IV–VI Ferromagnetic Semiconductors
Recent Studies

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Abstract:
In some IV–VI semimagnetic semiconductors, the RKKY interaction can dominate over the standard d–d superexchange and become the driving mechanism for ion–ion coupling. In effect, for low hole concentrations the Mn ion system is in a paramagnetic phase, whereas for higher ones it reveals typical ferromagnetic behavior. In this paper, recent work on IV–VI ferromagnetic (SnMnTe, PbSnMnTe and GeMnTe) systems will be presented. In particular, the influence of the presence of two types of magnetic ions (transition metal: Mn and rare earth metal: Eu or Er) incorporated into a semiconductor matrix on magnetic properties of resultant semimagnetic semiconductor will be described.

Keywords: IV–VI ferromagnetic semiconductor, RKKY interaction, Magnetic ions.

Introduction
Semiconductors exhibiting ferromagnetism have recently been intensively investigated on account of the emerging field of spintronics. Materials that display electrically tunable magnetism are of particular interest. Understanding of the carrier mediated ferromagnetism in semimagnetic semiconductors (SMSC) was initiated by a study of the ferromagnetism in IV–VI based materials [1]. In this class of materials, deviations from stoichiometry result in a carrier density sufficiently high to produce strong ferromagnetic interactions between the localized spins. The results of recent studies [2, 3] of the magnetic and transport properties of IV–VI based ferromagnetic semimagnetic semiconductors, namely PbSnMn(Eu,Er)Te and GeMnEuTe, will be presented in this paper.

Most IV–VI SMSC crystallize in the rock salt crystal structure. The lattice parameter \( a_0 \) changes linearly with the content of magnetic ions following the Vegard law. IV–VI materials are narrow gap semiconductors. Qualitatively, the electron band structure is analogous to the band structure of non-magnetic counterpart materials [4-7].

In general, all IV–VI SMSC show a metallic type of conductivity with a very large,
temperature independent, concentration of carriers. The carriers are generated by metal vacancies, and their concentration can be controlled by thermal annealing or doping.

**PB$_{1-x-y}$Sn$_x$Mn$_y$Te:Er,Eu mixed crystals**

In the present section the results of magnetic studies of Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te (0.022 $ \leq x \leq 0.031$, 0.002 $ \leq y \leq 0.017$, 0.0680 $ \leq z \leq 0.0850$) and Sn$_{1-x-y}$Mn$_x$Eu$_y$Te (0.055 $ \leq x \leq 0.131$, 0.003 $ \leq y \leq 0.023$) samples will be presented. All the investigated samples were $p$-type with a practically temperature independent concentration of carriers.

**Influence of Eu on the band structure**

In the range of high temperatures, all IV–VI SMSC are Curie–Weiss paramagnets with a temperature dependence of the magnetic susceptibility described by the Curie–Weiss law. At low temperatures, the transition to either a ferromagnetic or spin-glass phase takes place (see Fig. 1).

![Fig. 1. The low temperature behavior of both the real $\chi'$ and imaginary $\chi''$ component of susceptibility for two samples of Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te: 809_2 ($x = 0.031, y = 0.003, p = 1 \times 10^{21}$ cm$^{-3}$) and 809_12 ($x = 0.022, y = 0.003, p = 4 \times 10^{20}$ cm$^{-3}$). Typical ferromagnetic behavior is observed for the 809_12 sample and spin glass behavior is observed for the sample with a higher free hole concentration.](image)

Analysis of the data allowed us to notice a significant decrease of the Curie–Weiss temperature $\Theta$ with the Eu content. This is particularly clearly visible in the case of Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te. A few samples were characterized by very close values of Mn content and the free hole concentration. For Mn concentrations close to $x = 0.02$ and the free hole concentration of $p \approx 4 \times 10^{20}$ cm$^{-3}$, an increase of the Eu content from $y = 0.003$ to $y = 0.01$ lead to a decrease of the Curie–Weiss temperature from 4.55 K to 3.02 K and for $y = 0.017$ the paramagnetic Curie temperature is equal to 2.63 K. In the case of Sn$_{1-x-y}$Mn$_x$Eu$_y$Te crystals such a distinct tendency was not observed.

