Mössbauer investigations of Mn$_{2-x}$Fe$_x$P$_{0.5}$As$_{0.5}$

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Abstract. Magnetic and Mössbauer measurements were performed for Mn$_{2-x}$Fe$_x$P$_{0.5}$As$_{0.5}$, $0.5 \leq x \leq 1.0$. It was shown that with decreasing Fe content magnetic interaction significantly weakens. Low temperature magnetic structure could be explained as a superposition of ferromagnetic and antiferromagnetic contributions to the whole magnetic moment of the alloy.

Key words: Fe$_2$P-type crystal structure • local environment • magnetic interaction • Mössbauer effect

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Introduction

Numerous alloys are known to have a magnetic phase transition of first order accompanied by a big magnetic calorific effect at about room temperature. These types of magnetic materials are suitable for making magnetic ambient temperature range refrigerators [2]. One of the most perspective materials with a required combination of physical and chemical characteristics is MnFeP$_{1-y}$As$_y$.

The purpose of the present research was to determine the effect of varying compositions of cations on the magnetic properties and hyperfine interactions parameters of the solid solutions of Mn$_{2-x}$Fe$_x$P$_{0.5}$As$_{0.5}$ system.

Experimental

The following four compositions of solid solutions were chosen for the present study: Mn$_{2-x}$Fe$_x$P$_{0.5}$As$_{0.5}$, x = 0.5, 0.6, 0.7, 0.9. The solid solutions were prepared in two stages. Firstly, the preliminary two-component and ternary compounds were obtained: Mn$_2$As, Mn$_2$P MnFeAs and MnFeP. The homogeneous mixtures of powders Mn(99.9%), Fe(99.99%), As(99.9999%) and P(99.999%) were alloyed in the appropriate ratio in degasified (10^{-4} torr) quartz ampoules at 1000°C during 5 days, then sintered at 900°C for 3 days and cooled down slowly afterwards. Because of a high sublimity of As and P, the temperature was raised gradually (~10°C per hour). The preliminary obtained compounds were then used by the same method to prepare the final solid solutions of Mn$_{2-x}$Fe$_x$P$_{0.5}$As$_{0.5}$.
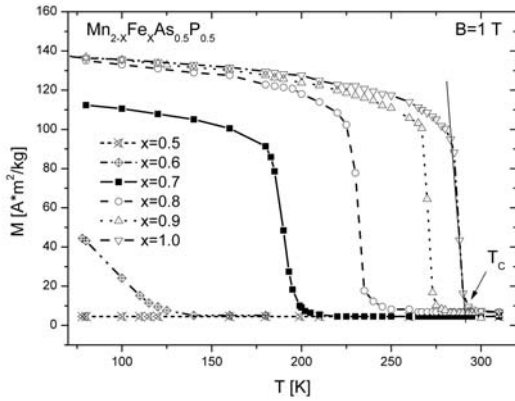
Fig. 1. The $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ magnetic measurement results.

X-ray diffraction (XRD) analysis was carried out with CuK_α-radiation, the scanning pitch was 0.03°, the scanning range was 20–90°, and the exposition in each point was 3 s.

Magnetic measurements were made by the Faraday method in the temperature range of 77 K – 300 K and a magnetic field of 0.86 T.

Mössbauer spectroscopy measurements were carried out in transmission geometry at room and liquid nitrogen temperatures and $^{57}Fe(Rh)$ was used as a source of resonance gamma radiation.

Results and discussion

XRD analysis of the $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ solid solutions ($x =$ 0.6; 0.5; 0.7, 0.9) proved that all the samples were monophasic and had the crystal structure of Fe_2P-type.

