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# Magnetic Properties of $Sn_{1-x}Cr_xTe$ Diluted Magnetic Semiconductors

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We present the studies of $Sn_{1-x}Cr_xTe$ semimagnetic semiconductors with chemical composition $x$ ranging from 0.004 to 0.012. The structural characterization indicates that even at low average Cr-content $x \leq 0.012$, the aggregation into micrometer size clusters appears in our samples. The magnetic properties are affected by the presence of clusters. In all our samples we observe the transition into the ordered state at temperatures between 130 and 140 K. The analysis of both static and dynamic magnetic susceptibility data indicates that the spin-glass-like state is observed in our samples. The addition of Cr to the alloy seems to shift the spin-glass-like transition from 130 K for $x = 0.004$ to 140 K for $x = 0.012$.

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## 1. Introduction

The transition metal alloyed IV–VI semiconductors are an intensively studied group of diluted magnetic semiconductors [1] due to the presence of itinerant ferromagnetism with the Curie temperatures, $T_C$, as high as 200 K for $Ge_{0.92}Mn_{0.08}Te$ [2]. The Mn alloying of SnTe crystals was also intensively studied [3–5] revealing itinerant ferromagnetism with $T_C$ ranging from 3 K up to 16 K for Mn-content, $x$, changing from 0.03 to 0.1, respectively [6–8]. The problem of alloying of IV–VI materials with chromium ions has not yet been well explored. The solubility of chromium in IV–VI materials is less than 0.01 in bulk PbTe [9] and up to about 0.06 in bulk GeTe [10, 11]. This is low comparing to Mn-doped IV–VI semiconductors. However, in $Ge_{1-x}Cr_xTe$ transition temperatures as high as 60 K for bulk crystals [10, 11] and 180 K for thin films [12] were observed. Chromium introduced into IV–VI semiconductor matrix may appear in mixed valence state: $Cr^{2+}$ with magnetic moment $J = S = 2$ (see Ref. [13]) and $Cr^{3+}$ with $J = S = 3/2$ (see Ref. [9]).

In the present paper we started investigating the problem of alloying SnTe with relatively small Cr-content, $x$ below 0.012. We wanted to see whether chromium can be successfully introduced into the SnTe lattice and explore the main exchange mechanisms in $Sn_{1-x}Cr_xTe$ alloy. In particular we would like to compare the magnetic properties of $Sn_{1-x}Cr_xTe$ to those of $Sn_{1-x}Mn_xTe$.

## 2. Basic characterization

The $Sn_{1-x}Cr_xTe$ crystals being the subject of the current research were synthesized with the use of the modified Bridgman method. The modifications of the growth procedure were similar to the ones applied for the growth of alumina crystals [14]. The modifications consisted of the presence of additional heating elements creating radial temperature gradients present in the growth furnace. This improved the crystal quality and thus reduced the number of individual crystal blocks in the as grown ingot from a few down to a single one.

The chemical composition of our samples was studied with the use of energy dispersive X-ray fluorescence technique (EDXRF). This method allows the determination of chemical composition of the alloy with maximum relative errors in the molar fraction of alloying elements, $x$, not exceeding 10%. The results of the EDXRF measurements show that the chemical composition of our $Sn_{1-x}Cr_xTe$ samples changes in the range of $0.004 \leq x \leq 0.012$. We focus, therefore, on samples of low chromium content due to the probable low solubility of Cr in SnTe.

The crystallographic quality of the $Sn_{1-x-y}Cr_xEu_yTe$ samples was studied with the use of a standard powder X-ray diffraction method (XRD). The XRD measurements were done at room temperature using Siemens D5000 diffractometer. The Rietveld refinement method was used in order to calculate the crystallographic parameters of our samples. The obtained XRD results indicate the presence of a single cubic NaCl phase in our samples. The lattice parameter $a$, calculated using the Rietveld method is close to the value for SnTe crystals, i.e. $a = 6.327$ Å [15].

