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Room temperature ferromagnetism in novel magnetic semiconductors based on II–IV–V₂ chalcopyrite compounds

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Abstract

Novel magnetic semiconductor compounds in the ternary system II–IV–V₂ with the 3d transition element Mn have been prepared. The use of alternative growth methods for CdGeP₂–Mn and ZnGeP₂–Mn quasi-binary systems proved the existence of material in both polycrystalline and single crystal forms. The prepared compounds share the chalcopyrite crystal structure and reveal ferromagnetic behavior over a wide temperature range. The Curie temperature has been measured for CdMnGeP₂ as 320 K (single crystal) and 310 K (polycrystalline bulk). © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Recently, ferromagnetic semiconductors have been attracting attention as promising materials for the next generation spintronics and information technology [1]. Intensive studies have been carried out in III–V-based diluted magnetic semiconductors (DMS), because III–V semiconductors inherently have high potential for fabrication of practical devices. Indeed, the use of advanced technology for heteroepitaxy has en-

abled realization of spin-injection devices employing III–V DMS. Recently, Ohno et al. succeeded in fabricating an LED structure having high spin-injection efficiency [2]. They also succeeded in fabricating a field effect transistor (FET) structure using a thin In_{0.97}Mn_{0.03}As layer as a channel, on which a gate is formed using a polyimide film as a gate insulator. They succeeded in changing ferromagnetic transition temperature by controlling the hole concentration by application of the gate voltage [3].

However, the main problem that hampers practical application of DMS is the low Curie temperature of these materials. The highest Curie temperature reported to date for the III–V-based DMSs is obtained in Ga_{1-x}Mn_xAs solid solutions with 5.3% Mn-content, which show the maximal

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Curie temperature of 110 K [4,5]. Magnetic semiconductors with room-temperature ferromagnetism have been strongly required for practical applications.

Since it has been known that high concentration of Mn can be incorporated in II–VI semiconductors as in the case of $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$, we looked for materials that contain group II element and have electrical property similar to III–V compounds.

Chalcopyrite materials II–IV–V₂ are close analogs to the well-developed III–V materials [6] and could be used in heterostructures based on them. Some of the materials belonging to this family show both p- and n-type conduction with mobility as high as III–V compounds. Compared with III–V semiconductors, in which Mn^{2+} should occupy the group III sites, Mn^{2+} can easily substitute for the group II site without any sacrifice of electrical neutrality. If a part of the Mn atoms occupy the group IV site, they will act as acceptors to supply holes to the Mn 3d band making the Mn ions partially trivalent, which may enable the Mn^{2+} – Mn^{3+} double exchange mechanism to be realized. Based on this postulation, we tried a incorporating Mn atoms into the ternary chalcopyrite type semiconductor and carried out crystallographic as well as magnetic and magneto-optical (MO) characterization. Recently, we have succeeded in incorporating high concentration of Mn atoms into CdGeP_2 , one of the ternary II–IV–V₂ compounds and reported ferromagnetism at room temperature [7,8].

2. Single crystal growth of CdGeP_2 and ZnGeP_2 and Mn-diffusion to these crystals

2.1. Growth of CdGeP_2 and ZnGeP_2 single crystals

CdGeP_2 single crystals were grown by directional crystallization of the stoichiometric melt in a quartz ampoule or graphite crucible (diameter 1 cm, length 10 cm). The method was developed at the Ioffe Institute [9,10]. 8–10 g of chemicals was weighed. Two-zone tubular oven was employed for re-crystallization with a small temperature gradient in height. After melt formation, the directional cooling was performed with a rate of

4 deg/h for 48 h until all the melt became solidified. Then the oven was cooled down at the rate of 60 deg/h. In that way, a large block crystalline ingot was obtained. It was possible to cut single crystal lumps of up to 100 mm³ and free of visible defects from the ingot. The crystals were oriented by optic asterism figures or X-ray diffraction method and cut to a rectangular shape of a convenient orientation. The crystals showed highly compensated n-type conductivity.

Prior to the growth of single crystals of ZnGeP_2 , the ternary compound was synthesized from constituent elements in polycrystalline form. Polycrystalline substance ZnGeP_2 was prepared by a two-temperature dynamic method [11] at Siberian Physical Technical Institute using calculated thermodynamic data [12]. The vertical Bridgman technique was employed thereafter to grow single crystal bulk ingots with a size of 28 mm in diameter and 150 mm in length. Single crystal plates with a required crystallographic orientation were cut from the ingots. The samples show p-type conductivity, high resistivity and may be prepared with a controlled optical transparency in the infrared spectral range.