It is known for the $MnFeP_{0.5}As_{0.5}$ compound ($x =$ 1) that Mn atoms occupy $3g$ sites of this type of crystal structure (with pyramidal anion surrounding), Fe atoms occupy the $3f$ sites (with tetragonal anion surrounding), As and P atoms are equally distributed at $2c$ and $1b$ sites. The lattice volume slightly increases with diminishing Fe-content (x), which harmonizes with the bigger atomic volume of Mn in comparison to Fe. When x decreases from $x = 1$ to $x = 0.5$, the hexagonal lattice parameter a increases by ~0.6% [3]. Meanwhile, the c parameter does not change. The magnetization temperature dependences for the solid solutions with $0.5 \leq x \leq 1$ [7, 12] showed a decrease of characteristic temperatures as x decreases; i.e. the Curie temperature T_C goes from 273 K ($x = 0.9$) down to 197 K ($x = 0.7$), while the Néel temperature T_N goes from 197 K ($x = 0.7$) down to 160 K ($x = 0.5$). Magnetic measurements results are presented in Fig. 1.

The Mössbauer spectra of $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ ($x = 0.5$, 0.6, 0.7, 0.9) solid solutions at room and liquid nitrogen temperatures ($T = 293$ K, $T = 77$ K) are shown in
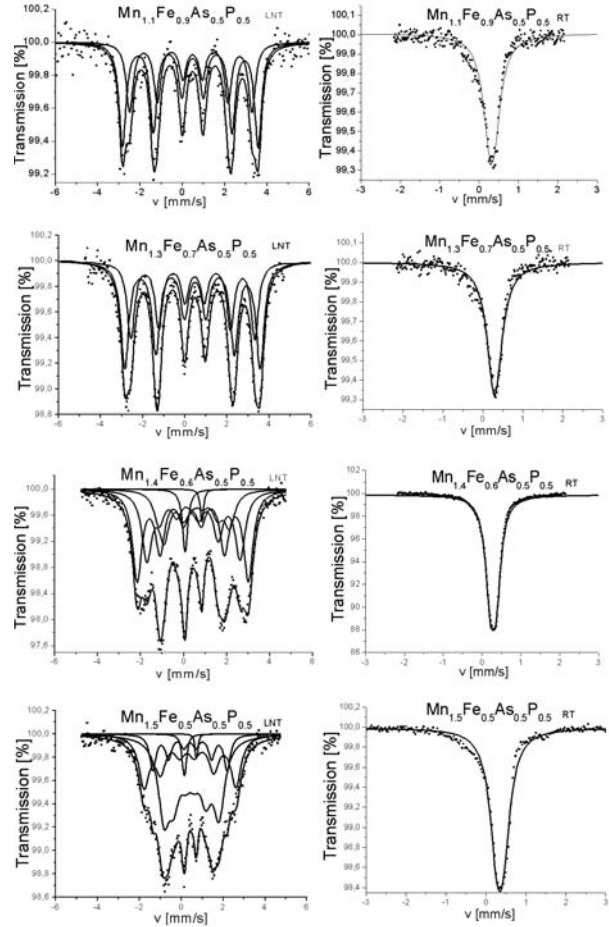

Fig. 2. The $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ Mössbauer spectra at 77 K (LNT) and 291 K (RT).

Fig. 2. The hyperfine interactions parameters are listed in Tables 1 and 2.

At room temperature, all the spectra consist of quadrupole split lines and do not have a magnetic component. This is in agreement with the results of magnetic measurements in accordance with which the Curie points lay below ambient temperatures for those samples. The isomer shifts (IS) of all the spectra at room temperature have practically the same values of about 0.4 mm/s (respectively α-Fe). Such IS values correspond to that in $MnFeP_{1-x}As_x$ for $x = 0.5$ [8, 9, 15]. An increase of IS value is observed at 77 K due to the addition of the second order Doppler shift to the IS value.

The quadrupole splitting (QS) values in all the spectra are nearly the same (~0.1 mm/s) which proves the stability of the Fe atom coordination. Though the symmetry around the Fe atom is not cubic, the values of QS are small, a similar situation was observed in Fe-Mn alloys [14].

