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Ferromagnetism of Narrow-Gap $Ge_{1-x-y}Sn_xMn_yTe$ and Layered $In_{1-x}Mn_xSe$ Semiconductors

G.V. Lashkarev[a,*], V.I. Sichkovskyi[a], M.V. Radchenko[a], A.I. Dmitriev[a], P.E. Butorin[a,c], V.E. Slyn'ko[a], E.I. Slyn'ko[a], Z.D. Kovalyuk[a], W. Knoff[b], T. Story[b], R. Szymczak[b], R. Jakieła[b], P. Aleshkevych[b] and W. Dobrowolski[b]

[a]Institute for Problems of Material Science
National Academy of Sciences of Ukraine
3 Krzhizhanovskogo str., Kyiv, Ukraine
[b]Institute of Physics, Polish Academy of Sciences
al. Lotników 32/46, 02-668 Warsaw, Poland
[c]Joint Institute for Nuclear Research, Dubna, Russia

Magnetic susceptibility, Hall effect and resistivity of narrow-gap $Ge_{1-x-y}Sn_xMn_yTe$ single crystals ($x = 0.083 \div 0.115$; $y = 0.025 \div 0.124$) were investigated in the temperature range 4.2–300 K revealing a ferromagnetic ordering at $T_C \approx 50$ K. Temperature dependence of magnetization indicates a superparamagnetic phase with magnetic clusters arranging in a spin glass state below the freezing temperature T_f. Magnetic structure of InSe⟨Mn⟩ 2D-ferromagnetic single crystals was studied by SQUID magnetometry, neutron diffraction, secondary ion mass spectroscopy, and wave dispersive spectra. Hysteresis loops of magnetization were observed at least up to 350 K. The cluster model of ferromagnetism is considered. The formation of self-assembled superlattice ferromagnetic InSe:Mn/antiferromagnetic MnSe during growth process and further annealing was established.

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1. Introduction

Ferromagnetic (FM) diluted magnetic semiconductors (DMSs) are of interest related to spintronics applications. DMSs possess charge and spin degrees of freedom leading to their interplay promising for novel devices. The main task is to

*corresponding author; e-mail: georgl@isp.kiev.ua

realize electrical or optical control of magnetic states as well as magnetic control of electrical signals. These properties allow combining information processing and its storage in one device.

The paper concerns DMSs which usually are solid solutions of d-transition metals (d-TM) with incomplete d-shell in narrow-gap IV–VI and layered III–VI semiconducting compounds as diamagnetic matrix.

Layered semiconductors are natural superlattices due to strong anisotropy of their chemical bond and display 2D conductivity of electron gas (EG). The studies of the III–VI (III — In, Ga; VI — S, Se) crystals doped with d-TM (Mn, Fe) have shown that these semiconductors display nontrivial magnetic properties. In InSe with 1.25 at.% Mn two magnetic subsystems containing Mn ions inside ionic--covalent layers and interlayer van der Waals gaps were discovered [1, 2]. The temperature hysteresis of magnetic susceptibility (MS) was observed in $In_{1-x}Mn_xSe$ ($x = 0.01$; 0.10) DMS in the temperature range 90–290 K [3]. According to [4], InS doped with 2 at.% of Mn forms the spin glass state below 20 K and exhibits the Curie–Weiss behavior of MS at high temperatures. Nevertheless, in previous studies the X-ray diffraction (XRD) phase analysis was not carried out and chemical composition was not exactly known.

$Ge_{1-x-y}Sn_xMn_yTe$ crystals are solid solutions from the family of IV–VI DMSs [5]. These materials exhibit FM transition due to indirect exchange interaction of the Mn^{2+} magnetic ions via the hole gas (the Ruderman–Kittel–Kasuya–Yosida (RKKY) mechanism) [6, 7]. Also these materials are characterized by phase transformations of ferroelectric (FE) type. Phase transition temperature depends on composition and the concentration of charge carriers. It is expected that the coexistence of FM properties and structural phase transition of FE type in IV–VI DMS will result in new possibilities of these materials. Temperature of FE transition for such crystals can be tuned by the change of Sn/Ge ratio.

In this paper we present the results of our recent investigations of $Ge_{1-x-y}Sn_xMn_yTe$ and InSe⟨Mn⟩ DMSs with a particular emphasis on the role of ferromagnetic clusters in both materials.

