Magnetic interactions in Ge$_{1-x}$Eu$_x$Te semiconductors: random distribution of magnetic Eu ions versus spinodal decompositions

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Abstract

We present the studies of structural, magnetotransport, and magnetic properties of Ge$_{1-x}$Eu$_x$Te bulk crystals with the chemical composition, $x$, changing from 0.008 to 0.025. For the samples with $x > 0.015$ the sample synthesis leads to formation of Ge$_{1-x}$Eu$_x$Te spinodal decompositions with a broad range of chemical contents. The presence of Ge$_{1-x}$Eu$_x$Te spinodal decompositions is responsible for the antiferromagnetic order in our samples with $x > 0.015$. For the samples with $x < 0.015$ the structural characterization shows no evidence for clusters, the samples are paramagnetic, but the analysis of the results of magnetic measurements indicates deviations from the random distribution of Eu ions.

1. Introduction

Among many studied IV–VI transition-metal-doped diluted magnetic semiconductors (DMS) GeTe compounds attracted significant attention during the past ten years [1–5]. Large scientific interest devoted to the studies of GeTe-based DMS is due to high Curie temperatures, $T_C$, attributed to carrier-induced ferromagnetic interactions. For Ge$_{1-x}$Mn$_x$Te the highest $T_C$ value was about 190 K [3, 4] and for Ge$_{1-x}$Cr$_x$Te about 180 K [5]. However, there have been no systematic investigations of GeTe doped with rare-earth ions. The present paper extends our earlier studies of Ge$_{1-x}$Eu$_x$Te crystals with $0.020 \leq x \leq 0.025$ [6] and is a continuation of the studies of magnetic properties of Eu-codoped Ge$_{1-x}$Mn$_x$Te [7] and Ge$_{1-x}$Cr$_x$Te [8] with the Eu content up to 0.04. Studies of DMS systems with more than one magnetic element are difficult due to problems with distinguishing different magnetic subsystems and interpreting the high Curie temperatures about 150 K for Ge$_{1-x-\gamma}$Mn$_x$Eu$_\gamma$Te and 80 K for Ge$_{1-x-\gamma}$Cr$_x$Eu$_\gamma$Te. Moreover, in all materials listed above there was a strong tendency to form different types of magnetic clusters. The clusters modified significantly the properties of the materials. Similar behavior was observed before in Sn$_{1-x}$Eu$_x$Te, where Eu clusters were detected for $x$ above 0.013 [9].

In the present paper we investigate magnetic interactions in Ge$_{1-x}$Eu$_x$Te crystals with the Eu-content, $x \leq 0.025$. We look at the influence of clusters and inhomogeneities on the magnetic properties of Ge$_{1-x}$Eu$_x$Te. We pay special attention to the problem of limited solubility of europium in the GeTe lattice. Our studies aim at an estimation of the limits of the Eu content in which the Ge$_{1-x}$Eu$_x$Te compounds are uniform DMS.

2. Sample preparation

We studied Ge$_{1-x}$Eu$_x$Te bulk crystals grown by the modified Bridgman method. We modified the Bridgman growth furnace introducing changes made by Aust and Chalmers in order to improve the structural quality of alumina crystals [10]. We installed the additional heating elements in the standard vertical Bridgman–Stockbarger system in order to create radial temperature gradient in addition to the longitudinal temperature gradient in the crystallization zone. The applied modification changed the angle between the crystallization front
observed three phases: of crystal blocks in the as-grown ingots from a few down to a single one. probably related to EuTe clusters, and

3. Structural characterization and the growth direction by about 15°. This angle was measured as the deviation of the normal to the end face of the cylindrical ingot from the axis of the cylinder. The modifications of the growth process reduced the number of crystal blocks in the as-grown ingots from a few down to a single one.

| x     | Ge$_{1-x}$Eu$_x$Te | EuTe | Ge  |
|-------|-------------------|------|-----|
| a$_1$ [Å] | α [deg] | a$_2$[Å] | [%] | a$_3$ [Å] | [%] |
| 0.025(1) | 5.98220 | 88.28826 | 6.5966(6) | 1.6(1) | 5.6566(3) | 1.3(1) |
| 0.023(1) | 5.98086 | 88.25981 | 6.5959(7) | 0.9(1) | 5.6554(8) | 0.3(1) |
| 0.020(1) | 5.980802 | 88.25692 | 6.5963(8) | 1.8(1) | 5.6571(1) | 1.2(1) |
| 0.015(1) | 5.977533 | 88.27498 | — | — | 5.6469(3) | 9.7(1) |

Results of the HRXRD characterization of the Ge$_{1-x}$Eu$_x$Te samples with different chemical Eu contents, x, including the crystallographic parameters of the detected Ge$_{1-x}$Eu$_x$Te, EuTe and Ge phases, i.e. the lattice parameters a$_1$, a$_2$, and a$_3$, the angle of rhombohedral distortion α, and the estimated phase content.