The most likely reason for the dependence of the Curie temperature on the Eu content is variation of band parameters with the alloy composition. In the qualitative analysis
of the above problem, the following points should be considered:

- In the PbMnSnTe matrix, the Eu atom is a magnetic impurity with a spin-only ground state: Eu$^{2+}$ has $S = 7/2$. The electrons of the half-filled f-shell, responsible for the magnetic moment of the Eu ion, are very weakly coupled to the band electrons. Thus, one cannot expect a substantial contribution of Eu magnetic ions to the average magnetization. The coupling constant $J_{sf}$ is much smaller than the $J_{sd}$ constant. However, a small contribution to the total energy from s–f coupling between Eu atoms and carriers exists. One can expect an increase of the Curie temperature with the Eu content from this mechanism. Since the experiment shows the opposite behavior, it can be assumed that the role of Eu as a magnetic impurity is negligible.

- Since EuTe is an antiferromagnet, one can expect a transition from positive (Curie) to negative (Néel) temperature of magnetic ordering of the PbMnEuSnTe system when the Eu content ($y$) changes from 0 to 1. For a small Eu content it can lead to a decrease of $T_C$.

- Eu is a component of the complex PbMnEuSnTe alloy and one should consider a variation of the band parameters as a function of the Eu content. For a qualitative analysis, let us assume here a simplified two-band model with some phenomenological parameters. It should be stressed that the real spectrum of IV–VI compounds is rather complicated and one should account for nonparabolicity and anisotropy of energy bands.

A careful analysis taking into account the peculiarities of the band structure (change of the energy gap, relative shifts of the light and heavy hole band position) enabled us to qualitatively explain the facts observed experimentally. The interaction energy between magnetic impurities is described by the Ruderman, Kittel, Kasuya, Yoshida (RKKY) formula:

$$
J_{RKKY}(R) = N \frac{m^* J_{sd}^2 a_0^3 k_F^2}{32 \pi^2 \hbar^2} \frac{\sin(2k_F R) - 2k_F R \cos(2k_F R)}{(2k_F R)^4}.
$$

where $k_F$ is the Fermi wave number, $m^*$ is the effective mass of the carriers, $J_{sd}$ is the Mn ion–electron exchange integral, $a_0$ is the lattice constant, $N$ is the number of valleys of the valence band and $R$ is the distance between the magnetic ions.

![Fig. 2. The Curie temperature calculated for Pb$_{1-x-y}$Mn$_x$Eu$_y$Sn$_z$Te mixed crystals as a function of the Eu content $y$ for various values of Sn concentration $0.6 \leq z \leq 1$ and Mn concentration $x = 0.02$.](image)

If one assumes that $R_0$ is equal to the mean distance $R$ between the magnetic ions
(Mn), this formula will give the mean interaction energy between magnetic impurities, which is roughly equal to the transition temperature $T_C \approx J_{RKKY}(R)/k_B$. It should be stressed that eq. 1 was obtained for a parabolic energy spectrum and does not take into account the anisotropy.

The obtained $T_C$ dependence on the Eu concentration $y$ for various values of the Sn content $(0.6 \leq z \leq 1)$ is shown in Fig. 2. It is clear that the obtained results of calculations performed within a simple two band model can explain the tendency of the Curie temperature to decrease with the Eu content that is observed experimentally. The obtained values of the Curie temperature are higher than those determined experimentally. However, it should be stressed that not all phenomenological parameters are precisely known and many assumptions are introduced to the model. Nevertheless, the calculated dependence of the Curie temperature on Eu content reflects very well the experimental observation of the $T_C$ decrease with Eu concentration $y$.

**Spin glass phase**

Fig. 1 presents characteristic behavior of the low temperature part of real as well as imaginary components of magnetic susceptibility for the spin glass (809_2) and ferromagnetic (809_12) samples of Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te. In the case of the ferromagnetic sample (with a concentration of free holes equal to $4.0 \cdot 10^{20}$ cm$^{-3}$), sharp transitions in both real and imaginary components of susceptibility occur. For the spin glass sample (characterized by a higher free hole concentration $p = 1 \cdot 10^{21}$ cm$^{-3}$), a cusp in $Re(\chi)$ is visible at the freezing temperature $T_f$. The magnitude of the susceptibility at this cusp is much lower than the susceptibility of the ferromagnetic sample. A corresponding maximum in the out of phase component of susceptibility, $Im(\chi)$, is observed at slightly lower temperature.