2. Experimental details

2.1. $Ge_{1-x-y}Sn_xMn_yTe$

Magnetic susceptibility, anomalous Hall effect (AHE), and electrical resistivity of $Ge_{1-x-y}Sn_xMn_yTe$ ($x = 0.083 \div 0.115$; $y = 0.025 \div 0.124$) bulk crystals grown by the Bridgman method were investigated in the temperature range 4.2–300 K. The chemical composition was determined by X-ray fluorescent analysis (XRFA). Multimeter Keithley 2700/E with data acquisition system was used for transport measurements. Magnetic measurements were carried out by the Faraday microbalances method over the temperature range 77–300 K. SQUID magnetometer was used in the temperature range 5–100 K.

2.2. $InSe\langle Mn\rangle$

Doped InSe single crystals were grown by the Bridgman method out of alloys containing Mn. Samples cut from the ingots were annealed at ≈ 600 K for 70 h. Mn content was determined by XRFA. The samples containing 5 at.% and 0.4 at.% Mn in cation sublattice were investigated. The phase composition (XRD), secondary ion mass spectroscopy (SIMS), wave dispersive spectra (WDS), as well as magnetization and neutron diffraction of $InSe\langle Mn\rangle$ single crystals in wide range of temperatures and magnetic fields were studied.

3. Experimental results and discussion

3.1. $Ge_{1-x-y}Sn_xMn_yTe$

Measurements performed by the Faraday balances showed that in the temperature range 77–300 K the magnetic susceptibility of GeSnMnTe follows the Curie–Weiss law $\chi = \chi_0 + C/(T-\theta)$ with χ_0 describing the diamagnetic contribution of the semiconductor matrix. The Curie–Weiss temperature θ is positive (ferromagnetic) and equals 42–64 K in various crystals. Its dependence on Mn content is nonlinear with a maximum at $y \approx 6$ at.%. The SQUID magnetometry studies of magnetization M of GeSnMnTe crystals with composition $x = 0.083$, $y = 0.124$ were carried out in zero field cooled (ZFC) and field cooled (FC) regimes (Fig. 1). The Curie–Weiss law is fulfilled in these crystals in the temperature interval 50–100 K. At temperatures $T \leq 45$ K the ZFC and FC magnetization curves $M(T)$ differ from each other which is a characteristic feature of various spin glass or superparamagnetic systems [8]. The freezing temperature of the system of ferromagnetic clusters equals $T_{\mathrm{f}} \approx T_{\mathrm{C}} \approx 45$ K. For this crystal composition the hysteresis loop is absent at $T < 45$ K and magnetization saturates at moderate magnetic field of $H \approx 450$ Oe.

Decrease in Mn content to $y = 0.082$ and $y = 0.044$ leads to the appearance of magnetization hysteresis loop at $T = 5$ K and to a decrease in the freezing temperature T_{f}. The samples demonstrate even two maxima on $M(T)$ dependence in ZFC regime indicating the existence of two types of FM clusters with different freezing temperature T_{f}.

Electrical resistivity of GeSnMnTe has a complicated temperature dependence. It increases with an increasing temperature which is characteristic of IV–VI semiconductors with degenerated hole gas (Fig. 2). Resistivity jump observed experimentally at temperature T_{f} points to the importance of both magnetic and electronic disorder present in GeSnMnTe crystals. Below $T = 25$ K one observes a behavior similar to the Kondo effect with spin dependent carrier scattering on localized magnetic moments. Negative magnetoresistance of a very small magnitude (0.2% at $H = 6$ kOe, $T = 4.2$ K) appears below 80 K. Its small value can be explained taking into account the dominant role on spin-independent scattering processes related to the very high concentration of metal vacancies always present in IV–VI semiconductors.

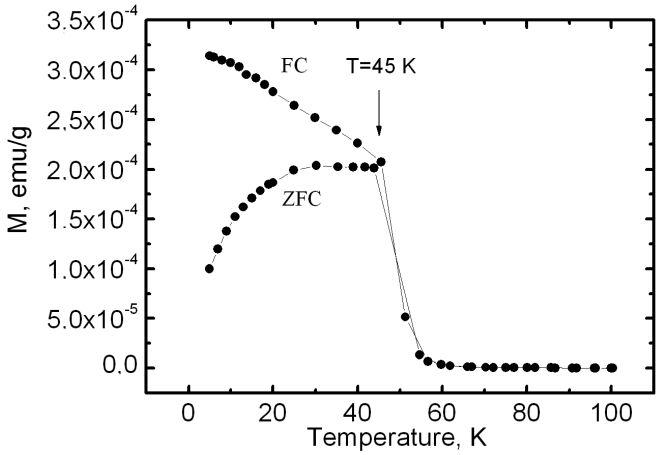

Fig. 1. Temperature dependence of magnetization for $Ge_{1-x-y}Sn_xMn_yTe$ ($x = 0.083$, $y = 0.124$).

