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Heterogeneous magnetic state in Mn-doped $CdGeP_2$ and $CuGaTe_2$

R.V. Demin[a], L.I. Koroleva[a,*], S.F. Marenkin[b], V.M. Novotortsev[b], B.M.Trukhan[b], S.A. Varnavskii[b], T.G. Aminov[b], G.G. Shabunina[b], R. Szymczak[c], M. Baran[c]

[a]*M.V. Lomonosov Moscow State University, Vorobyevy Gory, 119992 Moscow, Russia*
[b]*N.S. Kurnakov Institute of Inorganic and General Chemistry, Leninskii prosp. 31, 119991 Moscow, Russia*
[c]*Institute of Physics, Polish Academy of Science, Lotnikow al. 32/46, Warsaw 02668, Poland*

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Abstract

Polycrystalline samples $CdGeP_2$: Mn and $CuGaTe_2$: Mn of the chalcopyrite type have been synthesized. $CdGeP_2$ doped by 4.5 wt% Mn is heterogeneous magnet, it consists from a ferromagnetic and paramagnetic phases. Its Curie point has been determined to be 330 K. An origin of ferromagnetism in this sample is connected with the existence of vacancies (Cd, V_C, Mn)GeP_2 or non-stoichiometry (Cd, Ge, Mn)GeP_2. Superparamagnetism is found in $CuGaTe_2$:Mn.

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Diluted magnetic semiconductors have recently attracted new interest because of possible applications in spintronics devices [1, 2]. The $Ga_{1-x}Mn_xAs$ composition is the most extensively studied representative of this class of materials in which a ferromagnetism was found with the Curie point $T_C \leq 170$ K [3,4]. But the magnetic semiconductors with the room temperature ferromagnetism need for application in the spintronics devices. Recently the high temperature ferromagnetism was observed in a chalcopyrite semiconductors $A^{II}B^{IV}C^{V}_2$ doped by Mn. These were $CdGeP_2$:Mn, $ZnGeP_2$:Mn [5-7] and $ZnGeAs_2$:Mn [8] in which the Curie point achieved of 350 K. In our papers a new $CdGeAs_2$:Mn chalcopyrite was prepared in which the Curie point is reached of 355 K [9-11]. The ternary $A^{II}B^{IV}C^{V}_2$ semiconductors are long known. These compositions represent a crystallochemical analog of the $A^{III}B^{V}$ semiconductor. The interest was created in these ternary semiconductors of their unique nonlinear optical properties, namely, a high values of nonlinear polarization and a double refraction, that permits the use of its for the parametric frequency conversion of a laser radiation in mid-IR range. For this purpose the $CdGeP_2$, $CdGeAs_2$, and $ZnGeP_2$ crystals of a high-

* Corresponding author. Tel.:+7-095-939-28-47; fax: +7-095-932-88-20.
E-mail address:koroleva@phys.msu.ru

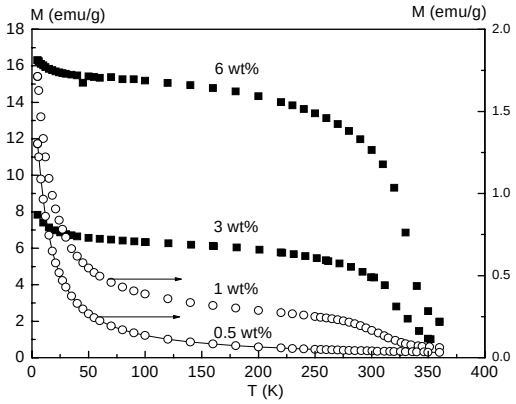

Fig. 1. The temperature dependence of magnetization M(T) in magnetic field 50 kOe of $CdGeAs_2$:Mn polycrystalline samples with 1, 3, and 6 wt. % Mn.

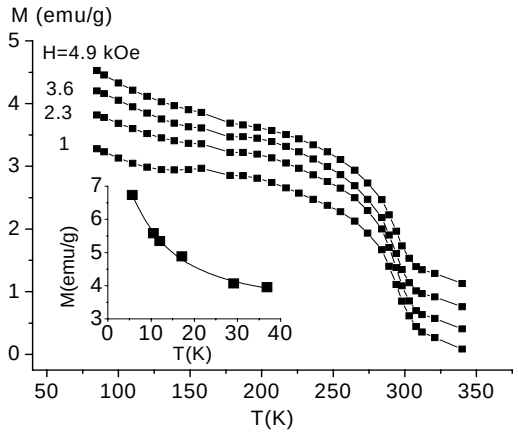

Fig.2. The temperature dependence of magnetization *M(T)* of $CdGeP_2$ with 4.5 wt% Mn polycrystalline sample in some magnetic field. Inset : experimental *M(T)* dependence in H=50 kOe (points), and the calculated one using experimental *H/T* values at $H \leq 50$ kOe, $M_0 = 5.3$ emu/g, $xM_{FM} = 3$ emu/g and $\mu = 5.8\ \mu_B$ (line).