Table 1. Results of the HRXRD characterization of the Ge$_{1-x}$Eu$_x$Te samples with different chemical Eu contents, x, including the crystallographic parameters of the detected Ge$_{1-x}$Eu$_x$Te, EuTe and Ge phases, i.e. the lattice parameters a$_1$, a$_2$, and a$_3$, the angle of rhombohedral distortion α, and the estimated phase content.

The as-grown Ge$_{1-x}$Eu$_x$Te ingot was cut into 1.5 mm thick slices along the plane perpendicular to the growth direction. The crystal slices were not subjected to post-growth annealing. We performed chemical composition measurements for all our Ge$_{1-x}$Eu$_x$Te crystal slices with the use of the energy dispersive x-ray fluorescence (EDXRF) technique. The EDXRF measurements were done with the use of the Tracor x-ray Spectrace 5000 EDXRF spectrometer. The intensity analysis of the EDXRF data allows the calculation of the average values of the Eu content, x, with the maximum relative error not exceeding 10% of the x value. As a result of the EDXRF data analysis we obtained molar fractions of each element in the studied Ge$_{1-x}$Eu$_x$Te ingot within the limits of the accuracy of the EDXRF method. The EDXRF results show that our samples have the correct stoichiometry of the Ge$_{1-x}$Eu$_x$Te alloy. From all the crystal slices we selected for further studies several samples in which the x values, gathered in table 1, changed from 0.008 up to 0.025. We will refer to these x values as chemical x values, because from the magnetic measurements we obtained for several samples different x values, x$_{po}$ which correspond to the number of magnetically active Eu ions.

We studied the crystallographic parameters of Ge$_{1-x}$Eu$_x$Te crystals with the use of the high resolution x-ray diffraction method (HRXRD). Measurements were done on powdered samples using the X’Pert MPD Pro Alpha1, Panalytical diffractometer (Cu K$_{α1}$ with λ = 1.540598 Å). The used X’Pert diffractometer utilizes the Bragg-Brentano geometry modified through installation of the Johansson Ge(111) monochromator in the incident beam and a linear semiconductor strip detector. The HRXRD diffraction patterns were measured during 20 h each in the 5 to 160 2θ range. Our diffractometer has high sensitivity and reflections of intensity as low as 0.06% can be detected. The obtained HRXRD patterns were analysed by using the Rietveld refinement method. This procedure allows to determine the crystal system, Bravais lattice, and to calculate the unit cell parameters. The selected HRXRD diffraction patterns for the Ge$_{1-x}$Eu$_x$Te samples with different chemical compositions, x, are presented in figure 1.

The Rietveld phase analysis of the obtained HRXRD patterns shows that for the samples with x ≥ 0.020 we observed three phases: (i) main rhombohedral NaCl structure related to GeTe, (ii) cubic NaCl structure most probably related to EuTe clusters, and (iii) cubic structure related to Ge inclusions. In contrast, for the samples with x ≤ 0.015, we observed the rhombohedral NaCl phase and a small concentration of Ge inclusions is observed. The rock salt structure of the EuTe clusters may be related to the fact that the rhombohedral deformation of the NaCl structure in IV–VI semiconductors occurs at temperatures inversely proportional to the cation mass. The transition from the cubic to the rhombohedral phase for GeTe is at about 700 K [11], for SnTe is below 100 K, (down to zero for high carrier concentrations) [12, 13], and PbTe is always cubic. Eu is heavier than Sn and much heavier than Ge, therefore clusters may have a tendency to preserve their rocksalt structure even in a slightly distorted environment. The lattice parameters of the observed phases are gathered in table 1. The most important fact is related to the small increase of the lattice parameter of the GeTe phase with x. It is a signature of the introduction of Eu ions (with much larger ionic radius than Ge ions) into the substitutional Ge sites in the GeTe lattice.