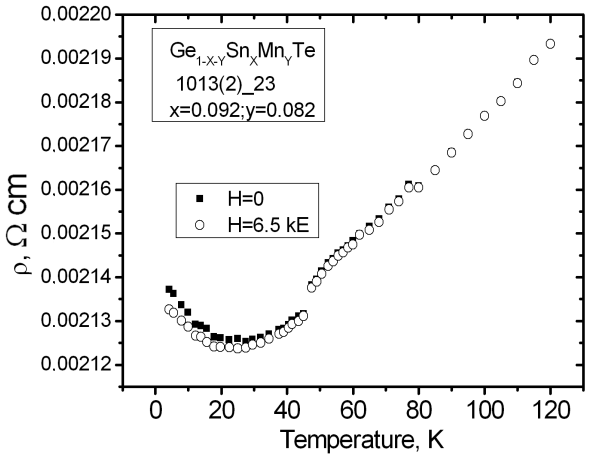

Fig. 2. Temperature dependence of resistivity for $Ge_{1-x-y}Sn_xMn_yTe$ ($x = 0.092$, $y = 0.082$).

The measurements of the Hall resistivity dependence on the external magnetic field $\rho_H(H)$ demonstrates very large contribution of the AHE, which is proportional to magnetization (Fig. 3). At $H > 2$ kOe, after the magnetic saturation of the AHE contribution, the weak increase in ρ_H is due to the normal Hall effect, which allows to calculate the conducting hole concentration in the crystal $p \approx 8 \times 10^{20}$ cm^{-3}.

It is necessary to note that the existence of the AHE in the media, which consists of FM clusters in the sea of conducting holes of very high concentration ($\approx 10^{21}$ cm^{-3}) is not a trivial one. This effect originates from the spin–orbit

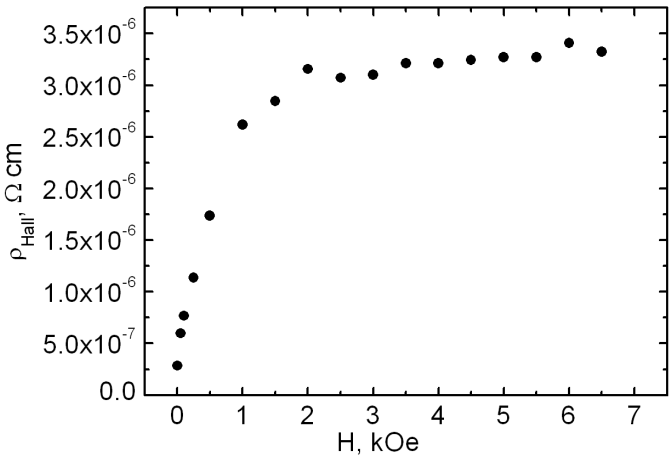

Fig. 3. Dependence of Hall resistivity ρ_{H} on magnetic field for $\mathrm{Ge}_{1-x-y}\mathrm{Sn}_x\mathrm{Mn}_y\mathrm{Te}$ ($x = 0.092$, $y = 0.082$) at $T = 4.2$ K.

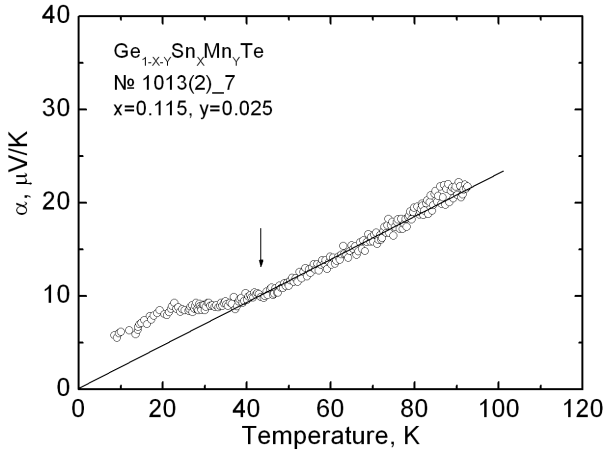

Fig. 4. Temperature dependence of thermoelectric power for $\mathrm{Ge}_{1-x-y}\mathrm{Sn}_x\mathrm{Mn}_y\mathrm{Te}$ ($x = 0.115$, $y = 0.025$).

interaction of free holes with one-domain FM inclusions in the crystal lattice of host material and is not considered theoretically.