2.2. Deposition and diffusion of Mn into single crystals

Oriented single crystals of CdGeP_2 {112} and ZnGeP_2 {001} with polished and etched faces were chosen as host substrates. Mn was evaporated from a Knudsen cell and was deposited on to the crystal surface of these single crystals in an MBE chamber.

In the case of CdGeP_2 , the temperature of the substrate during deposition was kept at 380°C. The total thickness of the deposited Mn-layer was 30 nm. After deposition, the sample was annealed in situ at 500°C for 30 min to assist a diffusion of Mn accompanied by the solid-phase chemical reaction with the host crystal.

On the other hand, in the case of ZnGeP_2 , the substrate temperature was elevated to 400°C during deposition. In this case, the deposition of Mn and subsequent solid-state reaction were simultaneously undertaken.

The process was monitored in situ using a reflection high-energy electron diffraction (RHEED) equipment. RHEED patterns for the case of $\text{CdGeP}_2\text{:Mn}$ are shown in Fig. 1: (a) Before deposition of Mn, the pattern with well-defined

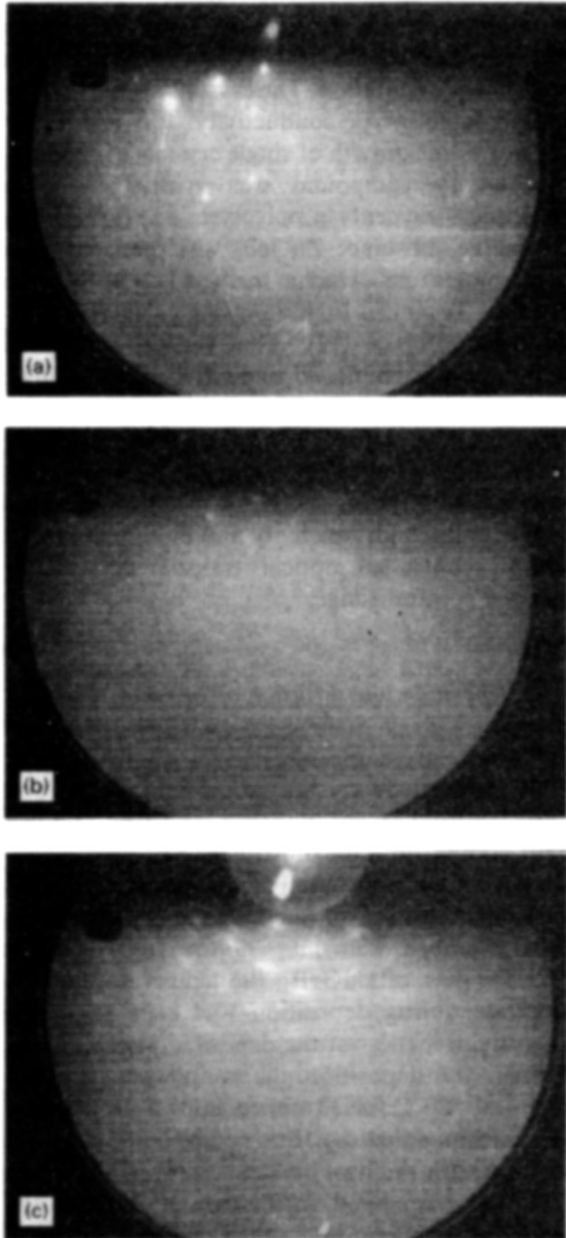


Fig. 1. RHEED patterns of $\text{ZnGeP}_2\text{-Mn}$: (a) before deposition; (b) and (c) at 300 and 1080 s after start of Mn deposition, respectively.

diffraction spots due to chalcopyrite lattice was observed. (b) After deposition of Mn, the spots disappeared and diffuse ring appeared, suggesting that amorphous Mn covered the surface. (c) During annealing process at elevated temperature, the single crystalline structure gradually recovered [13]. RHEED pattern of the material at initial and final stages of this reaction demonstrates a set of RHEED spots similar to each other and shares the same chalcopyrite-type lattice.

