

# CRYSTAL AND MAGNETIC STRUCTURE OF $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$ SYSTEM

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The crystal and magnetic properties of the intermetallic system  $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$  /for  $x=0, 1, 2, 2.5, 3$  and  $4$ / are investigated with X-ray and neutron diffraction and magnetometric methods. The compounds with  $0 \leq x \leq 2.5$  have  $\text{B8}_2$  type of crystal structure, whereas  $\text{Fe}_2\text{Mn}_3\text{Ge}_3$  is a two phase system, and  $\text{FeMn}_4\text{Ge}_3$  shows  $\text{D8}_8$  type structure. In both  $\text{B8}_2$  and  $\text{D8}_8$  structure the 3d metal atoms occupy two non-equivalent sites. The Mn atoms preferentially occupy the 2/a/ or 6/g/ positions. All investigated compounds /except for  $x=2.5$ / are ferromagnetic, and have collinear magnetic structure. The compound with  $x=2.5$  have ferrimagnetic structure with canted spin arrangement.

## 1. Introduction

The influence of substitution of Mn-atoms for Fe-atoms in polycrystalline  $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$  compounds on their crystal and magnetic properties was investigated.

The germanides of iron and manganese have related hexagonal crystal structures of  $\text{B8}_2$  type for  $\text{Fe}_5\text{Ge}_3$  [1] and  $\text{D8}_8$  type for  $\text{Mn}_5\text{Ge}_3$  [2]. In these structures, there are two types of sites for the metal atoms with alternate layers of just-metal atoms or metal-plus-germanium atoms. In the  $\text{B8}_2$  structure the space group is  $\text{P6}_3/\text{mmc}$  and the atoms occupy following positions: Fe atoms - 2/a/ and 2/d/, and Ge atoms - 2/c/. The structure  $\text{D8}_8$  belongs to space group  $\text{R}\bar{6}_3/\text{mcm}$  with atoms in following sites: Mn in 4/d/ and 6/g/, Ge in 6/g/. Both phases are ferromagnetic [3,4]. Neutron diffraction measurements yield following models of the magnetic structure of this compounds, in the case of -  $\text{Fe}_5\text{Ge}_3$  - collinear, magnetic moments of  $\text{Fe}_I$  atoms and  $\text{Fe}_{II}$  atoms mutually parallel and lie in the basal plane, -  $\text{Mn}_5\text{Ge}_3$  - collinear, the magnetic moments of the two sublattices aligned parallel to the c axis. The values of magnetic moments, are given in Table 2.

The purpose of this paper is to present the results of investigations of the crystal structure and magnetic properties of the intermetallic compounds  $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$  for  $x=0, 1, 2, 2.5, 3$  and  $4$  as obtained by means of X-ray and neutron diffraction and magnetometric methods.

## 2. Experimental and Results

The samples  $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$  were prepared by melting iron /4N/, manganese /4N/ and germanium /5N purity/ in an induction furnace. The samples were then annealed in a quartz tube at  $950^\circ\text{C}$  for 100 h and cooled to room temperature. The single-phase nature of the compounds was checked by X-ray analysis using  $\text{FeK}\alpha$  radiation. The samples with  $x=0, 1, 2$  and  $2.5$  have the  $\text{B8}_2$  structure, with  $x=4$  -  $\text{D8}_8$  structure.  $\text{Fe}_2\text{Mn}_3\text{Ge}_3$  / $x=3$ / appeared as a two-phase system, showing peaks corresponding to both  $\text{B8}_2$  and  $\text{D8}_8$  structures in X-ray and neutron diffraction patterns /see Fig. 1/. Lattice constants were determined with a diffractometer DRON-1. A least squares refinement using measured  $2\theta$  values yielded the lattice constants shown in Table 1.

Magnetometric measurements were carried out in the temperature range of 100 to 650 K, using a Sucksmith balance. The temperature dependence of the magnetization and reciprocal susceptibility are shown in Fig. 2. The inset presents the magnetization curves at 100 K. For all samples the spontaneous magnetization is observed at low temperatures. The magnetic susceptibility of all samples at high temperatures obeys the Curie-Weiss law. The Curie temperature values as well as the magnetic moments in the saturation and paramagnetic states were established from these measurements. The results are given in Table 1. In case of compounds with  $\text{B8}_2$  crystal structure, both Curie temperature  $T_c$  and magnetic moment  $\mu_s$  decrease with increasing Mn concentration.