The temperature dependence of thermoelectric power (TP) $\alpha(T)$ shown in Fig. 4 reveals below $T = 48$ K a deviation from the linear dependence expected for a semiconductor with a strongly degenerate electron or hole gas. This experimental finding can be explained by the mechanism discussed in our paper [9], where the $\alpha(T)$ dependence is modified by the structural phase transition of ferroelectric type. The broad maximum on $\alpha(T)$ dependence is also expected at the Curie temperature due to FM ordering. It should be underlined, however, that in our

crystals FM clusters do not occupy the whole crystal volume. The system consists of numerous FM clusters that do not provide the conditions of current flow through their volumes surrounded by conducting IV–VI matrix.

3.2. InSe⟨Mn⟩

The XRD investigations of the phase composition have shown that the hexagonal phase InSe ($P63/mmc$) with reduced value of the crystal lattice parameters $a = 4.0026$ Å and $c = 16.634$ Å is the dominant one. Decrease in lattice parameter with increasing Mn doping proves the creation of solid solution $In_{1-x}Mn_xSe$ which fills more than 90% of crystal volume. Besides that, samples contain the second (cubic) antiferromagnetic (AFM) phase MnSe ($Fm3m$, $a = 5.456$ Å) (with two Néel temperatures $T_{N1} = 130$ K, $T_{N2} = 260$ K) [10].

Magnetic susceptibility investigations of InSe⟨Mn⟩ crystals carried out in the temperature range 2.4–300 K in ZFC regime have shown that these crystals are paramagnetic but they do not obey the Curie–Weiss law (Fig. 5). Two pronounced peaks found experimentally at temperatures $T = 163$ and $T = 266$ K are due to antiferromagnetic transformations in MnSe additional crystal phase with their Néel temperatures shifted in comparison to bulk crystals reference values [11]. Cooling the sample down to 2.4 K in the magnetic field of 100 Oe (FC regime) increases the magnetic susceptibility in the whole temperature interval studied up to 300 K (Fig. 5) [10]. The difference between FC and ZFC regimes gives the preference to the cluster model of ferromagnetism which is a version of superparamagnetic model with spin glass state. In Fig. 5 we can see that the curves FC and ZFC tend to converge with temperature increasing. The freezing temperature T_f in this case is expected above 300 K.

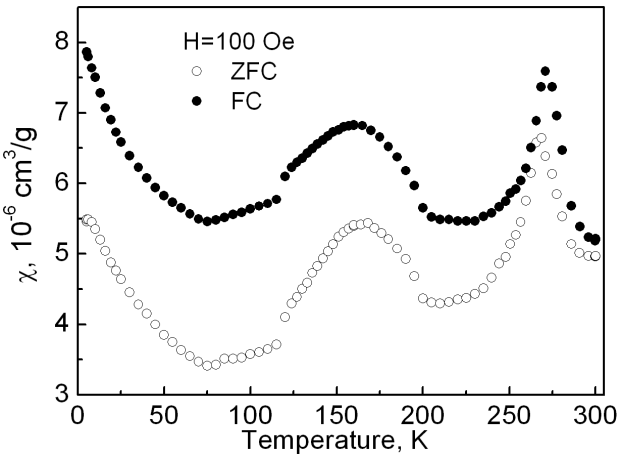

Fig. 5. Temperature dependence of magnetic susceptibility for InSe with 5 at.% Mn for ZFC and FC regimes at magnetic field $H = 100$ Oe.

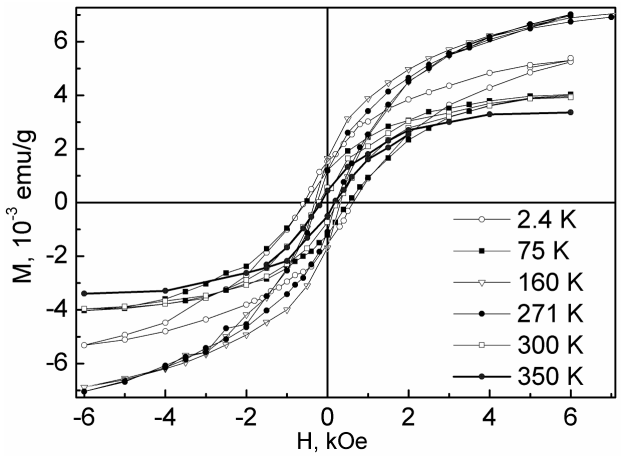

Fig. 6. Magnetization dependence on magnetic field for InSe with 5 at.%. Mn.