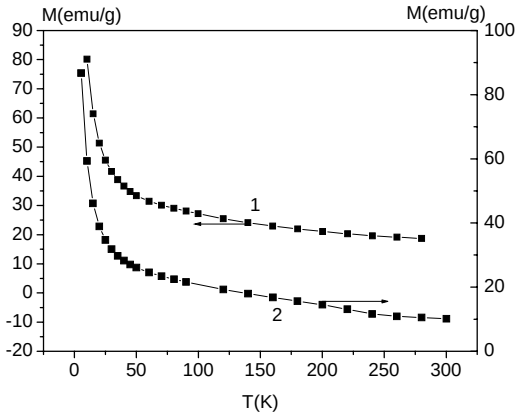

Fig. 3. The temperature dependence of magnetization *M*(*T*) of $Cu_{0.9}Ga_{0.9}Mn_{0.2}Te_2$ (1) and $Cu_{0.97}Ga_{0.97}Mn_{0.06}Te_2$ (2) samples in 10 kOe.

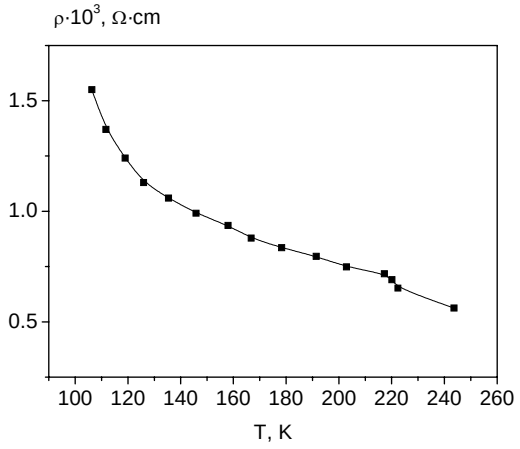

Fig. 4. The temperature dependence of the electric resistivity ρ of the polycrystalline sample $CdGeP_2$ with 4.5 wt% Mn.

purity hold much promise. By this means the $A^{II}B^{IV}C^{V}_2$:Mn compositions offer the promise for spintronics.

In polycrystalline volume $CdGeAs_2$:Mn samples a temperature dependence of the specific magnetization *M*(*T*), shown on Fig. 1, had a complicated character [9-11]. So, the *M*(*T*) shape is characteristic of the ferromagnetic at $T > 80$ K but at low temperatures a sharp increase of magnetization with a decrease of temperature is seen, which can be interpreted as an additional contribution of a paramagnetic-like phase. The non-uniform distribution of Mn ions in the polycrystalline samples can lead to a situation that a part of sample is ferromagnetic (FM) with a specific magnetization M_{FM} and other part is close to paramagnetic (PM) state with a specific magnetization M_{PM}. So, the whole magnetization $M = xM_{FM} + (1\text{-}x)M_{PM}$, where x is the portion of FM part. The xM_{FM} contribution at low temperatures can be roughly estimated by extrapolation of the rectilinear portions of the *M*(*T*) curves from the interval $T > 100$ K until they intersect the *M*-axis as using the relation:

$$M = M_0 L(\mu H/kT) + xM_{FM}, \qquad (1)$$

when L is Langevin function equal to $\mathrm{cth}(\mu H/kT) - kT/\mu H$, and μ is the mean magnetic moment of clusters. The μ-values of the $CdGeAs_2$:Mn samples equal to 7.4 ÷ 8 μ_B (see Table 1) that is the $(1-x)M_{PM}$ part is superparamagnetic-like. At 5 K the xM_{FM} contributions form 12 % of whole M for the sample with Mn concentration of 1 wt%, 76 % for 3 wt%, and 91 % for 6 wt% for $CdGeAs_2$:Mn. It was originally conjectured that clusters with μ = 7 ÷ 8 μ_B in superparamagnetic-like parts of sample can be consisted from Mn^{2+}-ions and 2 ÷ 3 holes, which magnetic moments are FM ordered.

The thin films and polycrystalline volume $CdGeAs_2$:Mn samples studied in work [5-7] had the admixture of another phases and the Mn content in them was not determined. Magnetization of these samples was not investigated in detail. Therefore a preparation and a magnetization investigation of single phase samples with determined Mn content are of considerable interest.

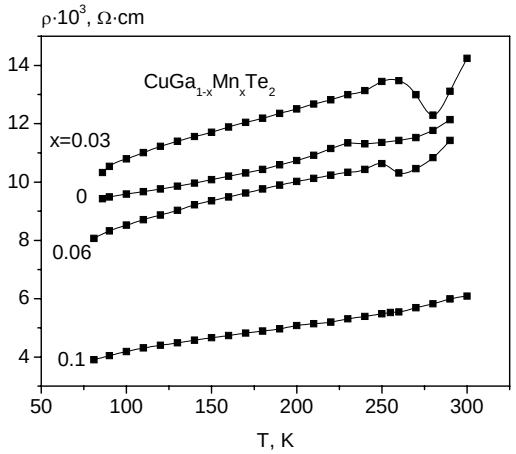

Fig. 5. The temperature dependence of the electric resistivity ρ of the polycrystalline samples $CuGa_{1-x}Mn_xTe_2$.

