

Mn-DOPED CdGeAs₂ AND CdGeP₂ CHALCOPYRITES – NOVEL MATERIALS FOR SPINTRONICS

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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^V₂ doped by Mn. These were CdGeP₂:Mn, ZnGeP₂:Mn [5-7] and ZnGeAs₂:Mn [8] in which the Curie point achieved of 350 K. In our paper a new CdGeAs₂:Mn chalcopyrite is described in which the Curie point is reached of 355 K. The ternary A^{II}B^{IV}C^V₂ 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 of light, that permits the use of its for the parametric frequency conversion of a laser radiation in mid-IR range. For this purpose the CdGeP₂, CdGeAs₂, and ZnGeP₂ crystals of a high-purity hold much promise. It has been found that CdGeP₂ accumulates up to 20 mol. % Mn [7]. By this means the A^{II}B^{IV}C^V₂:Mn compositions offer the promise for spintronics.

Polycrystalline CdGeAs₂:Mn, and CdGeP₂:Mn samples were synthesized by a solid-state reaction technique. No traces of MnAs, MnP or related compounds were found in them by accurate X-ray measurements. A magnetization was determined using SQUID and vibratory magnetometers. An electrical resistivity was measured by a four-probe method.

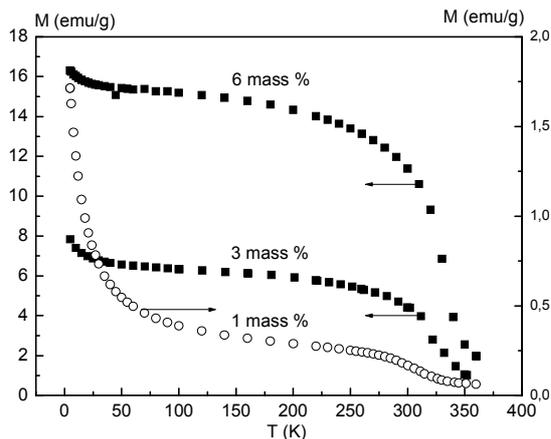


Fig. 1. The temperature dependence of magnetization $M(T)$ in magnetic field 50 kOe of CdGeAs₂:Mn polycrystalline samples with 1, 3, and 6 mass. % Mn.

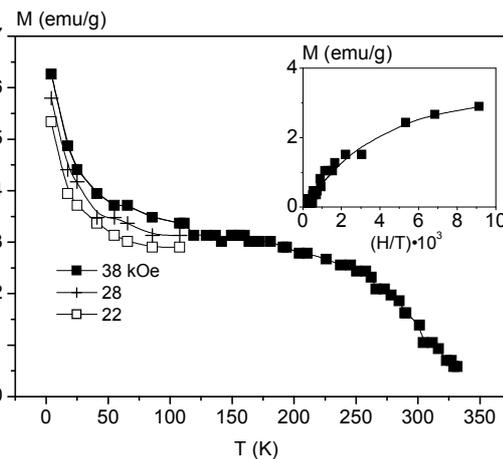


Fig. 2. The temperature dependence of magnetization $M(T)$ of CdGeP₂:Mn with 4.5 mass % polycrystalline sample with in some magnetic field; inset: line is the fitting on Langevin function, points are experiment.

The temperature dependence of specific magnetization, $M(T)$, of investigated samples is presented in Figs. 1,2. As one can see from Fig. 1 the $M(T)$ behavior of CdGeAs₂:Mn is distinctly dependent on the Mn concentration. As seen from Figs. 1 and 2, the $M(T)$ dependence for CdGeAs₂:Mn and CdGeP₂:Mn samples has a complicated character. So, the $M(T)$ shape is characteristic of the ferromagnet at $T > 80$ K for the first system and $T > 115$ K for the second compound 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 magnetization M_{FM} and other part is in state close to paramagnetic (PM) one with a magnetization M_{PM} . So, the whole magnetization $M = xM_{FM} + (1-x)M_{PM}$, 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 $T > 115$ K until they intersect the M -axis. Inset to Fig. 2 demonstrates that the $(1-x)M_{PM}$ experimental point, received at different values of T and H , is spaced on the curve, corresponding to Langevin function $L = \text{cth}(\mu H/kT) - kT/\mu H$:

$$(1-x)M_{PM} = M_0 L(\mu H/kT), \quad (1)$$

when μ is the mean magnetic moment of cluster. The μ -values of the CdGeAs₂:Mn and CdGeP₂:Mn samples equal to $7.4 \div 8 \mu_B$ and $8.6 \mu_B$ correspondingly (see Table 1) that is the $(1-x)M_{PM}$ part represents the superparamagnet.

