



Review

Manganese-doped CdGeAs₂, ZnGeAs₂ and ZnSiAs₂ chalcopyrites: A new materials for spintronics

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ABSTRACT

Based on Mn-doped chalcopyrites CdGeAs₂, ZnGeAs₂ and ZnSiAs₂ the new dilute magnetic semiconductors with p-type conductivity were produced. Magnetization, electrical resistivity, magnetoresistance and Hall effect of mentioned compositions were studied. Their curves of temperature dependence of magnetization have the similar form in spite of complicated character, for which the concentration and mobility of the charge carriers are responsible. Thus, for $T < 15$ K, these curves are characteristic for superparamagnetics and for $T > 15$ K for a frustrated ferromagnetics. In compounds with Zn these two states dilute by spinglass-like state. This specific feature is assigned to an attraction of Mn ions occupying neighboring sites and to the competition between the carrier-mediated exchange and superexchange interactions. Curie temperatures of these compounds are above room temperature. These are the highest Curie temperatures in the A^{II}B^{IV}C₂:Mn systems.

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1. Introduction

At the present time the new way of solid state physics is growing rapidly. This way relate with possibility of transfer oriented electronic spin from ferromagnetic to nonmagnetic semiconductor. These investigations will allow produce one electron logic structure and spin-information systems with using electron spin as a memory cell: one spin—one information bit. In order to achieve high polarized spins and to find solution of electrical contact between ferromagnetic and semiconductor, it is interesting to get ferromagnetic semiconductor with Curie temperature more that 300 K by dope of conventional semiconductor by element with the not fully filled 3d-shell. The best results were achieved on Ga_{1-x}Mn_xAs films with Curie temperature $T_C \sim 170$ K [1,2]. However for spintronics application ferromagnetic semiconductors with $T_C > 300$ K are desirable. Recently high temperature ferromagnetism was observed in Mn-doped A^{II}B^{IV}C₂ chalcopyrites. It were CdGeP₂:Mn [3], ZnGeP₂:Mn [4] and ZnSnAs₂:Mn [5] compounds with T_C up to 350 K. In our papers new chalcopyrites CdGeAs₂:Mn with $T_C = 355$ K [6], ZnGeAs₂:Mn with $T_C = 367$ K [7] and ZnSiAs₂:Mn with $T_C = 337$ K [8] were prepared and discussed. The value of the latter is in the fact that

they are combined with «siliceous technology», i.e. it is possibility to make on them of epitaxy and other technological processes allowed to create the devices of the solid state electronics.

It is well known that the semiconductor used in varies devices, can obtain the next properties: covalent type of chemical bond, small carrier effective mass, high carrier mobility and absolute minima and maxima of conduction and valence bands in the center of Brillouin zone. A^{III}B^V semiconductors, in particular GaAs, offer these properties. A^{II}B^{IV}C₂ ternary semiconductors being crystal-chemical and electronic analogy of A^{III}B^V semiconductors, obtain of the ones too. However high Curie point in A^{II}B^{IV}C₂:Mn compounds occur only at a large doping level as a result of which the ferromagnetic clusters are formed. It is shown in our works [6–8]. The ferromagnetic cluster presence increases the polarization of charge carriers and decreases of their mobility at this time. This latter is due to the fact that spins in ferromagnetic clusters are strongly correlated because of the coherently disperse the charge carriers. Therefore it is essential to search for ways of the preparation of the diluted magnetic semiconductors with the optimum properties for the spintronics devices. To attain a desired compromise it is necessary to elucidate a nature of ferromagnetism in them. In some works A^{II}B^{IV}C₂:Mn chalcopyrites were considered as homogeneous ferromagnetics [3–5,9,10]. Our study of CdGeAs₂:Mn [6], ZnGeAs₂:Mn [7] and ZnSiAs₂:Mn [8] magnetization was shown that these compounds are magnetic inhomogeneous materials. Here, we report that the curves of

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temperature dependence of magnetization $M(T)$ of mentioned chalcopyrites have the similar form in spite of its complicated character, for which the concentration and mobility of the charge are responsible.

Thus, for $T < 15$ K, it is characteristic of superparamagnetics, while for $T > 15$ K, it is a frustrated ferromagnetics. In compound with Zn these two states dilute by spinglass-like state. This specific feature is assigned to an attraction of Mn ions occupying neighboring sites and to the competition between the carrier-mediated exchange and superexchange interactions.

2. Samples producing and analysis

The CdGeAs_2 , ZnGeAs_2 and ZnSiAs_2 polycrystalline samples were prepared by the vacuum-ampoule method, using high purity powders of monocrystalline zinc diarsenide, cadmium diarsenide, and monocrystalline silicon and germanium, as along with double-sublimed manganese. The use of diarsenides allowed us to reduce the pressure of the saturated arsenic vapor over the melt solution, in contrast to synthesis by means of the immediate interaction of elements. This technique allowed the stoichiometric composition to be retained more precisely. To introduce substantial quantities of manganese into the CdGeAs_2 , ZnGeAs_2 and ZnSiAs_2 , the samples were prepared as oversaturated solid solutions. To keep the manganese in the soluble state at temperatures close to the melting points of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{As}_2$, we used quick cooling of the melt ($5\text{--}10^\circ/\text{s}$). To increase the manganese's solubility, the initial mixture was prepared according to the hypothetical profile $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{As}_2\text{--MnB}^{\text{IV}}\text{As}_2$ since (according to [11–15]) manganese ions in compositions of $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2$ tend to replace the elements of A^{II} . Samples were identified using a variety of physical–chemical analysis methods.