The structural homogeneity of our Ge$_{1-x}$Eu$_x$Te crystals was studied with the use of the Hitachi SU-70 Analytical UHR FE-SEM scanning electron microscope (SEM) coupled with Thermo Fisher NSS energy dispersive x-ray spectrometer (EDS) equipped with SDD-type detector. Prior to the SEM/EDS measurements we polished and chemically cleaned the sample surfaces of a few Ge$_{1-x}$Eu$_x$Te samples with different chemical compositions. We measured a series of high resolution SEM images of the crystal surface at different sample
spots and magnifications. Our SEM studies reveal the presence of micrometer-size inhomogeneities in the Ge\(_{1-x}\)Eu\(_x\)Te samples. The results for the sample with \(x = 0.015\) are presented in figure 2.

Our SEM results reveal that Ge\(_{1-x}\)Eu\(_x\)Te samples with \(x \geq 0.015\) contain Ge\(_{1-x}\)Eu\(_x\)Te spinodal decompositions. These inhomogeneities, most probably preserving the lattice structure of the host lattice, have Eu content much higher than the average \(x\) value. For all our samples the Ge\(_{1-x}\)Eu\(_x\)Te spinodal decompositions are accompanied with the presence of Ge clusters, randomly distributed in the host lattice. Eu diffusion in GeTe lattice at \(T \leq 300\) K is negligible and all the Ge\(_{1-x}\)Eu\(_x\)Te spinodal decompositions are created during the sample growth. It is also very probable that the presence of EuTe clusters may create Te deficiencies, which in turn can...
lead to the formation of Ge clusters. For the sample with \( x < 0.015 \) EuTe inhomogeneities are not observed. The \( \text{Ge}_{1-x}\text{Eu}_x\text{Te} \) spinodal decompositions have shapes of pillars with the average diameter of about 10 µm and length broadly distributed ranging from 100 µm up to about 200 µm. Our SEM/EDS studies consisted of measurements of EDS spectra made at several spots of the \( \text{Ge}_{1-x}\text{Eu}_x\text{Te} \) sample surface. The EDS results show that the Eu contents of the spinodal decompositions differ significantly between individual clusters. It might, however, be due to the fact that EDS probes not only the sample surface. The intersection of each individual cluster may have a crucial impact on the estimated microscopic chemical composition. It is therefore reasonable to assume the highest observed Eu content to be the most accurately measured. On the other hand for the homogeneous regions of the sample surface we observed a small Eu content (maximum of about \( x \approx 0.003 \)), most probably randomly distributed in the semiconductor lattice. This result is a clear signature that the Eu solubility in the GeTe lattice is smaller than \( x = 0.01 \). The SEM/EDS results lead to similar conclusions as those made upon the analysis of the HRXRD results.

4. Electrical characterization

We performed detailed studies of electrical transport and magnetotransport properties of the \( \text{Ge}_{1-x}\text{Eu}_x\text{Te} \) crystals. We measured the magnetoresistance and the Hall effect over the temperature range from \( T \approx 4 \) K up to 300 K and in the magnetic fields up to \( B = 1.5 \) T in order to calculate the magnetic and temperature dependencies of the resistivity tensor components, \( \rho_{xx} \) and \( \rho_{xy} \). The magnetotransport measurements done at several stabilized temperatures and selected stabilized magnetic field values allowed us to calculate values of the resistivity tensor component, \( \rho_{xx} \), the Hall carrier concentration, \( n \), and the Hall carrier mobility, \( \mu \), for each of the studied samples. Prior to measurements the samples, cut to the size of about \( 1 \times 1 \times 8 \) mm, were etched, polished, and cleaned in order to make electrical contacts. The contacts were made with the use of an indium solder and gold wires. The ohmic behavior of the prepared contacts was checked prior to proper measurements. Both \( \rho_{xx}(B) \) and \( \rho_{xy}(B) \) dependencies were measured simultaneously at dozens of selected stabilized temperatures. The samples were p-type, with the hole concentration and mobility similar to those in the as-grown GeTe. The parameters are shown in table 2 and presented in figure 3.

