Vol. **114** (2008) *ACTA PHYSICA POLONICA A* No. 5

Proc. XXXVII International School of Semiconducting Compounds, Jaszowiec 2008

AC Magnetic Susceptibility Studies of $Ge_{1-x-y}Sn_xMn_yTe$ Mixed Crystals

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We present preliminary studies of magnetic and transport properties of $Ge_{1-x-y}Sn_xMn_yTe$ mixed crystals with $0.091 \leq x \leq 0.105$ and $0.012 \leq y \leq 0.115$. Qualitative analysis of our experimental results showed the appearance of a spin-glass phase at $T < 50$ K. The transport characterization (resistivity and Hall effect measurements) showed that the investigated samples had semimetallic p-type conductivity with relatively large carrier concentrations ($p > 10^{21}$ cm^{-3}) and low mobilities ($\mu < 100$ cm^2 V^{-1} s^{-1}). The dependence of transport properties on the chemical composition of the samples was observed.

PACS numbers: 72.20.Fr, 72.80.Ga, 75.40.Gb, 75.50.Lk, 75.50.Pp

1. Introduction

Among many IV–VI compounds, PbTe, SnTe, and GeTe were the subject of considerable interest in the last decade. They offer very interesting physical properties, one of which is the possibility to tune carrier concentrations via changes in stoichiometry. They are also very interesting from the applicable point of view due to the possibility to utilize them in, e.g., optoelectronic [1] or thermoelectric [2] devices. Moreover, the addition of magnetic ions (such as Mn or Eu) further extends their possible applications. Studies of IV–VI compounds revealed the presence of the carrier induced ferromagnetism caused by the RKKY interaction [3, 4] enabling them to be used for future spintronic applications [5].

In this paper, we studied the effects of alloying GeTe with SnTe and MnTe on transport and magnetic properties of the resultant $Ge_{1-x-y}Sn_xMn_yTe$ alloy. Studying the quaternary compound, we expect to observe magnetic and transport properties originating from its two constituents: $Ge_{1-x}Mn_xTe$ and $Sn_{1-x}Mn_xTe$ ternary alloys. Both GeTe and SnTe compounds are characterized by the small energy gap (0.23 eV and 0.18 eV, respectively) [6, 7]. They crystallize in the

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NaCl structure distorted to the rhombohedral symmetry at temperatures below 720 K for GeTe [8] and 160 K for SnTe [9]. High carrier concentrations and the appearance of various magnetic phases were also reported in these compounds. The existence of a ferromagnetic phase with T_C up to 160 K in $Ge_{1-x}Mn_xTe$ [10] and 17 K in $Sn_{1-x}Mn_xTe$ [9] is the most interesting from the applicable point of view.

2. Experimental results and discussion

2.1. Sample preparation and basic characterization

The investigated $Ge_{1-x-y}Sn_xMn_yTe$ crystals were grown using a modified Bridgman method. The ingots were cut into thin slices (about 1 mm thick) perpendicular to the growth direction. The chemical composition of the samples was determined using X-ray dispersive fluorescence spectroscopy (see Table). A typical uncertainty of this method is about 10%.

TABLE

Results of the basic sample characterization including substitutional ions content x and y, resistivity ρ_{xx}, and carrier concentration n measured at 300 K, spin-glass transition temperature T_g, and factor R.

x Sn	y Mn	ρ_{xx} (10^{-5}) [Ω cm]	n (10^{21}) [cm^{-3}]	T_g [K]	R
0.105	0.012	4.78	1.30	9.77	0.025
0.103	0.041	13.8	1.44	23.51	0.010
0.092	0.058	7.69	2.23	27.14	0.015
0.094	0.079	12.6	1.14	45.11	0.005
0.091	0.115	6.03	4.08	29.91	0.016

The crystallographic quality of the studied samples was determined using X-ray diffraction (XRD) spectroscopy technique. The obtained diffractograms showed that the samples were monocrystalline. The crystallographic parameters were determined using the standard powder XRD technique. No other peaks except these attributed to GeTe were found indicating that the studied compound was a single phase. All the investigated samples crystallized in the NaCl crystal structure distorted in [111] direction ($R3mh$ symmetry group with Wyckoff indexes *edba*) similarly as their host GeTe crystals [11]. The diffractograms were fitted using the Rietveld method in order to determine the crystallographic parameters of the studied crystals. The lattice parameters showed small (around 1%) variations from the values reported for GeTe: lattice constant $a = 5.987$ Å and angle of distortion $\alpha = 88.3°$ [11].

The transport characterization was performed using a standard six contact DC current technique. Such configuration allowed us to measure simultaneously the voltage drop along the direction parallel (U_{xx}) and perpendicular (U_{xy}) to the current direction. Due to this, we were able to determine the resistivity of the sample ρ_{xx}, carrier concentration n, and carrier mobility μ. Transport measurements were performed at temperatures between 4.2 K and 300 K. The Hall effect was measured in a constant magnetic field $B = 1.4$ T.