X-ray phase analysis was performed on a Siemens D-5000 diffractometer ($\text{CuK}\alpha_1$, $\lambda = 1.54056 \text{ \AA}$), over the range of angles $2\theta = 0^\circ\text{--}160^\circ$. The experimental interplane distances were compared against the ICSD DATABASE (2004). The distribution of elements along the length of samples with a step of ~ 0.3 mm was monitored by X-ray fluorescence. According to the obtained data, manganese predominantly replaces the elements of A^{II} , leading to the formation of solid solutions of $\text{A}_{(1-x)}\text{Mn}_x\text{B}^{\text{IV}}\text{As}_2$ and has the valency equal to +2.

3. Experimental technique

At the present paper magnetization, electrical resistivity ρ , magnetoresistance $\Delta\rho/\rho = (\rho_H - \rho_{H=0})/\rho_{H=0}$ and Hall effect of aforementioned polycrystalline samples were studied. Magnetization (M) measurements have been performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) in the temperature region $5 \leq T \leq 300$ K and a weight method with electromagnetic compensation in $T \geq 290$ K. The last method is employed usually in measurements of the paramagnetic susceptibility, but the low value of magnetization resulting from small manganese contents made it applicable to magnetization studies. The determination of ρ and $\Delta\rho/\rho$ was effected by the standard four-point probe technique. The Hall effect was measured by the standard dc method (a homemade device). The electrical contacts were fixed to the sample with current-conducting glue.

4. Experimental results and their discussion

The curves #1 in Figs. 1–4 show the temperature dependence of the measured magnetization $M(T)$ of some compounds from

systems $\text{ZnSiAs}_2\text{:Mn}$, $\text{CdGeAs}_2\text{:Mn}$ and $\text{ZnGeAs}_2\text{:Mn}$ that are typical for another compounds of every system. One can see that these curves are similar although they have a complicated character. So, $M(T)$ curves under $T > 50$ K have shape characteristic for ferromagnetic. However, in case of $T < 15$ K magnetization rapid grows with T -decreasing and $M(T)$ -dependence obeys by Langevin's function

$$M/M_0 = \coth(\mu_c H/kT) - kT/\mu_c H, \quad (1)$$

that is evidence of superparamagnetic behavior. Here M_0 is equal to M at $T \rightarrow 0$ K and μ_c is magnetic moment of superparamagnetic cluster. We determined the M_0 -value by extrapolation of $M(T)$ curve to $T = 0$ K and μ_c -value by selection to experimental curve. Table 1 shows μ_c -values of the all studied compounds. These values are in the range from 8 to $80 \mu_B$. Difference between magnetizations of zero-field-cooled (ZFC) and field-cooled (FC) sample (see Fig. 5) and shift of the hysteresis loop of FC sample (see Fig. 6) observed at $T = 5$ K confirm the superparamagnetic clusters presence.

We proposed that at $T > 15$ K magnetization M is sum of magnetization of ensemble of superparamagnetic clusters and magnetization from phase with long-range magnetic order. We separate $M(T)$ -curve (curve # 1 in Figs. 1 and 2 and curve at 50 kOe in Fig. 3) on curve of the superparamagnetic clusters magnetization (curve # 2) and curve of T -dependence of magnetization from phase with long-range magnetic order $M_S(T)$ (curve # 3) using a computer subtraction of curve # 2 from curve # 1. A spontaneous magnetization appears at $T > 15$ K as Figs. 1–3 show. M_S -value does not almost depend from T at $100 \leq T \leq 250$ K and increases with magnetic field. From highest value of M_S in this T -region was determined a magnetic moment on formula unit. It is found this magnetic moment very understands comparison

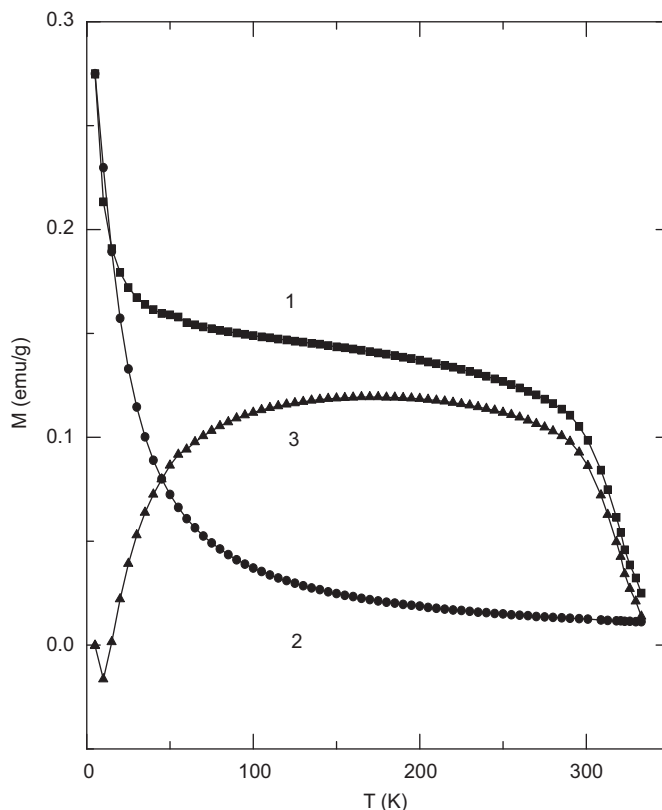


Fig. 1. ZnSiAs_2 composition with 2 wt% Mn. Temperature dependence: (1) of the magnetization M measured in a magnetic field of 10 kOe; (2) of $M_0 L(\mu_c H/kT)$ with $\mu_c = 55 \mu_B$; (3) of $M_S = M - M_0 L(\mu_c H/kT)$.

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