The Hall effect measurements showed that all our \( \text{Ge}_{1-x}\text{Eu}_x\text{Te} \) crystals are degenerate semiconductors with a p-type conductivity characterized by the high carrier concentrations changing from roughly \( 6 \times 10^{20} \) cm\(^{-3}\) up to about 1.2 \( \times 10^{21} \) cm\(^{-3}\). No signatures of anomalous Hall effect was observed in any of our samples, indicating that the magnetic europium ions do not have significant influence on the carrier transport in our material. The data gathered in figure 3(a) show that the Hall carrier concentration, \( p \), has generally higher values for the homogeneous samples with \( x \leq 0.015 \) than for the samples with EuTe-related clusters (\( x > 0.015 \)). Large concentration of holes in IV-VI semiconductors is due to cation vacancies [14]. P-type conductivity with high hole concentration in GeTe is related to the presence of Ge vacancies [15]. It is probable that the presence of EuTe clusters in the samples with \( x > 0.015 \) leads to an increase in excess Ge in the crystals which may in turn lead to a decrease of the Ge vacancy concentration and a decrease in the free carrier concentration. Electrical compensation of a part of Ge-vacancies leads to a small decrease of the Hall carrier concentration with increasing carrier scattering in the sample. The Hall carrier concentration does not show significant changes as a function of temperature (see figure 3(c)). It is a common feature in degenerate semiconductors where thermally activated carrier transport does not play a major role in the overall carrier transport. The Hall carrier mobility, \( \mu = (\rho_{xx}en)^{-1} \), where \( \rho_{xx} \) is the electrical resistivity and \( e \) is the elementary electron charge, is presented in figures 3(b) and (d). The data gathered in figure 3(b) show an increase of the carrier mobility with Eu content for homogeneous samples with \( x < 0.015 \). The increasing \( \mu(x) \) dependence is most probably related to weakening of the ionic Ge vacancy scattering mechanism due to the presence of interstitial europium ions screening Coulomb potential of the negative Ge vacancies and reducing their effective scattering cross-section. It is therefore probable that the addition of Eu ions to the \( \text{Ge}_{1-x}\text{Eu}_x\text{Te} \) crystals is an effective way to increase the mean free path of the conducting carriers. For the samples with \( x > 0.015 \) a rapid decrease of the carrier mobility is observed. The origin of this phenomenon is most probably complex and related to several effects. First of all the appearance of an increasing amount of EuTe phase for the samples with \( x > 0.015 \) can lead to an increase in the scattering due to interface barriers. It is also possible, that some Ge excess ions left after EuTe phase is formed are distributed in the GeTe crystal lattice, but are not localized in the cation positions and may be positioned in defect states such as interstitial defects increasing carrier scattering in the sample.

Temperature dependence of the carrier mobility shown in figure 3(d) has similar shape for all our samples. In general, for nondegenerate semiconductors such shape of the \( \mu(T) \) dependence can be ascribed to the phonon scattering mechanism influencing the carrier mobility. The mobility due to acoustic phonon scattering is expected to be proportional to \( T^{-1/2} \), while the mobility due to optical phonon scattering is expected to be proportional to \( T^{-1/2} \) [16, 17]. However, for our samples, even at low temperatures, the carrier mobility has
Table 2. Results of the characterization of the Ge$_{1-x}$Eu$_x$Te samples with different chemical compositions, $x$, including magnetotransport data obtained at room temperature: the hole concentration $p$, the carrier mobility $\mu$, and the magnetic properties: the Néel temperature $T_N$, the Curie-Weiss temperature $\theta$, the Curie constant $C$, the effective Eu content $x_\theta$, determined from equation (2), the effective numbers of isolated Eu ions $x_1$, and ions in pairs $x_2$, and the exchange parameter $J/k_B$, determined from equations (3)–(8).

| $x$ | $p$ $(10^{19} \text{cm}^{-3})$ | $\mu$ $(\text{cm}^2/(\text{V} \cdot \text{s}))$ | $T_N$ [K] | $\theta$ [K] | $C$ $(10^{-4} \text{emu} \cdot \text{K} / \text{g})$ | $x_\theta$ $(10^{-2})$ | $x_1$ $(10^{-2})$ | $x_2$ $(10^{-2})$ | $J/k_B$ [K] |
|-----|-----------------|-----------------|--------|--------|-----------------|-----------------|-----------------|-----------------|---------|
| 0.8 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 1.0 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 1.2 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 1.4 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 1.6 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 1.8 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 2.0 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 2.2 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 2.4 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 2.6 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 2.8 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |
| 3.0 | $0.8 \pm 0.1$  | $10 \pm 1$      | $22 \pm 1$ | $2 \pm 1$ | $23 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $111 \pm 0.2$   | $1.0 \pm 0.1$ |

Note: All values are given with uncertainties.
values lower than 120 cm$^2$/(V·s). This points to the conclusion that our samples contain many defects. Moreover, the $\mu(T)$ dependence for our samples cannot be fitted well with either optical or acoustic phonon scattering processes. In inhomogeneous semiconductors the $\mu(T)$ dependence is dominated by the scattering processes due to different defects and cannot be described by theories relevant for periodic crystals.