The Hitachi SU-70 Analytical ultrahigh resolution field emission scanning electron microscope (SEM) coupled with Thermo Fisher NSS 312 energy dispersive X-ray spectrometer (EDS) equipped with SDD-type detector was used in order to study chemical homogeneity of our $Sn_{1-x}Cr_xTe$ samples. A series of SEM micrographs

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done for our samples indicates the presence of microscopic regions (see Fig. 1) with the chemical composition different than the bulk of the crystal. Detailed measurements showed that the longitudinal precipitations of $Sn_{1-x}Cr_xTe$ with rather high Cr-content, $x \approx 0.25 \pm 0.03$, usually have a diameter of 1–2 $\mu$m and a length of up to 10–15 $\mu$m. Using the EDS microprobe, a series of surface maps with dimensions of $100 \times 100$ $\mu m^2$ was done for our $Sn_{1-x}Cr_xTe$ samples with different chemical composition, $x$. The results of these measurements show clearly that about $20 \pm 5\%$ of all the chromium ions do not form clusters and are most probably distributed randomly in the semiconductor lattice. It should be noted, however, that the limited resolution of the EDS microprobe (less than 1 $\mu$m) cannot definitely rule out the existence of clusters of chromium with sizes much smaller than 1 $\mu$m.

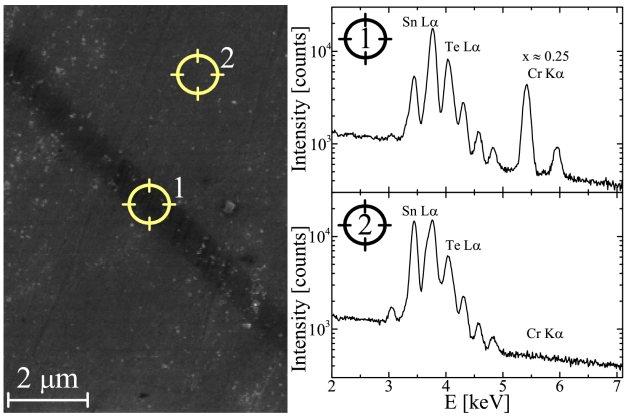


Fig. 1. The scanning electron microscope micrograph of the sample surface and the X-ray fluorescence spectra measured at selected spots of the selected $Sn_{0.988}Cr_{0.012}Te$ sample.

A basic magnetotransport characterization of our samples was performed. We used the standard six contact DC current Hall effect technique. The Hall effect measurements were done over the temperature range from 4.3 K up to 300 K in the presence of a constant magnetic field of induction not exceeding $B = 1.5$ T. The measurements indicate that in our samples the resistivity $\rho_{xx}$ as a function of the temperature is typical of degenerate semiconductors. The Hall effect measurements show that our samples have $p$-type conductivity with relatively high carrier concentration $n \approx 2 \times 10^{20}$ cm$^{-3}$ and the Hall mobility $\mu$ equal to 400 cm$^2$/(V s) at $T = 4.3$ K slowly decreasing as a function of the temperature down to $\mu = 130$ cm$^2$/(V s) at $T = 300$ K. The mobility reduction with increasing the temperature is an obvious consequence of phonon scattering increase in the $Sn_{1-x}Cr_xTe$ lattice.

### 3. Magnetic properties

Magnetic properties of our samples were studied with the use of LakeShore 7229 magnetometer/susceptometer system and Quantum Design XL-5 magnetometer.

At first, the detailed measurements of the magnetization, $M$, were performed over a wide temperature range from 2 K up to 250 K. During the measurements, the sample was put into the magnetic field $B$ with 3 different values 5, 10, and 20 mT. The $M(T)$ measurements were performed under two conditions at which the sample cooling was performed: (i) in the presence of the external magnetic field (FC — field curves) and (ii) in the absence of an external magnetic field (ZFC — zero field curves). Corrections were made for the magnetic contribution of the sample holder.

The results of the measurements are presented in Fig. 2. Our results indicate the presence of a magnetic transition in the $Sn_{1-x}Cr_xTe$ crystals, slightly increasing as a function of Cr content, $x$, from 130 for $x = 0.004$ up to about 140 K for $x = 0.012$. The ZFC magnetization, $M$, at $T < 120$ K decreases with decrease of the temperature indicating that we observe spin-glass-like, superparamagnetic, or possibly antiferromagnetic state in our samples. However, a more detailed interpretation of the observed data can be done using the static magnetic susceptibility.

