TRANSPORT AND MAGNETIC STUDY
OF Gd IONS IN Pb$_{1-y}$Sn$_y$Te


Institute of Physics Polish Academy of Sciences
Al. Lotników 32/46, 02-668 Warsaw, Poland

Electric conductivity, Hall effect and magnetic susceptibility of Pb$_{1-x-y}$Sn$_x$Gd$_y$Te mixed crystals with $0.13 \leq y \leq 0.93$ and $0.001 \leq x \leq 0.04$ were experimentally studied over the temperature range $4K \leq T \leq 300$ K. The incorporation of Gd ions into the Pb$_{1-y}$Sn$_y$Te matrix results in semi-metallic n-type conductivity of the crystals with $y < 0.6$. For crystals with $y > 0.6$ one observes only semi-metallic p-type conductivity. We present a model explaining these results in terms of the Sn composition dependence of the location of Gd$^{2+}$/3+ level with respect to the band edges of PbSnGdTe.

PACS numbers: 75.20.Ck, 75.30.Et

In recent investigations of magnetic and transport properties of Sn$_{1-x}$Gd$_x$Te it was established that in SnTe Gd forms a resonant donor state with Gd$^{2+}$/3+ energy level located about 0.2 eV below the top of the valence band [1]. Depending on the position of the Fermi level (governed by the concentration of two electrically active centers, Sn vacancies and Gd$^{3+}$ ions) with respect to the Gd$^{2+}$/3+ energy level, we expect the Gd ions to be present in SnTe matrix both in the usual 3+ charge state (electron configuration 4f$^7$) and in 2+ state (electron configuration 4f$^7$5d$^1$).

In SnTe Gd shows only limited donor action by partially compensating very high hole concentration due to native acceptor defects [1-3]. In related Pb$_{1-x}$Gd$_x$Te semiconducting crystals, Gd shows clear donor character generating the electron concentrations above $n \approx 10^{20}$ cm$^{-3}$. In PbTe the Gd$^{2+}$/3+ level is expected to be located far above the bottom of the conduction band. The purpose of our work is to examine the mixed Pb$_{1-y}$Sn$_y$Te crystals with Gd. It is expected that with an increasing content of Sn in Pb$_{1-x-y}$Sn$_y$Gd$_x$Te, the Gd$^{2+}$/3+ energy level will shift down from the conduction band to the valence band via the energy gap. It will result in a smooth change from the n-type to the p-type semi-metallic conductivity via a (possible) semi-insulating state. Similar effects were actually observed in PbSnTe with nonmagnetic In resonant donor [4].

We studied a set of bulk Pb$_{1-x-y}$Sn$_y$Gd$_x$Te crystals with $y = 0.14, 0.30, 0.50, 0.67, 0.73$ and $0.93$, and with Gd content up to 4 at.%. We measured the Hall effect and the electric conductivity over the temperature range $T = 4 \div 300$ K.
and the ac magnetic susceptibility in the temperature range \(T = 1.5 \div 70\) K. Both the as-grown crystals and the samples annealed in the atmosphere of metal were studied. The crystals with \(x \approx 0.1\) at.\% were also studied by electron paramagnetic resonance measurements. The chemical composition of our crystals was determined by X-ray fluorescent analysis. The concentration of Gd ions was independently verified by magnetic measurements.

In the as-grown crystals with \(y = 0.14\) we found the \(n\)-type semi-metallic conductivity with carrier concentrations up to \(n = 5 \times 10^{19}\) cm\(^{-3}\). For the crystals with \(y = 0.30\) and \(y = 0.50\) the \(n\)-type conductivity was observed only in samples annealed in Sn atmosphere in order to reduce the background native acceptor concentration. Neither as-grown nor Sn-annealed samples of \(\text{Pb}_{1-x-y}\text{Sn}_y\text{Gd}_x\text{Te}\) with \(y = 0.67, 0.73\) and 0.93 show \(n\)-type conductivity despite the introduction of up to 4 at.\% (i.e., about \(6 \times 10^{20}\) cm\(^{-3}\)) of Gd. These samples show semi-metallic \(p\)-type conductivity. At low Gd concentrations the carrier concentration in \(\text{PbSnGdTe}\) changes linearly with the rate of about \(1.5 \times 10^{22}x\), expected for the case when each Gd ion provides 1 conducting electron (or compensates 1 acceptor center). This dependence tends to level off for Gd concentrations above 1 at.\% indicating that only a part of Gd ions is electrically active. The maximal electron concentrations (for \(y < 0.6\)) or the minimal hole concentrations (for \(y > 0.6\)) established from these measurements are presented in Fig. 1a together with the corresponding Fermi level positions shown in Fig. 1b. The magnetic susceptibility measurements indicate that all our samples obey the Curie–Weiss law over the entire tempera-