5. Magnetic properties

Magnetic properties of our Ge$_{1-x}$Eu$_x$Te samples were studied with the use of the LakeShore 7229 susceptometer/magnetometer system allowing measurements of the dynamic magnetic susceptibility, $\chi_{AC}$, and the static magnetization, $M$. The measurements of the AC magnetic susceptibility were done with the use of the mutual inductance method and the magnetization measurements were done using the Weiss extraction method.

At first, for all our samples we performed the measurements of the AC magnetic susceptibility, $\chi_{AC}$, over the temperature range from $T = 4.3$ K up to 310 K. The magnetic susceptibility measurements were done with the sample put in the presence of an alternating magnetic field with the frequency, $f$, equal to 625 Hz and the amplitude, $H_{AC} = 10$ Oe. As a result, we obtained a series of temperature dependencies of both the real and the imaginary parts of the AC magnetic susceptibility, $\text{Re}(\chi_{AC})$ and $\text{Im}(\chi_{AC})$, respectively. The imaginary part of the AC magnetic susceptibility was close to zero for all our samples. The $\text{Re}(\chi_{AC})(T)$ results are presented in figure 4.

For the three samples with the chemical $x \geq 0.020$ we see a prominent maximum of the $\text{Re}(\chi_{AC})(T)$ at $T \approx 11$ K. It is a signature of a magnetic transition at about 11 K. The transition temperature we observe for Ge$_{1-x}$Eu$_x$Te samples is close to the paramagnet-antiferromagnet phase transition known for EuTe [14]. Therefore, we suppose that this transition is related to the presence of EuTe clusters in our samples. The estimated values of the Néel temperature, $T_N$, for the three mentioned samples are close to 11 K, a value slightly higher than that for EuTe bulk crystals with $T_N = 9.58$ K [18]. The values of the magnetic susceptibility roughly correspond to the susceptibility due to the chemical amount of Eu in the samples.

We see a different behavior for our samples with the chemical $x < 0.015$. We do not observe the presence of an antiferromagnetic transition about 10 K and the samples seem to be paramagnetic over the entire studied temperature range.

However, the magnetic susceptibility is about an order of magnitude less than it would be due to the amount of Eu corresponding to the chemical values of $x$.

We tried to describe the $\text{Re}(\chi_{AC})(T)$ dependence at $T \gg T_N$ in the paramagnetic region of our samples by using the modified Curie-Weiss expression of the form:
look we noticed in the two samples with the chemical content that turned out to be strongly dependent on the temperature range and varied between 12 and 40 K. At the closer examination it seemed to be reasonably far from the antiferromagnetic transition around 10 K. However, the results of our susceptibility measurements on the same samples at about 70 K. Such transition temperature does not correspond to any known Eu₃Te₇ structural analysis but in Ge₂−ₓEuₓTe₇, we obtained reliable results that fit to the Curie-Weiss law for the samples with x-values below 0.015 seem to be free of EuO inclusions. Unfortunately, the magnetic susceptibilities of these samples at temperatures above 100 K were very small, with the absolute values close to zero. That is characteristic of the EuTe antiferromagnet. However, it may indicate the presence of other EuₓTe₇ phases, which are close to the values of the antiferromagnetic Neel temperature 1%.

The reported paramagnetic Curie temperatures for different EuₓTe₇ phases were: −8 K for Eu₂Te₃, −10 K for Eu₃Te₄, −17 K for Eu₄Te₅, and −20 K for Eu₅Te₆ [21]. It could be due to a small amount of EuO, for which there is a ferromagnetic transition at about 70 K [22, 23]. This feature made it impossible to obtain reliable fits to the Curie-Weiss law for the samples with x = 0.023 and x = 0.025. The sample with x = 0.020 did not exhibit a trace of the maximum around 70 K and seemed to be free of the EuO inclusions. For this sample we obtained reliable fits to the Curie-Weiss law at the temperatures 80–300 K, independent of any specific part of the range. The Curie-Weiss temperature, θ, was about −12 K and the Curie constant, C, about 7 × 10⁻⁴ emu-K/g. That corresponds to the content of the magnetically active Eu ions, xₙ, about 0.018 and the absolute value of the paramagnetic Curie-Weiss temperature close to the value of the antiferromagnetic Neel temperature is characteristic of the EuTe antiferromagnet. However, it may indicate the presence of other EuₓTe₇ phases, mentioned above. The results of the fits are shown in table 2.

