Magnetic properties of Ge$_{1-x}$Mn$_x$Te ferromagnetic semiconductors doped with gadolinium

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Abstract. We report on magnetic measurements and X-band electron paramagnetic resonance for Ge$_{1-x}$Mn$_y$GdyTe (x=0.15-0.40, y=0, 0.02) single crystals. Ferromagnetic behavior was observed with the Curie temperature $T_C=70$-90 K depending on the alloy composition. Effective magnetic moment $\mu_{eff}$ per Mn ion estimated from the Curie constant increases with increasing x from 2.8 up to 4.3 $\mu_B$, while saturation magnetization per magnetic ion at 4.2 K gives 1.7-3.4 $\mu_B$. EPR spectra at low temperatures are described by Dysonian type line, which splits into two lines at $T \approx 150$ K. At temperature lower this value we observe distinct anomalies on temperature dependencies of the linewidths and g-factors. In paramagnetic region anomalous broadening of the linewidth with decreasing the temperature is revealed, while the g-factor is practically independent both on temperature and alloy composition.

1. Introduction
Diluted magnetic semiconductors (DMSs) are in focus of a great interest in recent years as promising materials for many spintronic devices due to the possibility of combining the advantage of tunable semiconductor and magnetic properties [1]. Since early 70$^{th}$ it has been known that introducing manganese in the host non-magnetic GeTe turns it into DMS and at certain critical Mn content the ferromagnetic ordering occurs with the highest among Mn-doped A$_4$B$_6$ compounds Curie temperature $T_C$ [2]. Ge$_{1-x}$Mn$_x$Te crystals are always p-type with high concentration of the holes and the ferromagnetism is accounted to Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, which proceeds via a coupling between the Mn ions and the mobile charge carriers. It was found, that with increasing of Mn content the Curie temperature $T_C$ increases in accordance with RKKY model, achieves 130 K for x=0.55 and then decreases for alloys with x>0.6 [3, 4]. Decrease of $T_C$ in the alloys with maximal x was associated with an increase of the antiferromagnetic exchange interaction between Mn ions.

In spite of numerous experimental investigations of Ge$_{1-x}$Mn$_x$Te performed in recent years, most part of these results obtained for thin layers and there is no report on electron paramagnetic resonance (EPR) study in these DMSs. Another interesting task is to examine the hypothesis reported in [5], according to which an additional doping of Ge$_{1-x}$Mn$_x$Te with another magnetic impurity, for example rare-earth elements, probably could block a creation of antiferromagnetic Mn$^{2+}$-Mn$^{2+}$ pairs, which presence causes $T_C$ to decrease. In the present paper we have investigated the magnetic properties and EPR in the Ge$_{1-x}$Mn$_x$Te single crystals doped with gadolinium under variation of the alloy composition.
2. Experimental details

Single crystals Ge\(_{1-x-y}\)Mn\(_x\)Gd\(_y\)Te (x=0.15-0.40, y=0, 0.02) were grown by the vertical Bridgman technique using growth charges prepared by melting appropriate amounts of components. The ampoule lowering rate in the growth furnace was about 1 mm/h and the thermal gradient in the growth zone was 35-40 K/cm. The chemical composition was determined using the X-ray fluorescence analysis. X-ray diffraction has shown that there were no secondary phases in all our samples. The temperature and magnetic field dependencies of the magnetization (5\(\leq\)T\(\leq\)300 K, B\(\leq\)0.5 T) were measured using vibrating sample magnetometer EG&G PARC M155 detecting the magnetic moments down to 5\(\times\)10\(^{-5}\) emu. Electron paramagnetic resonance for each sample were measured using X-band EPR spectrometer CMS 8400 (ADANI) (f=9.1-9.6 GHz, B\(\leq\)0.7 T) equipped by a low temperature mount with temperature controller tSTAT335, operating in the temperature range T=80-430 K.

3. Results and discussion

3.1. Magnetic measurements

Temperature and magnetic field dependencies of magnetization M demonstrate clear ferromagnetic behavior at T<100 K (figure 1). One can see that magnetic properties of the crystals are mainly driven by the manganese concentration in the alloys. With increase of the Mn content the magnetic moment increases and achieves about 23 emu/g. Practically no deviation between zero-field cooling (ZFC) and field cooling (FC) M(T) curves has been found. The ordering temperatures T\(_C\) for each sample have been determined by extrapolating the steep linear part of the M\(^2\)-vs–T plot to its temperature intercept. The values obtained are T\(_C\)=88\(\pm\)2 K for the samples with y=0 and T\(_C\)=70\(\pm\)5 K for the samples with y=0.02, that is in reasonable agreement with the previously reported data on Ge\(_{1-x}\)Mn\(_x\)Te of similar composition [2, 6]. At temperatures higher T\(_C\) the magnetic susceptibility \(\chi\) follows a Curie-Weiss law with the Curie-Weiss temperature \(\Theta\approx1.2\) T\(_C\). The effective magnetic moment p\(_{\text{eff}}\) per magnetic ion, estimated from the Curie constant, increases with increasing x from 2.8 to 4.3 \(\mu_B\). This is lower theoretical value 5.92 \(\mu_B\) for Mn\(^{2+}\) ion perhaps due to limited solubility of Mn atoms in the host lattice.