Fig. 2 illustrates RHEED patterns during Mn-deposition on ZnGeP_2 (001) crystal surface: (a) Spots of chalcopyrite structure are clearly observed in the initial surface. As Mn is deposited at 400°C , spots become gradually obscured and as shown in (b), a streaky pattern appears at 300 s after the start of deposition. At 1080 s after the start, the crystalline spots recovered as shown in (c). Simultaneously, we deposited Mn on InP (001) placed adjacent to the ZnGeP_2 substrate at the same substrate temperature. The RHEED pattern became obscured after Mn deposition but never recovered crystalline spots. It is important to emphasize that the solid-phase chemical reaction with manganese occurs differently in the chalcopyrite type ZnGeP_2 crystal and its binary zinc-blende analog InP. Mn atoms seem far more easily incorporated into the chalcopyrite crystals than into zinc-blende crystals.

After incorporation of manganese, appearance of MnP- and GeP-related phases along with Zn- and Cd-compounds was anticipated, since so many Mn-containing binary phases are known to exist [14]. Therefore, a special attention was paid to an accurate identification of the secondary phases.

3. Synthesis of polycrystalline II–IV–V₂ chalcopyrites and incorporation of Mn

3.1. Synthesis of CdGeP_2 and ZnGeP_2 polycrystalline powders

A series of growth methods suitable for II–IV–V₂ ternary compounds is known [15,16]. Herein we consider a specific technique to prepare polycrystalline materials of two ternary phosphides. Pure

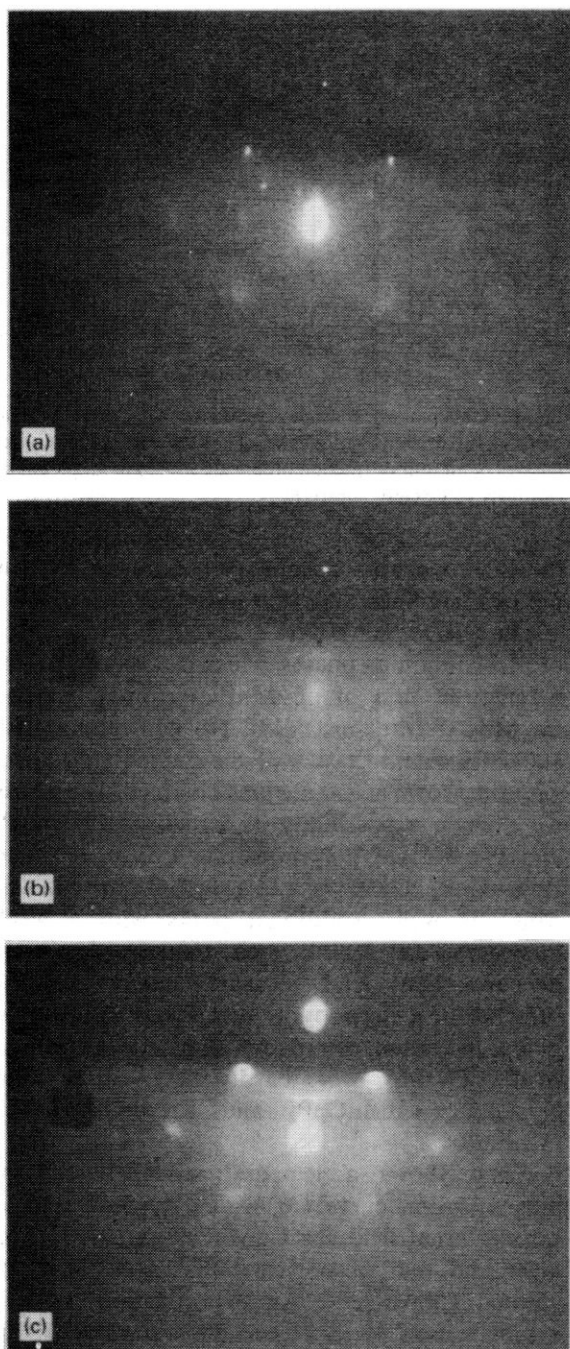


Fig. 2. RHEED patterns of ZnGeP_2 (a) before Mn-deposition, (b) 1080 s after the start of Mn-deposition and (c) 1800 s after the start of Mn-deposition.