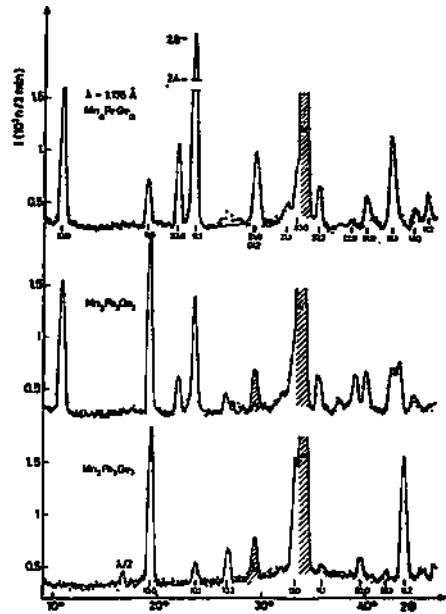


Fig. 1. Neutron diffraction patterns of  $\text{Fe}_3\text{Mn}_2\text{Ge}_3$ ,  $\text{Fe}_2\text{Mn}_3\text{Ge}_3$  and  $\text{FeMn}_4\text{Ge}_3$  at the room temperature.

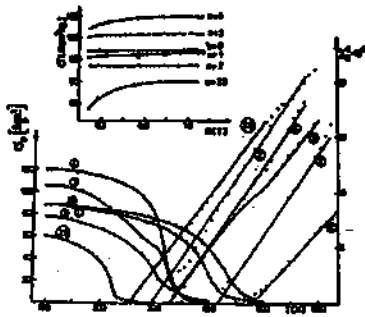


Fig. 2. Temperature dependence of the magnetization and reciprocal susceptibility for the  $Fe_{5-x}Mn_xGe_3$ . Inset presents magnetization curves at 80 K.

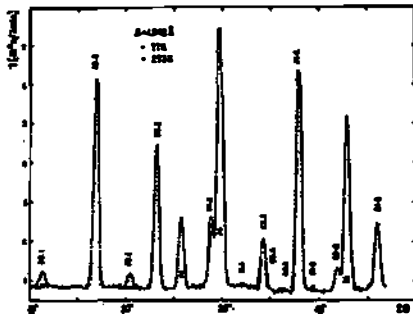


Fig. 4. Neutron diffraction patterns of  $Fe_{2.5}Mn_{2.5}Ge_3$  taken at 77 K and 293 K.

In order to separate the nuclear and magnetic contributions to the total scattering, a field of 0.6 T was applied parallel to the scattering vector. Fragments /from  $2\theta=9^\circ$  to  $47^\circ$ / of the patterns obtained in this way for the samples with  $x=1, 2$  and  $4$  are shown in Fig. 3. The peaks marked A1 originate from the sample holder and cryostat walls. Neutron diffraction patterns for the sample with  $x=2.5$  at 77 and 293 K are shown in Fig. 4. All the reflections observed in the patterns for  $x=1, 2$  and  $2.5$  could be indexed on the basis of the  $B8_2$  structure unit cell, and for  $x=4$  -  $DB_8$  structure. Since the nuclear scattering lengths of Mn and Fe atoms are very different,  $b_{Mn} = -0.39$  and  $b_{Fe} = +0.95 \times 10^{-14}$  m [6], the

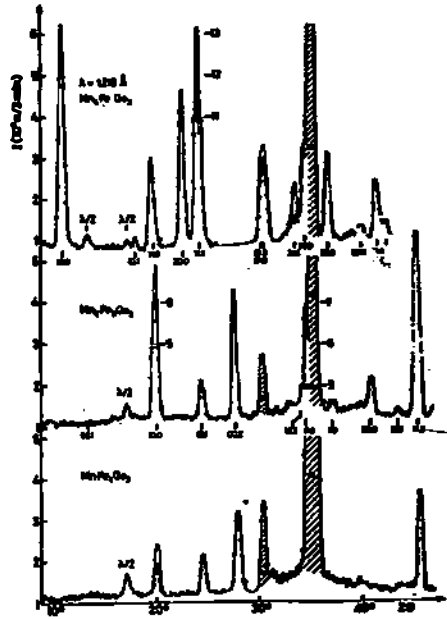


Fig. 3. Neutron diffraction patterns of  $Fe_4MnGe_3$ ,  $Fe_3Mn_2Ge_3$  and  $FeMn_4Ge_3$  at temperature of 80 K / $\theta=0$ ,  $x=H=0.6$  T/.

Neutron diffraction patterns were obtained on a diffractometer at the RA reactor in Boris Kidrič Institute at Vinča using neutrons wavelengths 1.048, 1.176 and 1.216 Å in the temperature range 77-293 K.