The resistivity vs. temperature dependence (typical result shown in Fig. 1) for all the investigated samples has the shape characteristic of degenerate semiconductors (i.e., an increase in ρ_{xx} with temperature). The resistivity shows small changes with temperature (30–40%). However, at temperatures $T \leq 50$ K we observed minimum in $\rho_{xx}(T)$ curves which is not a common feature of degenerate semiconductors. The values of ρ_{xx} determined at room temperature (see Table) varies in the range between 4.78×10^{-5} Ω cm for the sample with $y = 0.012$ and 1.38×10^{-4} Ω cm for the sample with $y = 0.041$. We did not observe any clear trend in variation of ρ_{xx} with chemical composition of the alloy.

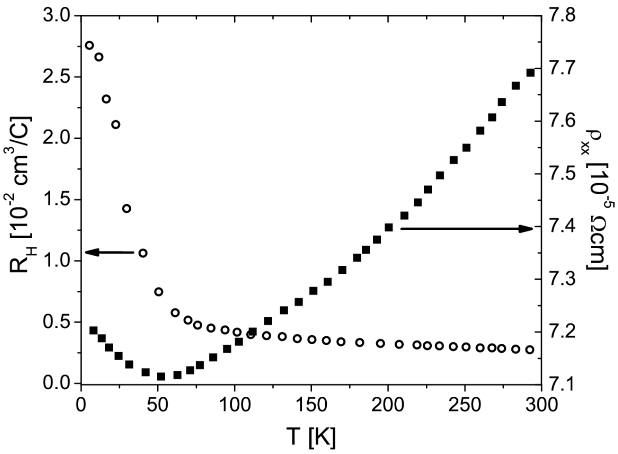

Fig. 1. Resistivity ρ_{xx} and Hall constant $R_{\rm H}$ as a function of temperature measured for $Ge_{0.85}Sn_{0.092}Mn_{0.058}Te$ sample.

The results of the Hall effect measurements showed that all studied samples exhibited p-type conductivity with relatively high hole concentrations $n = 1/eR_{\rm H}$ varying between 1.14×10^{21} cm^{-3} for the sample with $y = 0.079$ up to 4.08×10^{21} cm^{-3} for the sample with $y = 0.115$ (see Table). Table shows that generally n increases with the Mn content in the alloy. The temperature measurements of the Hall carrier concentration revealed large n variations for all the studied samples at low temperatures, $T < 100$ K (see Fig. 1). However, in the diluted magnetic semiconductors at temperatures below the transition to the magnetic ordered phase the total Hall effect can be strongly influenced by the anomalous Hall effect. Due to this fact, it is reasonable to analyze the Hall effect data taken for $T > 100$ K. Comparing n values at $T = 100$ K and 300 K, we did not observe large changes of n for the samples with $y \leq 0.058$. For the samples with Mn content higher than $y = 0.06$ we observed a significant increase in the Hall carrier concentration with temperature (n(300 K)/n(100 K)$\approx$ 4).

2.2. Magnetic investigations

The magnetic properties of $Ge_{1-x-y}Sn_xMn_yTe$ alloy were studied using the AC magnetometer (mutual inductance method). This technique allowed us to determine both real χ' and imaginary χ'' parts of the linear AC magnetic susceptibility. The studies were carried out in the temperature range between 4.2 K and 300 K. The magnetic measurements were performed applying the magnetic field of frequency $f = 625$ Hz and amplitude $H_{AC} = 0.5$ Oe. The results of measurements of AC magnetic susceptibility χ as a function of temperature for a few selected $Ge_{1-x-y}Sn_xMn_yTe$ samples are presented in Fig. 2.

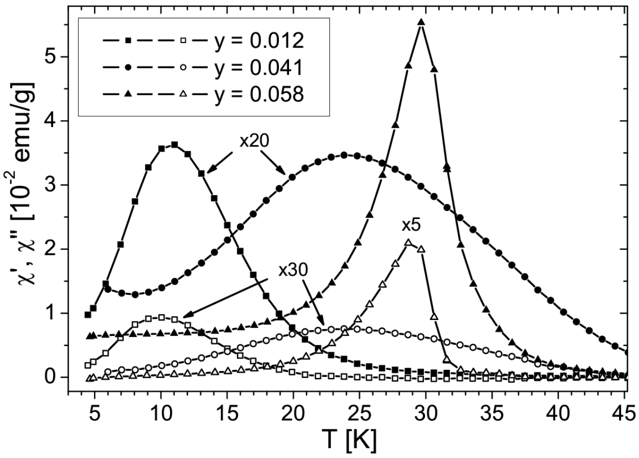

Fig. 2. Real (closed symbols) and imaginary (open symbols) parts of linear AC magnetic susceptibility measured as a function of temperature for a few selected $Ge_{1-x-y}Sn_xMn_yTe$ samples with different Mn molar fraction y (shown in legend).