All the spectra at liquid nitrogen temperature are magnetically split. The spectra of the samples with high

Table 1. Hyperfine interactions parameters of $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ solid solutions derived from the RT Mössbauer spectra. IS – isomer shift relative to α-Fe, QS – quadrupole splitting, Γ – HWHM

Sample	IS (mm/s)	QS (mm/s)	Γ (mm/s)
$Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}$	0.32	0.12	0.21
$Mn_{1.3}Fe_{0.7}P_{0.5}As_{0.5}$	0.29	0.08	0.21
$Mn_{1.4}Fe_{0.6}P_{0.5}As_{0.5}$	0.29	0.15	0.14
$Mn_{1.5}Fe_{0.5}P_{0.5}As_{0.5}$	0.36	0.18	0.19

Table 2. Hyperfine interactions parameters for $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ at $T = 293$ K and $T = 77$ K

Sample	No.	Magnetic subspectra					Non-magnetic subspectra		
		IS (mm/s)	QS (mm/s)	B_{eff} (T)	Γ (mm/s)	A (%)	IS (mm/s)	W (mm/s)	Γ (%)
$Mn_{1.1}Fe_{0.9}P_{0.5}As_{0.5}$	1	0.41	–0.05	19.9	0.19	60.3	–	–	–
	2	0.42	–0.04	17.9	0.19	39.7	–	–	–
$Mn_{1.3}Fe_{0.7}P_{0.5}As_{0.5}$	1	0.42	–0.06	19.9	0.22	59.8	–	–	–
	2	0.42	–0.04	18.3	0.20	40.2	–	–	–
$Mn_{1.4}Fe_{0.6}P_{0.5}As_{0.5}$	1	0.41	0.01	16.1	0.26	35.0	0.06	0.11	4.0
	2	0.40	0.05	13.5	0.28	38.7	0.81	0.099	1.3
	3	0.56	–0.04	10.2	0.29	20.9	–	–	–
$Mn_{1.5}Fe_{0.5}P_{0.5}As_{0.5}$	1	0.35	0.08	13.6	0.29	30.0	0.15	0.12	2.8
	2	0.42	0.02	11.0	0.17	13.0	0.73	0.10	1.1
	3	0.45	0.04	8.20	0.32	53.0	–	–	–

Fe content ($x = 0.7$ and $x = 0.9$) are quite well presented by two sextets with a broadened line width in relation to the natural one. Sextets correspond to the Fe sites with slightly different hyperfine magnetic field values at ^{57}Fe ($B_{eff.1} \approx 20$ T and $B_{eff.2} \approx 18$ T). These values are close to the B_{eff} value at Fe in the $MnFeP_{1-x}As_x$ system for $x = 0.5$ [8, 9, 14]. It is impossible to describe the $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ spectra for $x = 0.5$ and $x = 0.6$ by two subspectra. At least, there are 3 sextets and two single lines of weak intensity there. The presence of a single line in the spectrum at such a Mn-Fe ratio points out at a loss of the homogeneity of solid solution. There is no evidence of the presence of impurity phase in XRD patterns however, it is worth mentioning that this technique is not enough precise. The first single line has IS equal to 0.0 mm/s, the amount of the corresponding phase in the alloy is about 3–4% as follows from the subspectrum area ratio. This line could correspond to the phase of non-magnetic iron in the alloy. The second slight line with IS ~ 0.7–0.8 mm/s could be responsible for the small amount of MnO. But Fe_2P spectrum is characterized by the same value of IS [4, 10], that is why we cannot consider the origin of this line to be clearly established.