chemicals of Cd, Zn grains (99.9999), Ge grains (99.999), P chunks (99.9999) were used as starting materials for synthesis of CdGeP_2 and ZnGeP_2 compounds. Starting materials were sealed in vacuum into fused silica ampoule and placed in the furnace. A cylindrical furnace with a quartz reactor and thermocontroller was employed for growth. For polycrystalline ZnGeP_2 , temperature was raised at $6^\circ\text{C}/\text{h}$ to 1000°C , at which the sample was kept for 400 h. The resulting ZnGeP_2 polycrystalline powder was sealed together with Mn and appropriate amount of iodine for chemical vapor transport with the growth temperature kept at 680°C and the source temperature varied from 700°C to 1000°C . The temperature profile for growth of CdGeP_2 and MnP polycrystalline materials was similar to the case of ZnGeP_2 . Polycrystalline substances of CdGeP_2 and ZnGeP_2 have been grown with a composition 1:1:2 corresponding to II–IV–V₂ ternary compounds. In spite of repeated iodine transport experiments, CdGeP_2 and ZnGeP_2 could not be obtained in single crystalline forms, but in a polycrystalline bulk. The obtained Zn-compound showed presence of Ge-excess, while no additional germanium was found in the Cd-compound. This fact indicates different homogeneity areas of these compounds. The situation with Ge-excess in ZnGeP_2 is usual because of an elevated solubility of germanium in this ternary compound.

3.2. Synthesis of Mn-containing polycrystalline materials of CdMnGeP_2 and ZnMnGeP_2

We employed two-stage crystallization-substitution approaches to crystal growth of polycrystalline phases of CdMnGeP_2 and ZnMnGeP_2 [17,18]. The polycrystalline host ternary compound was synthesized directly from elemental components Cd (Zn), Ge, P as described in the above section. Then a chemical reaction of ternary chalcopyrite compound with Mn was carried out at 500°C for 2 h in N_2 -flow to realize CdMnGeP_2 or ZnMnGeP_2 solid solution in a polycrystalline form. Polycrystalline ZnMnGeP_2 after the second stage was grown as a chalcopyrite compound with Ge-excess (like the starting ZnGeP_2), whereas the

CdMnGeP_2 powder did not show any detectable amount of Ge-excess.

MnP polycrystalline ingots were synthesized from Mn and P elements to obtain a reference substance. XRD analysis revealed that the obtained material contained the ordinary manganese phosphide MnP as the main phase. However, weak XRD peaks showed the presence of small amount of triphosphide $\text{Mn}_{5.6}\text{P}_3$.

4. Characterization of magnetic chalcopyrites

The crystal structure and chemical composition were measured with a Rigaku type RAD-IIC X-ray diffractometer (XRD) and scanning electron microscope (SEM) Hitachi S-4500. Magnetization effect was measured with a Toei type VSM-5 vibrating sample magnetometer (VSM) in the temperature range 80–350 K.

XRD patterns of single crystal CdMnGeP_2 and ZnMnGeP_2 showed strong chalcopyrite peaks. In the single crystal layer of CdMnGeP_2 , slight shift of the chalcopyrite peaks to larger angles 2θ with increasing Mn-content was observed in a careful XRD experiment (Fig. 3). It was found that the lattice constant changes as $a = 5.741 \text{ \AA} \rightarrow 5.710 \text{ \AA} \rightarrow 5.695 \text{ \AA}$ in a series of compounds $\text{CdGeP}_2 \rightarrow \text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2 \rightarrow \text{Cd}_{1-y}\text{Mn}_y\text{GeP}_2$ ($x < y$). Although no trace of second phase compounds was observed in this XRD study, very weak diffraction rings that can be assigned to MnP were observed in the accurate XRD measurement using a Rigaku type RINT-RAPID system with a glancing angle incidence of X-rays. We still believe that the main thickness (about 1000 nm) of the layer of CdGeP_2 crystal reacted with Mn belongs to the chalcopyrite phase of CdMnGeP_2 . On the contrary, the position of XRD peaks in polycrystalline Cd-compound practically does not undergo a shift with increasing Mn concentration (0% \rightarrow 20% \rightarrow 50%).