The sample 809_2 shows obvious characteristics of a spin glass-like phase. The cusp observed in magnetic susceptibility $\chi$ versus temperature $T$ shifts to higher temperatures when the frequency $f$ of the applied AC field is increased. This feature – the increase of the freezing temperature when the frequency is higher – was observed in the well-known canonical spin glass systems (see, e.g., [8]). The increase of $T_f$ per decade of frequency is approximately constant and the frequency dependence occurs in both the real and imaginary part of AC magnetic susceptibility. Fig. 3 presents the frequency dependence of the low temperature part of real component of magnetic susceptibility for the 809_2 sample. The relative shift of the freezing temperature $T_f$ per decade of frequency $R = \Delta T_f/T_f \Delta \log f$ is equal to 0.021.

![Fig. 3. The frequency dependence of the real component of susceptibility $Re(\chi)$ for the Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te 809_2: $x = 0.031, y = 0.003, p = 1 \cdot 10^{21}$ cm$^{-3}$ sample. The shift of the](image-url)
freezing temperature $T_f$ towards higher temperatures with the frequency increase is clearly visible.

The analogous rate of the changes observed for the imaginary part of magnetic susceptibility is higher and equals $R = 0.048$.

The values of $R$ reported for known spin glass systems range from 0.005 (Cu) to 0.11 (La$_{1-x}$Gd$_x$Al$_2$ [9]) and the rate of the change in $\text{Im} (\chi)$ is the same as the rate of the change in $\text{Re} (\chi)$. The values of $R$ reported for Sn$_{1-x}$Mn$_x$Te are equal: $R = 0.027$ ($x = 0.04$) [10], $R = 0.022$ ($x = 0.008$), $R = 0.027$ ($x = 0.022$) [11]. It appears that in the case of Sn$_{1-x}$Mn$_x$Te mixed crystals the character of the spin glass phase does not depend on the manganese concentration. In the case of Pb$_{1-x-y-z}$Mn$_x$Eu$_y$Sn$_z$Te mixed crystals, with a comparable Mn composition, a significant difference is visible in the inequality of frequency shift in $\text{Re} (\chi)$ and $\text{Im} (\chi)$.

**Anomalous Hall effect**

The Anomalous Hall Effect (AHE) has recently attracted much attention. Due to AHE universality, it has often been applied even without a full understanding of its complicated nature. For our studies, crystals with the following compositions were chosen:

- Sn$_{1-x}$Mn$_x$Te: 7.5% and 12% of manganese,
- Sn$_{1-x-y}$Mn$_x$Er$_y$Te: 5.8% or 6% of manganese, and about 0.05% of erbium,
- Sn$_{1-x-y-z}$Mn$_x$Eu$_y$Te: 13% of manganese and 1% of europium.

Complementary measurements of the Hall effect and high field magnetization using the same samples allow determination of the anomalous Hall coefficient value and its temperature behavior.

![Graph](image)

**Fig. 4.** The anomalous Hall coefficient in Sn$_{1-x}$Mn$_x$Te (squares and circles), Sn$_{1-x}$Mn$_x$Er$_y$Te (stars and pentagons) and Sn$_{1-x}$Mn$_x$Eu$_y$Te (triangles) crystals.

Thus obtained anomalous Hall coefficient values for all investigated crystals are shown in Fig. 4. No temperature dependence of $R_S$ is observed in all crystals except in one of the two Sn$_{1-x-y-z}$Mn$_x$Er$_y$Te samples.

The data obtained lead to the following conclusions:
1. Increase of the carrier concentration results in a decrease of the anomalous Hall coefficient.
2. Introduction of rare earth atoms into the system significantly lowers the anomalous Hall coefficient value.