![Graphs](image)

Fig. 1. (a) The dependence of the maximal electron concentration (for \(y < 0.6\)) or minimal hole concentration (for \(y > 0.6\)) obtained in \(\text{Pb}_{1-x-y}\text{Sn}_y\text{Gd}_x\text{Te}\). (b) The Sn composition dependence of the position of the Fermi level corresponding to the carrier concentrations shown in (a).
Transport and Magnetic Study of Gd Ions in Pb$_{1-y}$Sn$_y$Te

This allows for the precise determination of the concentration of Gd ions from the value of the Curie constant. We found good agreement between the results of X-ray measurements and magnetic data analyzed for $S = \frac{7}{2}$ spin magnetic moment of Gd ion. The paramagnetic Curie temperatures determined from magnetic susceptibility measurements are very small, typically below 1 K. This indicates the presence of only very weak $f-f$ exchange interaction between magnetic ions with the $f-f$ exchange integral of the order of 0.1 K. Our results show the antiferromagnetic sign of the exchange integral for the samples with $y > 0.6$ and the ferromagnetic sign of this parameter for the crystals with Sn composition $y < 0.6$. As the observed values of the paramagnetic Curie temperature are of the order of 0.5–1 K and the experimental error for this parameter is ±0.5 K, we refrain from further analysis of this observation.

The transport properties of PbSnGdTe can be explained within the frames of the model presented in Fig. 2. The key point of this model is the Sn composition dependence of the PbSnGdTe conduction and valence band edge location with respect to the Gd$^{2+/3+}$ level position. We have assumed that the band edges of PbSnGdTe follow the same dependence as in Pb$_{1-y}$Sn$_y$Te matrix [3–6], and that Gd ions influence the energy gaps of PbTe and SnTe in a way similar to other rare earth ions [5]. The position of the Gd$^{2+/3+}$ level in SnTe was taken in accordance with the results of Ref. [1]. We have also assumed that the Gd$^{2+/3+}$ level may serve as a certain energy reference level [7].

One can see that for $y > 0.6$ the Gd$^{2+/3+}$ level is expected to be resonant with the valence band of PbSnGdTe whereas for $y < 0.45$ it is in resonance with...
the conduction band. We expect that the well-known effect of pinning of the Fermi level to the resonant levels (Gd$^{2+/3+}$ level in our case) will determine the effect of Gd on the carrier concentration in PbSnGdTe. The model correctly predicts the switch from the $n$-type to $p$-type conductivity for about $y = 0.5 \div 0.6$. The experimentally observed shift of the Gd$^{2+/3+}$ level (see Fig. 2b) agrees with the trend obtained in the model. The complete quantitative analysis would require a detailed knowledge of the band structure dependence on the Gd concentration which is not available.

An analysis of the experimental results indicates that the composition-induced changes of the band ordering in PbSnTe may result in the mid-gap position of the Gd$^{2+/3+}$ level for $y = 0.45 \div 0.65$, therefore creating a semi-insulating system. We have observed unusually low concentrations of carriers $n \approx 5 \times 10^{18}$ cm$^{-3}$ and low carrier mobilities $\mu \approx 10$ cm$^2/(V \cdot s)$ in the crystals with $y = 0.53$. They, however, possess semi-metallic electric properties, i.e., show finite temperature-independent low temperature conductivity. In the set of samples studied by us we found no definite experimental evidence for the formation of the semi-insulating state. It is yet not clear whether it is a matter of precise choice of the chemical composition of the alloy or it is related to the very narrow energy gap of PbSnGdTe expected for this composition range, $E_g \leq 50$ meV. The energy gap may be of the order of the width of the density of states related to the Gd$^{2+/3+}$ energy states. Also the fluctuations of the energy of the band edges due to disorder present in the electronic system of PbSnGdTe may be an important factor.

In conclusion, we presented the experimental results and the physical model of the Sn composition dependence of the transport and magnetic properties of PbSnGdTe mixed crystals. The key element of the proposed interpretation of experimental results is the continuous shift of the Gd$^{2+/3+}$ energy level from the position high above the bottom of the conduction band in PbTe-based PbSnGdTe crystals to the position of about 0.2 eV below the top of the valence band for the SnTe-based crystals. The magnetic susceptibility measurements show the existence of only very weak $f-f$ exchange interaction between Gd ions.

This work was supported in part by the Committee for Scientific Research grant 2 P03 B 103 08.

References