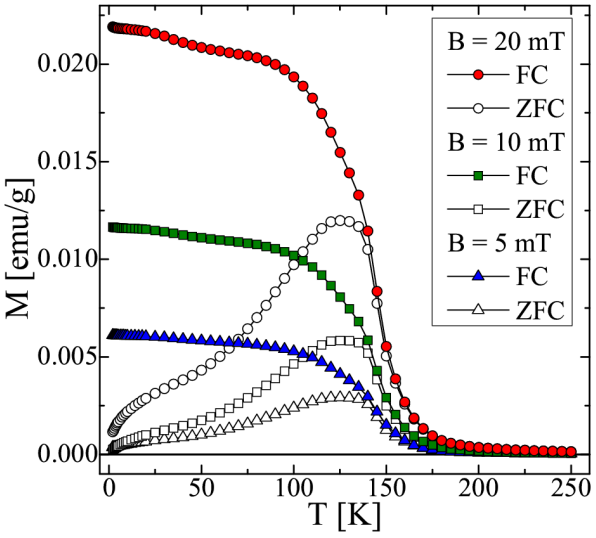


Fig. 2. The magnetization $M$ as a function of temperature measured at selected magnetic fields $B$ with the sample cooled in the absence (ZFC curves) and in the presence of an external magnetic field (FC curves) for the selected $Sn_{0.988}Cr_{0.012}Te$ sample.

The DC magnetic susceptibility $\chi_{DC}$ can be calculated as $\frac{\delta M}{\delta B}\big|_{T=\text{const}}$ for both ZFC and FC $M(T)$ curves. The results of our calculation in a form of temperature dependences of both ZFC and FC static susceptibility $\chi_{DC}$ are presented in Fig. 3. The ZFC static magnetic susceptibility $\chi_{DC}$ shows a maximum between 130 and 140 K, which is a signature of a presence of a magnetic order in our samples. The shape of the $\chi_{DC}(T)$ shows the large bifurcations between the FC and ZFC curve for $T < 120$ K. It indicates that we do not observe clear ferromagnetic alignment in our samples. It is difficult to determine the

type of magnetic phase only from the behavior of the magnetic susceptibility, $\chi_{DC}$, versus temperature. The problem of distinguishing between the spin glass and superparamagnetic phase transition cannot be solved by measuring a difference between magnetic susceptibilities in ZFC and FC conditions.

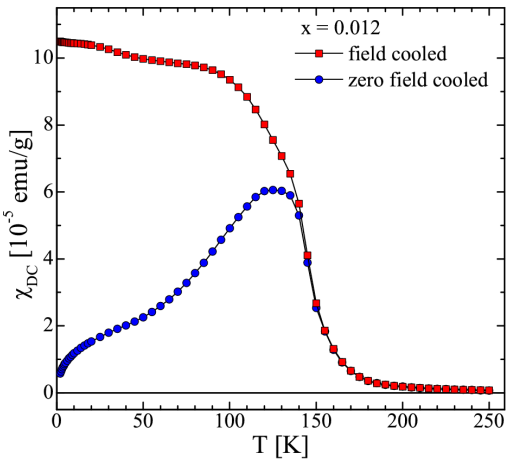


Fig. 3. The static magnetic susceptibility as a function of the temperature measured with sample cooled in the absence (ZFC curve) and in the presence of an external magnetic field (FC curve) for the selected $Sn_{0.988}Cr_{0.012}Te$ sample.

In order to determine the type of magnetic ordering in the studied material, the measurements of the AC magnetic susceptibility as a function of temperature for different magnetic field amplitudes and frequencies were performed. The dynamic magnetic properties of our $Sn_{1-x}Cr_xTe$ samples were studied with the use of LakeShore 7229 magnetometer system. The measurements of the temperature dependence of the dynamic magnetic susceptibility $\chi_{AC}$ were done in the presence of an alternating magnetic field with four different frequencies $f$ equal to 7, 80, 625, and 9970 Hz and the amplitude $H_{AC}$ equal to 20 Oe for $f \leq 625$ Hz and $H_{AC} = 1$ Oe for $f = 9970$ Hz. For example, the real part of the AC magnetic susceptibility, $\chi_{AC}$, is shown in Fig. 4. The data presented in Fig. 4 indicate the slight shift of the maxima in the $\chi_{AC}(T)$ dependences towards higher temperatures with an increase in the AC magnetic field frequency. Such behavior is a signature of either superparamagnetic or spin-glass-like state in the material. The simplest way to decide between the two above magnetic states can be done with the use of the phenomenological factor, $R$, defined by Mydosh [16]. The frequency shifting of the peak in the dynamic susceptibility at the temperature scale can be expressed as