Table 1: Structural and magnetic parameters in  $Fe_{5-x}Mn_xGe_3$

x	Type of crystal structure	Lattice constants		$T_C/K/$	$\theta_p/K/$	$\mu_s/\mu_B/$	$\mu_{eff}/\mu_B/$
		a/R/	c/R/				
0	B8 <sub>2</sub>	4.020/2/	5.024/2/	485	480	1.57	3.5
1	B8 <sub>2</sub>	4.022/2/	5.063/2/	405	395	1.55	3.5
2	B8 <sub>2</sub>	4.064/2/	5.168/3/	314	305	1.33	3.5
2.5	B8 <sub>2</sub>	4.088/2/	5.204/2/	227	225	1.04	3.3
4	D8 <sub>8</sub>	7.138/2/	5.013/2/	320	325	2.10	3.3

Table 2. The distributions of atoms and values of magnetic moment in  $Fe_{5-x}Mn_xGe_3$

x	The distributions of atoms in sites		Values of magnetic moments	
	2/a/	2/d/	2/a/ $\mu_B/$	2/d/
0	2 Fe	1.34 Fe	1.4 $\pm$ 0.1	1.8 $\pm$ 0.1 [5]
1	1.38Fe+0.62Mn	1.30Fe+0.04Mn	1.25 $\pm$ 0.15	1.75 $\pm$ 0.15
2	0.84Fe+1.16Mn	1.16Fe+0.18Mn	1.15 $\pm$ 0.15	1.60 $\pm$ 0.15
2.5	0.33Fe+1.67Mn	1.34Fe	1.18 $\pm$ 0.15	2.17 $\pm$ 0.15
	4/d/	6/g/	4/d/	6/g/
4	0.78Fe+1.22Mn	0.22Fe+2.78Mn	1.55 $\pm$ 0.15	2.45 $\pm$ 0.15
5	2 Mn	3 Mn	1.7 $\pm$ 0.1	2.7 $\pm$ 0.1 [5]

nuclear data indicate very readily the degree of preferred ordering on each of the crystallographic sites. Refinement of the neutron diffraction data were carried out using the profile technique developed by Rietveld [7]. The refined parameters and corresponding minimum values of R-factors are given in Table 2. For the structures of B8<sub>2</sub> type the Mn atoms preferentially occupy the 2/a/ position. For  $FeMn_4Ge_3$  the iron substitution takes place initially in the 4/d/ sites of the D8<sub>8</sub> structure. The positional parameters are  $x_{Mn}=0.22/2/$  and  $x_{Ge}=0.60/3/$ .

In the second step the magnetic structures were determined. In the neutron diagrams of these compounds all peaks can be indexed on the basis of the crystallographic unit cells. The magnetic structures were determined from the field dependent contributions to the neutron reflections obtained at 80 K. In the case of compounds with x=1 and 2 the relative variation of neutron diffraction intensities for (10,0), (10,1) and (00,2) reflections produced by applied magnetic field is

consistent with placing ferromagnetic components in the basal plane. The absence of (00,1) reflection indicates that the antiferromagnetic components do not appeared. The diffraction pattern of sample with  $x=2.5$  at 77 K has shown two extra reflections which could be indexed as (00,1) and (10,1) corresponding to the same chemical cell. Similar diffraction pattern Suzuoka et al.[8] observed for a single crystal of  $\text{Fe}_{0.9}\text{Mn}_{0.9}\text{Ge}$ . With these results he showed, that  $\text{Fe}_{0.9}\text{Mn}_{0.9}\text{Ge}$  has a ferrimagnetic structure with canted spin arrangement. The results of our calculations given similar model of magnetic structure. The magnetic structure of  $\text{FeMn}_4\text{Ge}_3$  is similar to that of  $\text{Mn}_5\text{Ge}_3$ . Since Fe and Mn atoms occupy two nonequivalent positions with slight disorder, one can calculate average magnetic moments. Those, corresponding to the minima of R-factor, are given in Table 2.

### 3. Conclusion

In this paper we have presented the first results of neutron diffraction measurements for the  $\text{Fe}_{5-x}\text{Mn}_x\text{Ge}_3$  compounds. For all compositions /except  $x=2.5$ / the collinear magnetic structure is observed. For the compounds with  $\text{B8}_2$  type of crystal structure the Curie temperature decreases with increasing concentration of Mn. This result suggests that the magnetic interaction between Mn and surrounding of Fe atoms has the negative sign.

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