No second phase was observed at all in the Mn-diffused single crystalline layer of ZnGeP_2 in the accurate XRD using the RINT-RAPID system. However, in ZnMnGeP_2 polycrystalline substance, a secondary phase of Ge accompanies the main chalcopyrite phase, although chalcopyrite phase

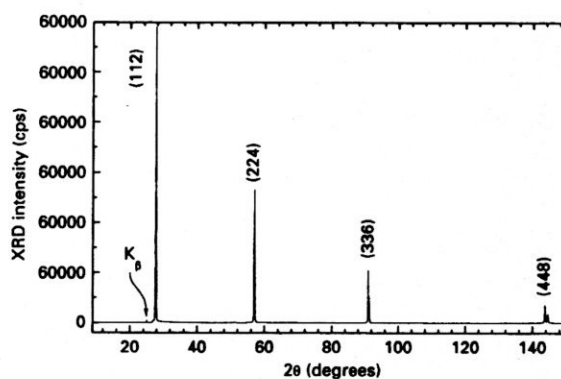


Fig. 3. XRD pattern of single crystal layer $\text{Cd}_{1-y}\text{Mn}_y\text{GeP}_2$ (at $T = 300 \text{ K}$, orientation of CdGeP_2 substrate- (112)). The reflexes of all four diffraction orders are shifted to larger angles relatively to CdGeP_2 substrate

prevails over the secondary Ge-phase. A few unidentified lines were also observed.

The XRD spectra were analyzed in the presence of Mn-containing phases, which can be a source of magnetism, first of all MnP (ferromagnet) and Ge_2Mn_3 (ferrimagnet) [14]. No conformity with 100–20% intense peaks of the quoted substances with the grown substance was obtained. Therefore, we exclude a possibility of formation of Mn_xP_y and Ge_xMn_y in polycrystalline CdMnGeP_2 and ZnMnGeP_2 . There was not a trace of pure Mn and MnO as well. Additional peaks with a weak intensity were found; their nature remains in question. Thus, XRD measurements revealed the presence of a chalcopyrite compound as the main phase, whereas, extraneous magnetic phases as MnP_x , Ge_xMn_y were hardly observed in polycrystalline CdMnGeP_2 and ZnMnGeP_2 with $[\text{Mn}] = 20\%$.

Fig. 4 shows a temperature dependence of magnetization curve ($M-T$ curve) measured at zero external field for CdMnGeP_2 single crystal layer and that of polycrystalline 20% Mn-substituted CdMnGeP_2 . An extrapolation to zero magnetization gives Curie temperature of 320 K for single crystal and a little lower as 310 K for polycrystalline materials. Recent measurement has revealed that the $M-H$ curve of the CdMnGeP_2 single crystal layer shows the same saturation magnetization at elevated temperature up to 423 K.

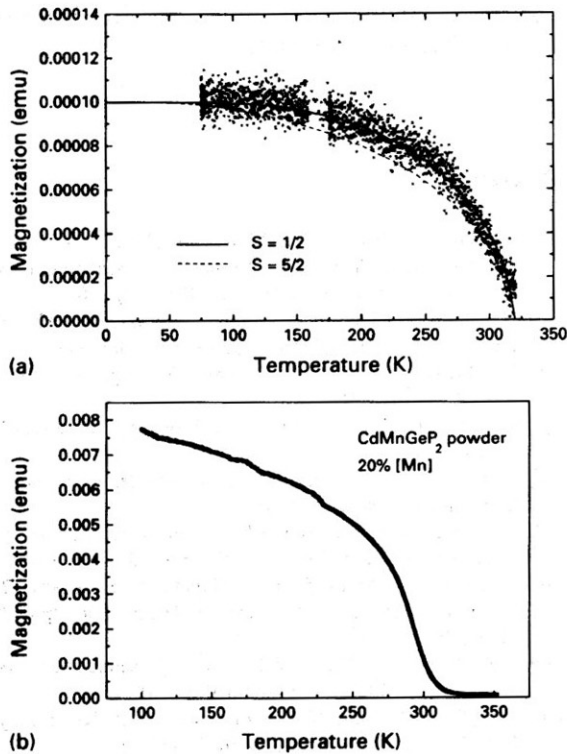


Fig. 4. Magnetization versus temperature of $\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$ single crystal layer (a) grown on CdGeP_2 crystal and of $(\text{Cd,Mn})\text{GeP}_2$ polycrystalline powder (b) with 20% [Mn] substitution.