Polycrystalline $CdGeP_2$:Mn and $CuGaTe_2$:Mn samples were synthesized by a solid-state reaction technique. No traces of MnP or related compounds were found in them by accurate X-ray diffraction measurements. A magnetization was determined using SQUID and vibrating sample magnetometers. An electrical resistivity was measured by a four-probe method.

The temperature dependence of specific magnetization of $CdGeP_2$ doped by 4.5 wt% Mn is presented in Figs. 2. As one can see in comparison Figs 1 and 2, the $M(T)$ behavior of $CdGeP_2$:Mn is similar to the one of $CdGeAs_2$:Mn: the $M(T)$ curve are characteristic of the FM at $T > 190$ K and a sharp increase of M with a decrease of T, due to PM-like phase, is observed at $T < 150$ K. FM contribution in M at 5 K, received as well as for $CdGeAs_2$:Mn, forms 45 %. Mean magnetic moment μ, determined with use relation (1), is equal to 5.8 μ_B. Inset to Fig. 2 show the experimental $M(T)$ dependence (points) in magnetic field H =50 kOe and the calculated one using experimental H/T values at $H \le 50$ kOe, M_0 = 5.3 emu/g, xM_{FM} = 3 emu/g and μ = 5.8 μ_B. The points are well disposed on line. The μ value is near close to magnetic moment of Mn^{2+} ion therefore this part of sample is paramagnetic-like.

The Curie temperature T_C of such magnetic two-phase sample is T_C of its FM part. The determination of T_C–value with use of the Belov-Arrott method or the fitting under the Brillouin function fails because of the magnetic heterogeneity of samples. So, we

Table 1 Magnetic characteristics of $CdGeAs_2$:Mn, $CdGeP_2$:Mn and $CuGaTe_2$:Mn.

Compound	T_C,K	μ, μ_B
$CdGeAs_2$ with		
1 wt% Mn	350	7.4
3 wt% Mn	355	8.0
6 wt% Mn	355	8.0
$CdGeP_2$ with		
4.5 wt% Mn	330	5.8
$CuGa_{0,9}Mn_{0,1}Te_2$		25.75
$CuGa_{0,94}Mn_{0,06}Te_2$		20.72
$CuGa_{0,97}Mn_{0,03}Te_2$		16.73
$Cu_{0,88}Ga_{0,88}Mn_{0,24}Te_2$		17.89
$Cu_{0,9}Ga_{0,9}Mn_{0,2}Te_2$		19.12
$Cu_{0,93}Ga_{0,93}Mn_{0,14}Te_2$		17.39
$Cu_{0,95}Ga_{0,95}Mn_{0,1}Te_2$		15.27
$Cu_{0,97}Ga_{0,97}Mn_{0,06}Te_2$		16.76

determined T_C–value by an extrapolation of the steepest part of the $M(T)$ curve until it intersects the T-axis, similarly as was done in Ref. 7 and 8. The obtained T_C–value is equal to 330 K. It is given in Table 1. Application of that method of the T_C determination is easily justified since a $(1\text{-}x)M_{PM}$ contribution near T_C is less than xM_{FM} by a factor ~ 100 and nearly constant.

Three types of $CuGaTe_2$:Mn samples were investigated: the first type in which Mn partly replaces Cu, the second type in which Mn partly replaces Ga and the third type in which Mn partly replaces the both Cu and Ga. The part of compounds has a deviation from stoichiometry. Table demonstrates the all investigated compounds and their magnetic properties. As seen from Fig. 3, the $M(T)$ dependence of $CuGaTe_2$:Mn samples is characteristic for superparamagnetic. Fitting of the $M(T)$ data to Langevin function allows to determine the moment of clusters; it is $16 \div 25$ μ_B, (see Table). That clusters contain $3 \div 5$ Mn^{2+} ions in which magnetic moments are FM-ordered.

Figs. 4, 5 show the temperature dependence of an electrical resistivity ρ of the $CdGeP_2$:Mn and $CuGaTe_2$:Mn samples correspondingly. The $CdGeP_2$:Mn sample has semiconductive type of conductance. The ρ-dependence of $CuGaTe_2$:Mn samples is metallic type of conductance. Magnetoresistance was absent in the all samples in the investigated interval $80 \le T \le 400$ K within the limits of experimental error 0.01%. The sign of charge carriers was determined at 300 K using thermopower measurements. It has been found that the hole type of the conductivity prevails in the all investigated compounds.

Recent electronic structure calculations [12] found that Mn-doped $CdGeP_2$ was antiferromagnetic, just as Mn-doped CdTe [13]. But the holes for FM exchange between Mn^{2+}-ions can produce by intrinsic defects. The central point is that chalcopyrite structure are known [14] to be stabilized by certain intrinsic defects such as cation (Cd,Ge) vacancies, vacancy-antisite pairs, and the presence of hole-producing defects which could result in FM being favored even when Mn dopes the Cd site. In work [15] the hole-producing defects, that form stable complexes with substitution, were identified. Calculation of the formation energies of various kinds of defects and the prediction the conditions favoring the substitution of Cd sites and Ge sites by Mn were made too.

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