The observed variances in numbers of subspectra in the Mössbauer spectra of the samples with different compositions x could be explained as follows. As Mössbauer effect is observed at Fe atoms, we consider the nearest neighbourhood of that one. For the case $x = 1$ ($MnFeP_{0.5}As_{0.5}$-compound, see the fragment of the structure in Fig. 3), the shortest interatomic distances are Fe-As and Fe-P, they are respectively equal to 2.3083 Å and 2.3525 Å (see Table 3). The interatomic distances are calculated by the program described in
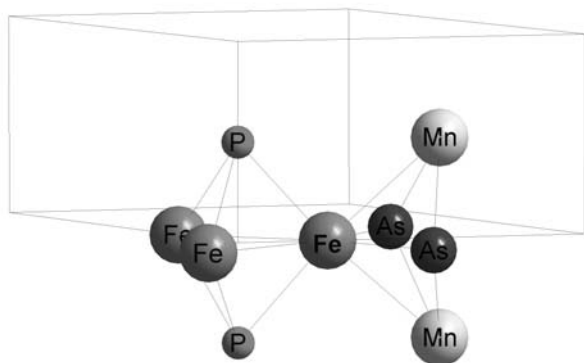
[13]. There are four nearest atoms of As or P for each Fe atom in 3f position. Fe atom is involved into indirect magnetic exchange with neighbouring Fe or Mn via these four closest P or As. Thus, for the $MnFeP_{0.5}As_{0.5}$ two Fe atoms and two Mn atoms influence the hyperfine interactions at the Fe via the nearest P and As atoms. If x in $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ goes down to $x = 0$, two Fe atoms are replaced by Mn atoms. Evidently there is a possibility of replacing of 0 (zero), 1 (one) or 2 (two) Fe atoms closest to the fixed Fe-atom by Mn atom. It is clear, that the number of the possible configurations of resonance Fe atom is reflected in the number of subspectra in each Mössbauer spectrum at Fe and in the values of its hyperfine interactions parameters.

1) Results for the samples with $x = 0.7$ and 0.9.

We considered the spectra of $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ with $x = 0.7$ and $x = 0.9$ in terms of two sextets. The reason is that we consider the most probable configurations of ^{57}Fe local environment the configurations with 0 or 1 Mn atom in closest Fe places. Earlier [1, 5, 6, 11] it was shown that the $Mn_{2-x}Fe_xAs$-system in the concentration region about $x = 0.7$ ($Mn_{1.3}Fe_{0.7}As$) and at low temperatures exhibits ferromagnetic properties. The existence of two values of hyperfine magnetic fields was interpreted as a result of a coexistence of ferromagnetic and antiferromagnetic contributions to the magnetic moment of Fe atom [6]. The results obtained in the present study could also prove the $Mn_{1.3}Fe_{0.7}P_{0.5}As_{0.5}$ magnetic structure to be a superposition of ferromagnetic and antiferromagnetic properties. The ferromagnetic component contributes to spontaneous magnetization; the antiferromagnetic one is responsible for the sharp decrease of the spontaneous magnetization value with x decreasing (especially at $x < 0.8$ [7, 12]).

2) Results for the samples with $x = 0.5$ and $x = 0.6$.

The spectra of $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ with $x = 0.5$ and

Fig. 3. Fragment of $MnFeP_{0.5}As_{0.5}$ structure.

Table 3. The interatomic distances in $MnFeP_{0.5}As_{0.5}$

No.	Atom 1	Atom 2	Distance (Å)
1	P	Fe	2.3525
2	P	Mn	2.5694
3	Mn	Fe	2.6395
4	Mn	As	2.5339
5	Fe	Fe	2.7231
6	Fe	As	2.3084
7	Mn	Fe	2.6395

$x = 0.6$ were considered in terms of three sextets. If we suppose that Fe is replaced by Mn randomly in $3f$ positions, then at $x = 0.5$ and $x = 0.6$ all three variants of local configurations around Fe could take place. There could be one or two or none of Fe atoms replaced by Mn atoms in $3f$ position. The $Mn_{1.5}Fe_{0.5}P_{0.5}As_{0.5}$ and $Mn_{1.6}Fe_{0.4}P_{0.5}As_{0.5}$ spectra were fitted using the model of three sextets (see Table 3). The fitting result is in good agreement with the experimental data. The hyperfine magnetic interaction field values at ^{57}Fe site are between 16 T and ~8 T. The proper understanding of correlation between the hyperfine magnetic field values and the number and type of magnetic phases occurred in the solid solution is in progress.

Conclusions

The Mössbauer data reveal that with decreasing x from $x = 1.0$ to $x = 0.5$, the substitution of $3f$-Fe atoms for Mn atoms in the $Mn_{2-x}Fe_xP_{0.5}As_{0.5}$ solid solutions occurs randomly. Simultaneously, magnetic interaction significantly weakens. Low temperature magnetic structure could be explained as a superposition of ferromagnetic and antiferromagnetic contributions into the whole magnetic moment of the alloy.

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