$$R = \frac{\Delta T_F}{T_F \log(\Delta f)}, \tag{1}$$

where $\Delta T_F = T_F(f_1) - T_F(f_2)$ is the difference between freezing temperatures determined at frequencies $f_1$ and $f_2$, respectively, and $\Delta f = f_2 - f_1$. The calculated values of $R$ for our samples are similar and close to 0.02. Such a value (smaller than $R = 0.1$) indicates that we observe the spin-glass-like state in our samples.

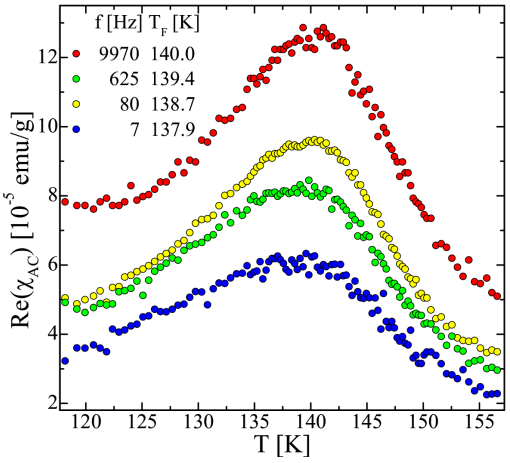


Fig. 4. The dynamic magnetic susceptibility as a function of the temperature measured at four selected frequencies of the alternating magnetic field for the selected $Sn_{0.988}Cr_{0.012}Te$ sample.

For all our $Sn_{1-x}Cr_xTe$ samples we can distinguish two magnetic subsystems, i.e., clusters with a high content of chromium around $x = 0.25 \pm 0.03$ and the bulk matrix with randomly distributed Cr ions having the concentration equal to about $20 \pm 5\%$ of the average composition $x$. We believe that the spin-glass-like state observed in our samples cannot be associated with itinerant ferromagnetism. In the case of $Ge_{1-x}Cr_xTe$ [10] and $Ge_{1-x}Mn_xTe$ [17] crystals the conducting carrier–magnetic ion exchange constant values are similar. Let us assume that the value of the conducting hole–Cr ion exchange constant in $Sn_{1-x}Cr_xTe$ is close to $J_{pd} = 0.1$ eV, known for $Sn_{1-x}Mn_xTe$ system [7]. For $J_{pd} = 0.1$ eV both magnetic subsystems present in our samples would not be able to form a spin-glass-like state with freezing temperatures of the order of 130–140 K. Therefore, we believe that the direct magnetic interactions within the clusters together with the presence of a strong structural disorder are responsible for the observed magnetic state.

## 4. Summary

The presence of Cr-ion rich regions (with about 20–25 mol.% of Cr) is observed in $Sn_{1-x}Cr_xTe$ crystals with low chromium content, $x$, ranging from 0.004 up to 0.012. The inhomogeneities are not related to any $Cr_{1-\delta}Te$ phases. The Cr solubility in SnTe seems to be lower than $x = 0.01$. For all our samples, only about 20% of all chromium ions are distributed randomly in the host semiconductor. The magnetic properties of the alloy are dominated by the presence of inhomogeneities. The spin-glass-like state at $T < 130$ K is identified in all our samples, with the transition temperature changing

by about 10 K with increasing the average Cr-content, $x$. The observed spin-glass-like state is present at temperatures about an order of magnitude higher than the Curie temperatures, $T_C$, reported by various authors in the literature for homogeneous $Sn_{1-x}Mn_xTe$ crystals, in which the carrier mediated ferromagnetism is observed. The magnetic properties of $Sn_{1-x}Cr_xTe$ resemble more those of $Ge_{1-x}Cr_xTe$ than of $Sn_{1-x}Mn_xTe$. We believe that the short range direct magnetic interactions present in Cr-rich clusters are responsible for the observed spin--glass-like state.

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