Compound	T _c , K	μ , μ_B	T _{ρ_{max}} , K
CdGeAs ₂ with:			
1 mass% Mn	350	7.4	276
3 mass% Mn	355	8.0	324
6 mass% Mn	355	8.0	291
CdGeP ₂ with:			
4.5 mass% Mn	330	8.6	-

The presence of superparamagnetic part in samples is responsible for the difference between FC and ZFC curves in low magnetic fields which was observed in these samples. At 5 K the xM_{FM} contributions form 12% of whole M for the sample with Mn concentration of 1 mass %, 76 % for 3 mass %, and 91 % for 6 mass % for CdGeAs₂:Mn and 52% for CdGeP₂ with 4.5 mass % Mn.

The Curie temperature 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 fit under the Brillouin function fails because of the magnetic inhomogeneity of samples. So, we 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 – values are given in Table 1. Application of that method of the T_C determination is easily justified since a $(1-x)M_{PM}$ contribution near T_C is less than xM_{FM} by a factor ~ 100 and nearly constant.

Fig. 3 shows the temperature dependences of an electrical resistivity ρ of the CdGeAs₂:Mn and CdGeP₂:Mn samples. The $\rho(T)$ curves of CdGeAs₂:Mn have the large maximum at $T_{\rho_{max}} < T_C$ (see Table 1 for the $T_{\rho_{max}}$ values). At $T > T_{\rho_{max}}$ the conductivity has a semiconductor character and a metallic one at $T < T_{\rho_{max}}$. The CdGeP₂:Mn has semiconductive type of conductance. 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 except the CdGeAs₂:Mn compound with 6 mass. % Mn, in which the type of conductivity is an electronic one.

It was shown that Mn²⁺-ions substitute of Cd²⁺-ions up to 3 mass. % and for compound with 6 mass % Mn²⁺-ions substitutes of Ge⁴⁺-ions mainly. In first case the free charge carriers are absent

and FM exchange interaction between Mn^{2+} -ions is impossible.

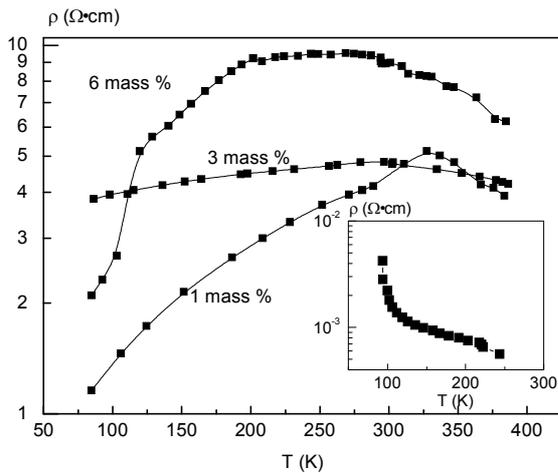


Fig. 3. The temperature dependence of the electric resistivity ρ the polycrystalline samples $CdGeAs_2:Mn$ and on inset the one for $CdGeP_2:Mn$.

Recent electronic structure calculations [9] found that Mn-doped $CdGeP_2$ was antiferromagnetic. But the hopes for FM exchange between Mn^{2+} -ions can produce by intrinsic defects. The central point is that chalcopyrite semiconductors are known [10] 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 [11] 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. In this case the clusters with $\mu = 7 \div 8 \mu_B$ in superparamagnetic parts of samples can be consisted from Mn^{2+} -ions and 2 \div 3 hopes, which magnetic moments are FM ordered.

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