Magnetization curves at helium temperature display a clear hysteresis loop for all samples under study. The value of coercive field decreases with increase of Mn content and achieves 0.14 T. With the

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Temperature (left column) and magnetic field (right column) dependencies of magnetization for Ge\(_{1-x}\)Mn\(_x\)Gd\(_y\)Te (1 – x=0.15, y=0.02; 2 – x=0.21, y=0; 3 – x=0.25, y=0.02; 4 – x=0.26, y=0). On inset – residual magnetization versus temperature for samples 2 and 3.
increase of temperature the saturation moment and coercive field decreases and at T>Tc we have observed the linear magnetization curves typical for paramagnets. Estimation of effective number of Bohr magneton per Mn ion from saturation magnetization at T=4.2 K gives \( m_B = 1.7-3.4 \), that is well comparable with values 2.38 \( \mu_B \) and 2.74 \( \mu_B \) reported for the Ge\(_{1-x}\)Mn\(_x\)Te\((x=0.13)\) layers [6].

Thus, one can conclude that unlike Eu doping action in Ge\(_{1-x}\)Mn\(_x\)Te [5] the introducing of Gd does not essentially change the magnetic properties, just lowering slightly the saturation magnetic moment and the Curie temperature \( T_C \). Our results are in agreement with the data obtained for Pb\(_{1-x-y}\)Mn\(_x\)Eu\(_y\)Te and Sn\(_{1-x-y}\)Mn\(_x\)Eu\(_y\)Te [7], where it was shown that doping with Eu leads to the decrease of \( T_C \).

3.2. EPR study

It was found that for all samples the derivative absorption line \( dP/dB \) at low temperature (figure 2) is satisfactorily described by one asymmetrical line of Dysonian shape, taken in form given in [8]:

\[
\frac{dP}{dB} \propto \frac{d}{dB} \left[ \frac{\Delta B + \alpha (B - B_r)}{B^2 + (B - B_r)^2} + \frac{\Delta B - \alpha (B + B_r)}{B^2 + (B + B_r)^2} \right]
\]

which is a combination of the absorption and the dispersion components of a symmetric Lorenzian, where \( \alpha \) denotes asymmetry parameter, \( B \) – magnetic field, \( B_r \) – resonance field, \( \Delta B \) – the linewidth.

With increasing the temperature the shape of EPR line is changed dramatically (see right column in figure 2) and accurate analysis of line shape indicates that at certain critical temperature \( (T_{anom} \approx 150 \text{ K}) \) resonance line splits into two lines – wide and narrow ones. An example of fitting along with the resolved lines (dashed and dotted lines) is given on inset in figure 2. The wide line appears to introduce the main contribution into absorption signal. The amplitude of this line varies with temperature in accordance with the Curie-Weiss law, while the narrow line amplitude falls down more quickly and remains practically unchanged at \( T>200 \text{ K} \) (paramagnetic region). At temperatures lower the critical temperature \( T_{anom} \) we observed the anomalies on temperature dependencies of the linewidth and \( g \)-factor, which are manifested for wide line in more distinct manner (see inset b in figure 2). In paramagnetic region the linewidths of both lines vary in unusual manner: they decrease smoothly with the temperature increasing. Over the whole temperature range studied the asymmetry parameter \( \alpha \) is

![Figure 2. First derivative absorption line for Ge\(_{1-x,y}\)Mn\(_x\)Gd\(_y\)Te \((x=0.21, y=0)\) at various temperatures: points – experimental data, solid lines – fits using (1). On insets – a) an example of fitting along with two resolved lines, b) effective g-factors for Ge\(_{1-x,y}\)Mn\(_x\)Gd\(_y\)Te \((y=0.02)\).](image-url)
practically identical for both components and decreases with increasing the temperature.

It is worth to note that like in magnetic measurements there was practically no effect of the gadolinium doping action on the EPR spectra detected in our experiments. The variation of manganese content does not essentially change the parameters of narrow line in paramagnetic region, whereas the linewidth of wide line increases with increasing the manganese content.

Since the EPR spectra are similar both for Gd–doped and undoped samples, we can attribute the features revealed to the magnetic activity of Mn ions. We ascribe the availability of two lines to the inhomogeneity of the Mn ions distribution. We suppose that the wide line corresponds to the regions with high Mn content and fairly strong short-range interactions between Mn ions while the narrow one – with low concentration of isolated paramagnetic Mn ions. The anomalous decrease of the linewidths with the increase of temperature in paramagnetic phase indicates predominance of the spin-spin relaxation over spin-phonon one. This feature has been observed earlier for Mn-doped A$^2$B$^6$ DMSs demonstrating spin glass behavior at low temperature [9, 10] and was explained by dynamic distribution of internal fields impressed upon the spin system by the slowing down of the spins as the freezing temperature was approached from above. At T>200 K, in spite of the decrease of the linewidth, we obtain temperature independent g-factor with average values for wide line – $g_1=2.02-2.07$ and $g_2=1.99\pm0.01$ for narrow one, those are typical for Mn$^{3+}$ ion in semiconductor compounds.

4. Conclusion

In summary, we have observed ferromagnetic ordering in the Ge$_{1-x-y}$Mn$_x$Gd$_y$Te single crystals with the Curie temperature and coercive force achieving 90 K and 0.013 T respectively. Introducing of Gd has been found to decrease the Curie temperature and the saturation magnetic moment. The main mechanism responsible for ferromagnetic ordering was thought to be RKKY interaction. The EPR spectra revealed a superposition of two Dysonian type lines attributed to two nonequivalent magnetic coupling between Mn ions. Average values of effective g-factors at room temperature are $g_1=2.02-2.07$ and $g_2=1.99\pm0.01$ those are typical for Mn$^{3+}$ ion. Temperature dependencies of linewidths and g-factors revealed the sharp peculiarities at approaching of ferromagnetic ordering transition from above. An anomalous broadening of the linewidth with lowering temperature has been observed and related to predominance of the dipole-dipole relaxation over spin-phonon one.

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