. It indicates the van Vleck type of magnetic behavior which may be attributed to the $3d^4$ states of Cr^{2+} ions which are expected to have non-magnetic ground state in the octahedral crystal field [5].

One may attempt to interpret the experimental findings presented above in a model assuming the shift of the Cr^{2+} level from the conduction band in the case of PbTe and PbSnTe to the valence band in the case of SnTe. It will induce the decrease of electron concentration and the changes in the relative concentrations of Cr^{2+} and Cr^{3+} ions. In SnTe:Cr one would expect the Cr^{2+} level to be located below the Fermi level of the crystal. Only magnetically and electrically "neutral" Cr^{2+} ions are expected to be present in this case. In conclusion, we have observed that Cr acts as a resonant donor both in PbTe and Pb$_{1-x}$Sn$_x$Te with small tin content ($x \leq 0.2$). Magnetic properties of PbTe:Cr and Pb$_{1-x}$Sn$_x$Te:Cr are typical for Curie paramagnets and are probably due to the spin magnetic moments of Cr^{3+} ions. The van Vleck type of paramagnetism observed in SnTe:Cr is attributed
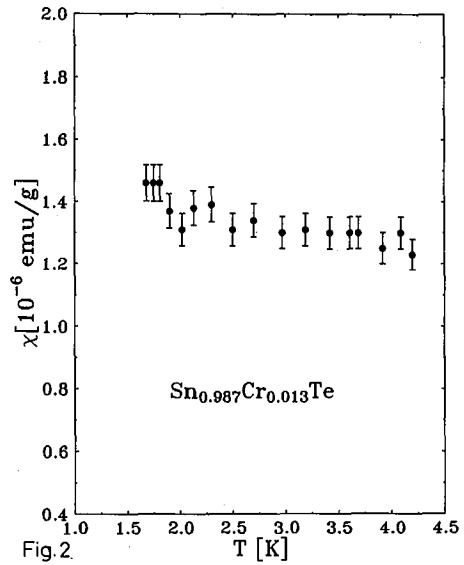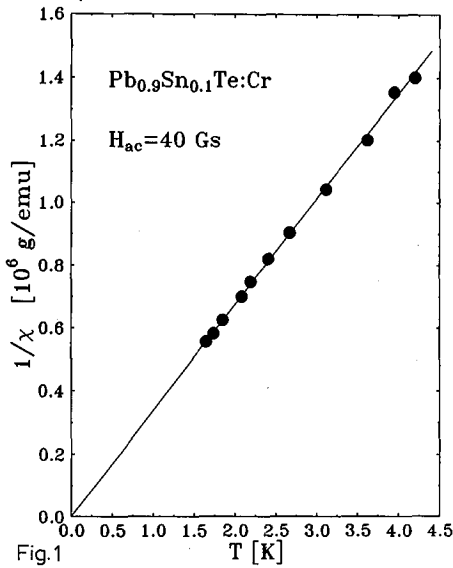
Fig. 1.   The temperature dependence of the inverse magnetic susceptibility of the $Pb_{0.9}Sn_{0.1}Te$ sample doped with $N_{Cr} \cong 2 \times 10^{19}$ cm^{-3} of chromium. Qualitatively the same behavior is observed for PbTe:Cr and $Pb_{0.8}Sn_{0.2}Te$:Cr samples.

Fig. 2   The temperature dependence of the magnetic susceptibility of the sample of $Sn_{0.987}Cr_{0.013}Te$. The weak influence of temperature on the magnetic susceptibility and the very small magnitude of it suggest the van Vleck paramagnetism.

to the Cr^{2+} ions. The magnetic properties of PbSnTe:Cr seem to support the model describing the Cr impurity in IV–VI matrices as a resonant donor with a Cr^{2+}/Cr^{3+} state depending on the relative position of the Fermi level and the energy level of Cr^{2+}.

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