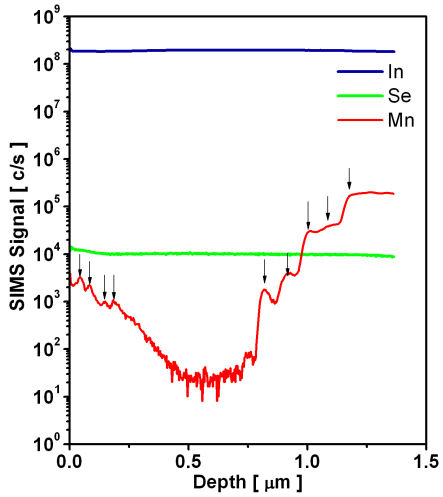

Fig. 7. SIMS depth profiles for InSe with 0.4 at.% Mn measured under oxygen ion sputtering.

Magnetization hysteresis loops were observed by SQUID magnetometry at temperatures up to 350 K (Fig. 6) indicating the existence of ferromagnetic order above the room temperature. We suggest that the ferromagnetic interactions are due to indirect coupling between Mn ions in ferromagnetic clusters via degenerated 2DEG or/and the superexchange via anions (Se). No magnetic hysteresis loops were found for undoped InSe crystals.

Neutron diffraction structural studies of InSe with Mn were carried out for two goals, first — phase analysis independent of the XRD method, and the second — revealing the detailed magnetic structure of FM matrix ($In_{1-x}Mn_xSe$) with

inclusions of AFM phase (MnSe). The analysis of neutron diffraction studies of layered semiconductor InSe doped by Mn (total amount of 0.4 at.%) has shown that the material consists of $In_{1-x}Mn_xSe$, α-MnSe and traces of In_4Se_3 crystal phases.

Well pronounced diffraction reflections of MnSe inclusions into layered InSe⟨Mn⟩ single crystal prove the layer form of these inclusions. The last conclusion became possible because of the large penetration ability of neutrons (about several centimeters) opposite to X-rays (≈ 4 μm). Manifestation of ferromagnetic ($T_C \geq 350$ K) as well as antiferromagnetic ($T_{N1} = 166$, $T_{N2} = 266$ K) behavior of this sophisticated magnetic system demonstrates that InSe⟨Mn⟩ represents the self-assembled magnetic superlattice consisting of alternating layers of ferromagnetic $In_{1-x}Mn_xSe$ and antiferromagnetic MnSe. This conclusion was confirmed by SIMS investigations of Mn oscillating distribution with a depth of a sample. In the case of the sample with 0.4 at.% of Mn we have observed well pronounced oscillations of Mn content (Fig. 7). Period of oscillations was about 40–85 nm. It is naturally to suppose that the above mentioned superlattice was formed during single crystal growth and its further annealing.

Strong change of Mn content within the depth of ≈ 1.5 μm shows to nonuniform distribution of manganese in InSe crystal lattice, which was also confirmed by WDS studies.

4. Conclusions

Investigations of the bulk crystals of $Ge_{1-x-y}Sn_xMn_yTe$ containing Mn in the amount of $y = 0.044 \div 0.124$ have revealed that its magnetic structure is superparamagnetic one. Below the freezing temperature T_f magnetic clusters become ferromagnetic, i.e. T_f is close to the Curie point. Weak negative magnetoresistance and strong anomalous Hall effect found experimentally below the T_f are due to spin dependent interactions of ferromagnetic clusters with holes in surrounding semiconductor matrix.

The magnetic structure of the crystal $In_{1-x}Mn_xSe$ is governed by the superposition of various magnetic states: a basic ferromagnetic phase with the Curie temperature $T_C > 350$ K and an antiferromagnetic MnSe phase in the form of planar inclusions. The creation of such self-assembled superlattice FM $In_{1-x}Mn_xSe$/AFM MnSe was confirmed by neutron diffraction and SIMS studies.

It is worth stressing that such different semiconductor materials as narrow-gap GeSnMnTe and layered InMnSe crystals display the features characteristic of superparamagnetism related to the creation of magnetic clusters during the growth process. These clusters become ferromagnetic below the Curie temperature coinciding with the freezing temperature. Thus, the separation in additional phases and non-uniform distribution of magnetic impurities seems to be the feature inherent to many diluted magnetic semiconductors.

Acknowledgments

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