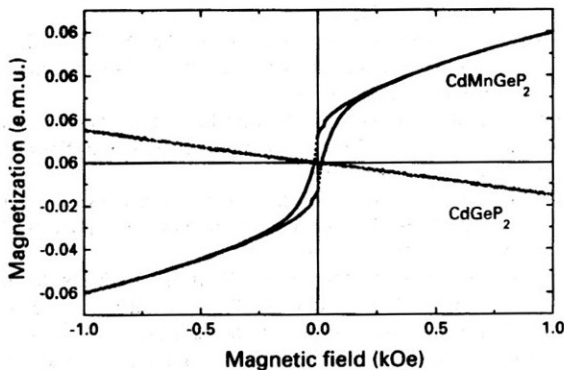


Fig. 5. Magnetization of polycrystalline substances at 298 K-undoped CdGeP_2 and CdMnGeP_2 annealed at $T = 500^\circ\text{C}$ for 30 min.

Fig. 5 presents magnetization versus magnetic field curve ($M-H$ curve) for polycrystalline substances CdGeP_2 and CdMnGeP_2 . A distinct

magnetic hysteresis was measured at room temperature in Mn-containing chalcopyrite compound, whereas the starting CdGeP_2 gives only a straight line with a negative slope, characteristic of diamagnetic behavior.

It is important to emphasize that the treatment with manganese under equal conditions does not result in a magnetization in InP:Mn in contrast with the ternary Zn-compound [18]. The converted layer of $\text{ZnGeP}_2:\text{Mn}$ shows a weak ferromagnetism up to 350 K by SQUID measurement. On the contrary, independently prepared ZnMnGeP_2 in a polycrystalline form revealed an evident ferromagnetic behavior. The hysteresis loop of the latter gave values of coercivity $H_c = 0.22$ kOe and saturation field $H_s = 16$ kOe at room temperature. The magnetization effect of ZnMnGeP_2 polycrystalline sample does not disappear at $T = 296$ K, although M_s value decreases by a factor of 2.2 as compared to the value at 123 K. This begs the question why magnetization comes from the magnetic chalcopyrite but not from MnP ($T_c = 289$ K).

Recently, a notice about ferromagnetic behavior in other II–IV–V₂ chalcopyrite compounds, e.g. ZnGeAs_2 , has become available [19]. It became known that the Mn-containing ZnGeAs_2 material prepared by MBE showed Curie temperature higher than room temperature. Theoretical calculations carried out recently for gaining a knowledge of the nature of ferromagnetism in $\text{Cd}_{1-x}\text{Mn}_x\text{GeP}_2$ [20] disclosed the ferromagnetic alignment between Mn and P increases the total energy and makes antiferromagnetic ordering preferable. On the contrary, Akai et al. [21] showed that ordering of Mn and introduction of defects could explain the ferromagnetism observed experimentally in this material. Freeman with co-authors [20] predicted also a widening of the band gap due to the addition of Mn, which is in agreement with our experimental data on photoluminescence [7]. MO Kerr spectra were measured in a single crystal layer CdMnGeP_2 grown on a non-magnetic CdGeP_2 substrate. The spectrum of MO Kerr ellipticity peaks at photon energy 1.75 eV close to the energy gap of CdGeP_2 and then shows a gradual decrease with individual spectral features of CdMnGeP_2 at higher photon

energies up to 3.7 eV [8]. Since MO spectra reflect the electronic structures of the magnetic materials, they can be used as a powerful tool for discrimination of the main phase materials from the secondary phases. It is a future problem to pursue MO measurements in all the related materials.

5. Conclusion and unsolved problems

The new ferromagnetic materials in II–IV–V₂–Mn chalcopyrite system have been described in comparison with known binary phosphides MnP and InP. The chalcopyrites can be prepared under different techniques; the two-stage fusion/I₂-transport/N₂-flow method and solid-phase chemical reaction. Both polycrystalline and single crystal materials of Cd- and the Zn-phosphides with manganese share the crystal structure of chalcopyrite as a major phase. The distinct magnetic hysteresis has been measured in single crystalline CdMnGeP₂ and in polycrystalline ZnMnGeP₂ and CdMnGeP₂ compounds with 20% [Mn] and at temperature as high as room temperature. We believe that the main contribution to room temperature ferromagnetism is from the magnetic chalcopyrite.

Epitaxial growth of thin films of CdMnGeP₂ and ZnMnGeP₂ compounds on appropriate single crystalline substrates is now under planning to ascertain the compatibility of these quaternary substances with standard type substrates widely used, which will open up a possibility of using these materials as spin-injection electrodes.

Theoretical calculations of ordering in the magnetic chalcopyrites should support technological search and give prognosis for relative magneto-optical, polarization, magneto-transport and other phenomena.

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