One can see that for all the studied samples both parts of the AC magnetic susceptibility χ exhibited maximum at low temperatures. Usually the presence of cusps in both parts of χ indicates the appearance of magnetic phase transition in the studied alloy. The values of χ' near maximum are around 10^{-3} emu/g for samples with $y \leq 0.041$ (broad and symmetric cusp), while for Mn content $y \geq 0.058$ are around 10^{-2} emu/g (narrow and asymmetric cusp). The observed critical behavior of χ may be attributed to the transition from paramagnetic phase to various magnetic phases (e.g., ferromagnetic, antiferromagnetic, superparamagnetic, or spin-glass). The vanishing of both χ' and χ'' observed below the very broad maximum is not typical of the ferromagnetic phase. However, the positive values of the Curie–Weiss temperature $\Theta \approx 25.4-41.5$ K (determined from the extrapolation of the $\chi'^{-1}(T)$ curve) indicate that ferromagnetic interactions play a dominant role in determining the magnetic behavior of the $Ge_{1-x-y}Sn_xMn_yTe$ system.

In order to experimentally determine the nature of the observed transitions, we performed measurements of both χ' and χ'' as a function of temperature for a few selected frequencies varying between 7 Hz and 9970 Hz and amplitudes changing between 0.5 Oe and 5 Oe. Exemplary results of χ' vs. temperature measurements for different frequencies are presented in Fig. 3.

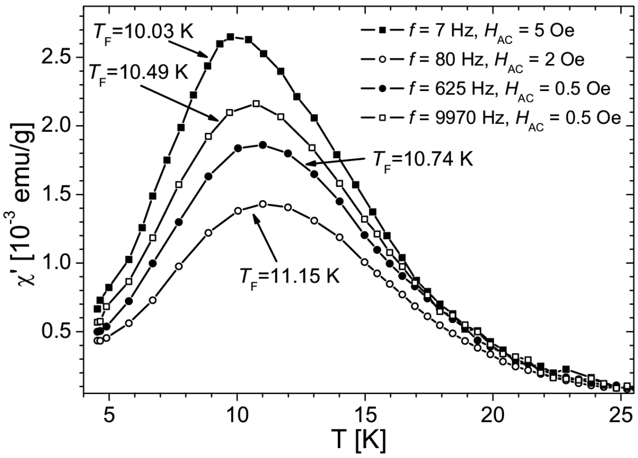

Fig. 3. The in-phase part of linear AC magnetic susceptibility χ' as a function of temperature measured for different AC magnetic field frequencies and amplitudes (shown in legend) for $Ge_{0.883}Sn_{0.105}Mn_{0.012}Te$ sample.

As we can see in Fig. 3, the cusp in χ' shifts towards higher temperatures with increasing frequency. The same tendency was observed in the χ'' vs. temperature dependence. Frequency shift of the linear AC magnetic susceptibilities is a common feature of the magnetically inhomogeneous systems, such as spin-glasses, cluster-glasses, or superparamagnetics. The factor $R = \Delta T_F/(T_F \log(\Delta f))$ proposed by Mydosh [12], where T_F is the freezing temperature, defined as the temperature position of the maximum in χ', is usually used for the determination of the type of the observed phase transitions. The parameter R describes the cusp shift per decade of frequency. The values of R calculated for investigated $Ge_{1-x-y}Sn_xMn_yTe$ samples are gathered in Table. According to Mydosh [12], the values of R for canonical spin-glass systems are around 0.01, while for superparamagnetic compounds R is usually higher than 0.1. The inspection of Table shows that the values of R are not exceeding 0.025. This indicates that cusps in both parts of χ can be attributed to the appearance of a spin-glass phase at temperatures $T \leq 50$ K.

The spin-glass transition temperature T_g is an equivalent of the freezing temperature measured in $f \to 0$. The value of T_g can be determined from the extrapolation of the T_F vs. f dependence to zero frequency. The values of the spin-glass transition temperatures T_g determined in the way presented above are listed in Table. The obtained values of T_g are composition dependent changing between 9.77 K and 45.11 K for samples with $y = 0.012$ and 0.079, respectively. One can see that the spin-glass transition temperature is increasing with Mn molar fraction y for $y \leq 0.078$. For the sample with the highest Mn content the decrease in T_g was observed.

3. Summary

We reported the results of experimental studies of $Ge_{1-x-y}Sn_xMn_yTe$ mixed crystals including magnetic and transport properties.

The transport characterization revealed, typical of this class of compounds, metallic ($\rho_{xx} \leq 10^{-4}$ Ω cm) p-type conductivity with relatively large hole concentrations $n \geq 10^{21}$ cm^{-3} and low carrier mobilities $\mu \leq 100$ cm^2/(V s). We have observed that the transport properties were composition dependent. We have also observed large changes of n with temperature for the samples with $y \geq 0.078$.

The magnetic investigations showed the appearance of the magnetic phase transition which in the studied $Ge_{1-x-y}Sn_xMn_yTe$ samples takes place at temperatures $T \leq 50$ K. Experimental investigations of the frequency shift of the cusp in the $\chi'_1(T)$ curves connected with the quantitative analysis of the obtained results showed that the observed critical behavior of magnetic susceptibility can be attributed to the paramagnet–spin-glass transition. Thus, via alloying we were able to tune the temperature of the spin-glass transition in the range $T = 10-50$ K.

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