Figure 4. Temperature dependence of: (a) the real part of the AC magnetic susceptibility and (b) the inverse of the real part of the AC magnetic susceptibility obtained for Ge₁−ₓEuₓTe₇ samples with different chemical contents. Markers—experimental data, solid lines—fits to the Curie-Weiss law, dashed lines—extrapolated fits.

\[
\text{Re}(\chi_{AC}) = \frac{C}{T - \theta} + \chi_{dia},
\]

where θ is the Curie-Weiss temperature, and C is the Curie constant described with the equation

\[
C = \frac{N_B g^2 \mu_B^2 J(J + 1)x_n}{3k_B},
\]

where \(N_B\) is the number of cation sites per gram, \(g\) is the effective spin splitting factor (for Eu ions \(g = 1.993 ± 0.006 [19]\)), \(J\) is the total magnetic momentum of the Eu ion (for Eu²⁺ we assumed \(J = S = 7/2\)), \(\mu_B\) is the Bohr magneton, \(x_n\) is the content of the magnetically active Eu ions, \(k_B\) is the Boltzmann constant, and \(\chi_{dia}\) is the diamagnetic susceptibility of the host lattice. For GeTe \(\chi_{dia} = −3 \times 10^{-7} \text{emu/g} [20]\). We assumed the \(\chi_{dia}\) in our materials equal to \(\chi_{dia}\) in GeTe. We tried to fit the experimental \(\text{Re}(\chi_{AC}))(T)\) curves shown in figure 4 to the equation (1) in the temperature range above 80 K with two fitting parameters: θ and C. Such temperature range seemed to be reasonably far from the antiferromagnetic transition around 10 K. However, the results of fits turned out to be strongly dependent on the temperature range and varied between 12 and 40 K. At the closer look we noticed in the two samples with the chemical x = 0.023 and x = 0.025 a trace of a small maximum in the susceptibility around 70 K. Such transition temperature does not correspond to any known Eu₃Te₇ compound. The reported paramagnetic Curie temperatures for different EuₓTe₇ phases are: −8 K for Eu₂Te₃, −10 K for Eu₃Te₄, −17 K for Eu₄Te₅, and −20 K for Eu₅Te₆ [21]. It could be due to a small amount of EuO, for which there is a ferromagnetic transition at about 70 K [22, 23]. This feature made it impossible to obtain reliable fits to the Curie-Weiss law for the samples with x = 0.023 and x = 0.025. The sample with x = 0.020 did not exhibit a trace of the maximum around 70 K and seemed to be free of the EuO inclusions. For this sample we obtained reliable fits to the Curie-Weiss law at the temperatures 80–300 K, independent of any specific part of the range. The Curie-Weiss temperature, θ, was about −12 K and the Curie constant, C, about 7 × 10⁻⁴ emu-K/g. That corresponds to the content of the magnetically active Eu ions, xₙ, about 0.018 and the absolute value of the paramagnetic Curie-Weiss temperature close to the value of the antiferromagnetic Neel temperature is characteristic of the EuTe antiferromagnet. However, it may indicate the presence of other EuₓTe₇ phases, mentioned above. The results of the fits are shown in table 2.

Figure 4. Temperature dependence of: (a) the real part of the AC magnetic susceptibility and (b) the inverse of the real part of the AC magnetic susceptibility obtained for Ge₁−ₓEuₓTe₇ samples with different chemical contents. Markers—experimental data, solid lines—fits to the Curie-Weiss law, dashed lines—extrapolated fits.
The AC magnetic susceptibility measurements were supplemented with the DC magnetization measurements. We performed a series of measurements of the magnetization as a function of the magnetic field at several stabilized temperatures, $T < 200$ K, for all our samples. The magnetization $M(B)$ curves were measured using the LakeShore 7229 magnetometer system employed with the Weiss extraction method and equipped with the superconducting magnet allowing the measurements at constant magnetic fields with induction, $B$, up to 9 T. All of the obtained experimental results were corrected by subtracting the contribution of the sample holder from the total magnetic moment. The $M(B)$ curves measured at low temperatures and up to high magnetic field values carry most information about the physical mechanisms responsible for the behavior of the Eu ions in the samples. The selected $M(B)$ curves, are presented in figure 5.