**Ge\(_{1-x-y}\)Mn\(_x\)Eu\(_y\)Te mixed crystals**

Co-occurrence of ferro-electric and ferromagnetic properties gives interesting application possibilities. Ge\(_{1-x}\)Mn\(_x\)Te is a material with such unique properties. From the early 70’s it is well known (see, e.g., [12], [13], [14]) that even a small admixture of MnTe in GeTe leads to ferromagnetic behavior. Ge\(_{1-x}\)Mn\(_x\)Te crystallizes in the NaCl structure. For \(x = 0.00\) to \(x = 0.18\) rhombohedral distortion is observed [15]. Ge\(_{1-x}\)Mn\(_x\)Te is a strongly degenerate semiconductor with \(10^{20}-10^{21}\) cm\(^{-3}\) holes. Similar to the facts described in the previous paragraphs for the case of PbSnMnTe, the source of ferromagnetism is a RKKY interaction between mobile holes and localized magnetic moments. The Curie temperature depends on both the Mn content and carrier concentration and its highest reported value (for \(x_{\text{Mn}} = 0.6\)) does not exceed 160 K.

In the present section, preliminary results of studies of a quaternary GeMnEuTe system will be presented. We investigated crystals grown using the Bridgman method with a Mn content about 0.07 and of Eu content of 0.04. An X-ray investigation revealed that the samples were single phase and showed that the crystal is rhombohedrally distorted with a lattice constant \(a_0 = 5.9754\) Å and rhombohedral distortion angle \(\alpha = 88.37^\circ\).

The results of AC magnetic susceptibility measurements for one of the investigated samples are shown in Fig. 5.

![Fig. 5. The magnetic susceptibility vs. temperature for the Ge\(_{1-x}\)Mn\(_x\)Te, \(x = 0.07\), \(y = 0.04\) sample.](image)

The Curie temperature obtained for the GeMnEuTe system substantially exceeds the values of \(T_C\) reported for Ge\(_{1-x}\)Mn\(_x\)Te crystals and layers with a similar composition, i.e. \(\approx 40\) K [13]. The origin of this substantial Curie temperature enlargement is yet not fully explained. One of the hypotheses assumes that addition of Eu ions to GeMnTe can block creation of antiferromagnetic Mn–Mn pairs, whose presence decreases the Curie temperature. Anyway, the increase of \(T_C\) seems to be too large to be explained by the above hypothesis. The result of
nuclear magnetic resonance studies may shed some light on the anomaly observed. The spin-echo resonance does not correspond to the anticipated position of Mn$^{2+}$ ions, but occurs at lower frequencies. This may suggest that the system is in a mixed valence state and that an additional channel of interaction between magnetic ions is open.

**Conclusion**

Two important features give IV–VI semimagnetic materials a distinguished position within the whole family of semimagnetic semiconductors. First, are a variety of magnetic properties observed in Mn based IV–VI SMSC. Second are semi-metallic electric properties with well developed methods of carrier concentration control. However, one has to admit that in the case of SnTe-based materials, the ferromagnetic characteristics (magnetic anisotropy, coercive field and Curie temperature) are not superior to other magnetic materials. An additional obstacle for these materials is the low temperature of ferromagnetic phase transition. Thus, applications (if any) related to ferromagnetic properties of these materials will be limited to hybrid systems with IV–VI electronic devices incorporating the ferromagnetic element with controlled magnetic properties. On the other hand, the case of GeTe-based ferromagnetic semiconductors seems to be promising. Preliminary data presented here show that the presence of Eu ions enhances the Curie temperature of GeMnTe, and $T_C$ in crystals containing a few percent of Mn and Eu substantially exceeds liquid nitrogen temperature. This property, in addition to ferroelectricity, opens a wide field of potential applications.

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**References**


Садржај: За неке IV-VI полупроводнике RKKY интеракција може превладати стандардне d-d суперизмене и постати покретачки механизам за јон-јон куповање. Ефективно, за ниске концентрације шупљина Mn јонски систем је у парамагнетној фази, док за више испољава типично феромагнетно понашање. У овом раду приказан је скорашњи рад на IV-VI феромагнетним системима (SnMnTe, PbSuMnTe и GeMnTe). Нарочито је описан утицај присуства два типа магнетних јона (прелазни метод: Mn и метал ретке земље Еу или Er), који су инкорпорирани у полупроводну матрицу на својства добијеног паразеног магнетног полупроводника.

Кључне речи: IV-VI феромагнетни полупроводници, RKKY интеракције, магнетни јони.