As we see in figure 5(a) the three samples with the highest Eu content show a nearly linear behavior $M(B)$ up to about 7 T. At about 7 T the slope changes, $M$ still increases with $H$ but on much slower rate. Such behavior is typical of EuTe, as can be seen in [25, 26]. We tried to describe this magnetic behavior in the molecular field approximation by the modified Brillouin function, but such approach did not give any conclusive results. Therefore, we used an expression which includes a modified Brillouin function plus an explicit term for the magnetization due to magnetic ion pairs.

We fitted the magnetization data versus magnetic field $H$ to an expression containing the magnetization for isolated ions, $M_\text{S}$, and pairs, $M_\text{P}$ [27–29]:

$$M = M_\text{S} + M_\text{P} + \chi_\text{dia} H,$$

where

$$M_\text{S} = M_0 S x_1 B_3(\zeta),$$

$$M_0 = g\mu_B N_0,$$

and $B_3(\zeta)$ is the modified Brillouin function:

$$B_3(\zeta) = \frac{25}{25} \cot h\left(\frac{25 + 1}{25} \zeta\right) - \frac{1}{25} \cot h\left(\frac{\zeta}{25}\right).$$

![Figure 5. Magnetization as a function of the magnetic field obtained at $T = 4.5$ K: (a) samples with $x > 0.015$, (b) samples with $x < 0.015$. The markers represent the data, the dashed lines are fits to the modified Brillouin function and the solid lines are three-parameter fits.](image-url)
we are observing pairs and actually there is a contribution from clusters with some ions, and the Curie-Weiss temperature, $T_0$. The pair term contains two additional parameters: the number of magnetic ions in pairs, $x_2$, and the pair exchange, $J_p/k_B$. In addition we have one more parameter, $\chi_{dia}$, which represents the diamagnetic susceptibility of the non-magnetic host lattice. The simple modified Brillouin function did not fit well the magnetization data, significantly better fits were obtained by including the pair interaction explicitly. In the latter case, $T_0$ represents a mean-field contribution from magnetic ions other than pairs. For the results presented here, in which the pair term has been included in the fit, $T_0$ has been fixed at zero because the magnetic ion concentrations are small and the fit is not very sensitive to the value of $T_0$. We will refer to fits in which the pair term is included as three-parameter fits. The results of fits for three samples with the highest Eu-content are shown in figure 5(a).

The knee observed at about 7 T cannot be obtained from our fitting expressions. We attribute the knee to the presence of antiferromagnetic EuTe clusters in our samples. Such characteristic structures have been observed in EuTe by Busch et al [25] and Hori et al [26]. EuTe clusters also produce a cusp in our low-field susceptibility data on the same Ge$_{1-x}$Eu$_x$Te samples. The cusp was not observed in four samples with the lowest Eu-content.

In figure 5(b) we see the magnetization data for four samples with the lower Eu content. For the three samples with the lowest Eu content the fits to the modified Brillouin function are close to the three-parameter fits. We still see some deviations from the modified Brillouin function, but within our experimental error. For the sample with the nominal $x = 0.013$ the deviations are more noticeable.

Parameter values for our three-parameter fits are given in table 2 in the last three columns. The values of $J_p/k_B$ are about $-0.7$ K for the three samples with the chemical $x$ values above 0.015 and about $-0.6$ K for the four samples with the lower $x$, roughly the same within our experimental accuracy. The antiferromagnetic exchange interaction in EuTe obtained from the Néel temperature, $T_N$, and the Curie-Weiss temperature, $\theta$, has been reported to be about $-0.15$ K. [30] We obtained the exchange parameter, $J_p/k_B$, about $-0.65$ K both for samples displaying the features characteristic of EuTe and for samples with very small $x$-values, showing no direct evidence of Eu-rich phases. It is possible that in our disordered samples we do not see long-range interactions due to the antiferromagnetic order but only short-range nearest-neighbor pair interactions.

Therefore, the pair interaction parameters in our three samples with the higher Eu-contents and four samples with the lower Eu-contents have similar values. The absolute values are slightly larger than those reported for Pb$_{1-x}$Eu$_x$Te [29] and Sn$_{1-x}$Eu$_x$Te [31]. This may be explained by the fact that the superexchange interaction in IV–VI DMS is inversely proportional to the anion-cation distance, and that distance in Ge$_{1-x}$Eu$_x$Te is smaller than that in Pb$_{1-x}$Eu$_x$Te and Sn$_{1-x}$Eu$_x$Te. In the $p$-type IV–VI DMS with rare-earth-ion exchange parameter depends also on the positions of the $d$ level and $f$ level with respect to the top of the valence band [29]. Our samples containing spinodal decompositions are not suitable for such analysis. We should also remember, that in our fits, the exchange parameter times the magnetic moment is treated as a unit. We cannot distinguish between the exchange of a pair, $J_{p}^{\text{ex}}$, times the moment of a pair, $m_p$, and the exchange of a higher cluster, $J_{\text{clus}}$, times the moment of the cluster, $m_{\text{clus}}$ which is proportional to the number of ions in the cluster, $n$. If we assume we are observing pairs and actually there is a contribution from clusters with $n > 2$, then the exchange will appear to be larger than it actually is. The assumption that we take only pairs into account is quite good for $x < 0.05$, the value corresponding to maximum pair probability, but larger clusters may be present. Therefore, we should treat the value of the parameter $J_p$ obtained from our three-parameter fits rather as an upper limit, not as an exact value. Similar problem concerning Pb$_{1-x}$Eu$_x$Te was described by us before [29].
Next we consider the values of $x_1$ and $x_2$ obtained from the fits. Table 1 shows that the values of $x_1$ and $x_2$ do not conform to the random probability distribution, in which a probability of an ion in a pair is less than the probability of an isolated ion, up to an $x$ value of about 0.06 [32]. For our samples the numbers of pairs are considerably greater that the numbers of singles, even for the sample with the lowest Eu-content. That suggests a non-random distribution with very few isolated Eu ions. That, again, is not surprising for the samples with $x > 0.015$, since our x-ray analysis and the knee in the $M$ versus $B$ data clearly indicate a presence of EuTe, Eu-rich clusters and/or spinodal decompositions. For the samples with $x < 0.015$ the structural analysis did not provide evidence for clusters, but the magnetic measurements indicate deviations from the random distribution of Eu ions. The sum of $x_1$ and $x_2$, in all samples is a little lower than $x_0$, obtained from fits to the Curie-Weiss law. That may be due to the lack of the magnetic saturation.

6. Conclusions

We have investigated structural, transport, and magnetic properties of Ge$_{1-x}$Eu$_x$Te crystals with $x$-values ranging from 0.0008 to 0.025. The structural analysis indicated a presence of EuTe with NaCl structure in samples with $x \geq 0.020$. In the samples with $x < 0.015$ we did not see clusters with the NaCl structure but spinodal decompositions with the structure of the host lattice. Some of these inhomogeneities have Eu-contents much higher than the average $x$ value. The solubility of Eu in GeTe lattice turned out to be below 0.01. Transport properties of our samples were similar to the properties of other DMS with rare-earth-ions.

For chemical concentrations $x > 0.020$ we observed a cusp in the magnetic susceptibility versus temperature plot at about 11 K. This we attribute to the formation of an antiferromagnetic phase, possibly EuTe. In two samples we also observed structures which could be due to EuO inclusions. For concentrations less than 0.015 we did not observe a cusp or direct evidence of other Eu-rich inclusions. From the fits of $\chi$ to the Curie-Weiss law we have estimated the concentration of the Eu$^{2+}$ ions in the samples. This concentration turned out to be an order of magnitude less than the nominal one. The Curie-Weiss temperatures estimated from the fits were close to zero.

From our high-field magnetization studies we have determined the antiferromagnetic pair exchange parameters to be from $-0.6$ to $-0.74$ K. For $x$-values greater than 0.015 we see a knee in the magnetization curve. That may be evidence for EuTe antiferromagnetic clusters. This result is confirmed by the cusp in the susceptibility at about 11 K, which is present in our samples with larger concentrations and has also been observed in EuTe [14]. The analysis of the high-field magnetization in all samples indicated a non-random distribution of magnetically active Eu-ions, especially very few isolated ions. That may account for the magnetic susceptibilities of samples with $x < 0.015$ much lower than in case of randomly distributed Eu ions, even in samples with the chemical $x$ smaller than 0.001.

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