Magnetic state features of $Mn_{1.4}Fe_{0.6}P_{0.5}As_{0.5}$

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ABSTRACT

Mössbauer spectroscopy in the temperature range between 4 K and 270 K was used to more clearly define the magnetic phase diagram of $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$. It is shown that antiferromagnetic and paramagnetic states coexist in the alloy $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ in the temperature range of $150\,K \leq T \leq 160\,K$.

INTRODUCTION

Some of the most promising materials for the development of magnetic refrigerators operating under normal conditions,[1,2] are $MnFeP_{1-y}As_y$ alloys. Previously,[3,4] when magnetic properties of $Mn_{2-x}Fe_xAs_{0.5}P_{0.5}$ alloys were studied, it has been shown that the alloy $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ is in an antiferromagnetic state at temperatures between 120 and 180 K. This research was conducted with the purpose of specifying the magnetic phase diagram at low temperatures using the Mössbauer effect method.

EXPERIMENT

The test $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ solid solution was synthesized in two stages. Binary and ternary compounds MnFeAs and MnFeP were preliminarily obtained using powder metallurgy technology. Homogeneous mixtures of powders Mn(99.9%), Fe(99.99%), As (99.9999%), P (99.999%) taken in corresponding weight proportions were baked in quartz ampoules evacuated to 10^{-4} Torr at 1000°C for 5 days, followed by annealing at 900°C for 3 days, and slow cooling. Due to an intensive sublimation of phosphorus and arsenic, the temperature was increased at a rate of ~10 degrees per hour.

Then, the same scheme was followed using the powders of pre-obtained ternary compounds to acquire a sample of $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$.

X-ray diffraction analysis was carried out on a DRON-3 M diffractometer using CuK_α monochromatic radiation, with a scan step of 0.03°, scanning range 20°–90°, and exposure of 3 sec at each point.

Mössbauer measurements were taken in transmission geometry, constant acceleration mode, in the temperature range between 4 K and 291 K. The source of resonance γ-radiation ^{57m}Fe (Rh) was used.

RESULTS AND DISCUSSION

The X-ray studies showed that the sample of $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ has a hexagonal structure such as Fe_2P (Fig. 1). In this structure, at $x = 1$, Mn atoms occupy positions like $3\,g$ (with a pyramidal anionic environment), Fe atoms occupy positions such as $3f$ (with a tetrahedral anionic environment), and the As and P atoms are distributed between $2c$ and $1b$ positions with equal probability.[5]

The Mössbauer spectra of the sample are shown in Fig. 2, and the specified spectrum parameters are provided in Table I.

Each of the sample spectra in the temperature range between 5 K and 150 K were calculated in the three-sextet model. Each spectrum in the temperature range 150–160 K is represented by three sextets and a paramagnetic component, and at 160 K the paramagnetic line already makes up ~80% of the integral spectrum.

The number of sub-spectra in the sample's Mössbauer spectra that were obtained upon calculation of the experimental results can be explained as follows. It is believed that 4 atoms of arsenic or phosphorus are located near each of the Fe 3f-atoms in the $MnFeP_{0.5}As_{0.5}$ compound $(x = 1)$. The distance between atoms
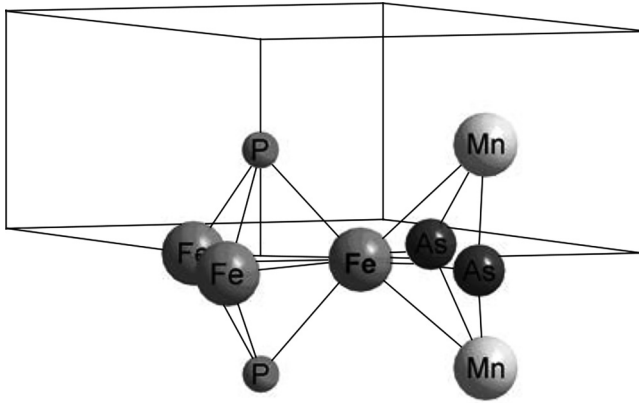
FIG. 1. A fragment of $MnFeP_{0.5}As_{0.5}$ sample structure.

Fe–As is 2.3084 Å; the distance Fe–P is 2.3525 Å (see Table II), the interatomic distances are calculated using the program described in Ref. 6. The distances between the nearest iron atoms Fe–Fe and Fe–Mn in $MnFeP_{0.5}As_{0.5}$ are 2.7231 Å and 2.6395 Å, respectively; both exceed the distance Fe–As and Fe–P. An assumption can be made that in $MnFeP_{0.5}As_{0.5}$ ($x = 1$), each Fe atom, for which the Mössbauer effect study registers hyperfine parameters, is significantly affected by two nearest manganese atoms and two nearest iron atoms through anions P and As (indirect antiferromagnetic interaction). At the same time, there is a statistical probability that manganese will replace one, two, or none of the two iron atoms closest to the fixed Fe atom. That is, for $MnFeP_{0.5}As_{0.5}$, three variants of the local environment around the iron atom are most likely, statistically. The three most probable electron configurations of the Fe atom are reflected in the experimentally observed values of the effective magnetic fields at Fe nuclei.[7] Assuming that these local environment configurations of the resonant iron atoms are also most probable for a sample $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$, the composition of which is close to that of $MnFeP_{0.5}As_{0.5}$, then the spectral representation via the model of three sub-spectra seems to be reasonable. The calculations are quite consistent with the experiment. However, the multiplicity of possible environments around the resonant atom, which is unaccounted for, for gives the observed broadening of the sub-spectrum lines (see Table I). The magnetic interactions become noticeably weaker with increasing temperature, which is reflected in the reduction of hyperfine magnetic fields at the ^{57}Fe atom nuclei from ~16–20 T down to ~2–6 T.

The sample spectra at temperatures above 160 K represent a single paramagnetic line, which indicates an entirely non-magnetic state of the alloy.

According to Refs. 3 and 4, the $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ solid solution is in an antiferromagnetic state in the temperature range between ~120–130 K and 160 K, and in a paramagnetic state in the temperature above 160 K. According to the refined data obtained by Mössbauer spectroscopy, two phases—paramagnetic and antiferromagnetic (PM and AFM)—coexist in the alloy $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ at 150–160 K. Furthermore, the Mössbauer data convincingly indicate that the alloy is structurally single-phased.
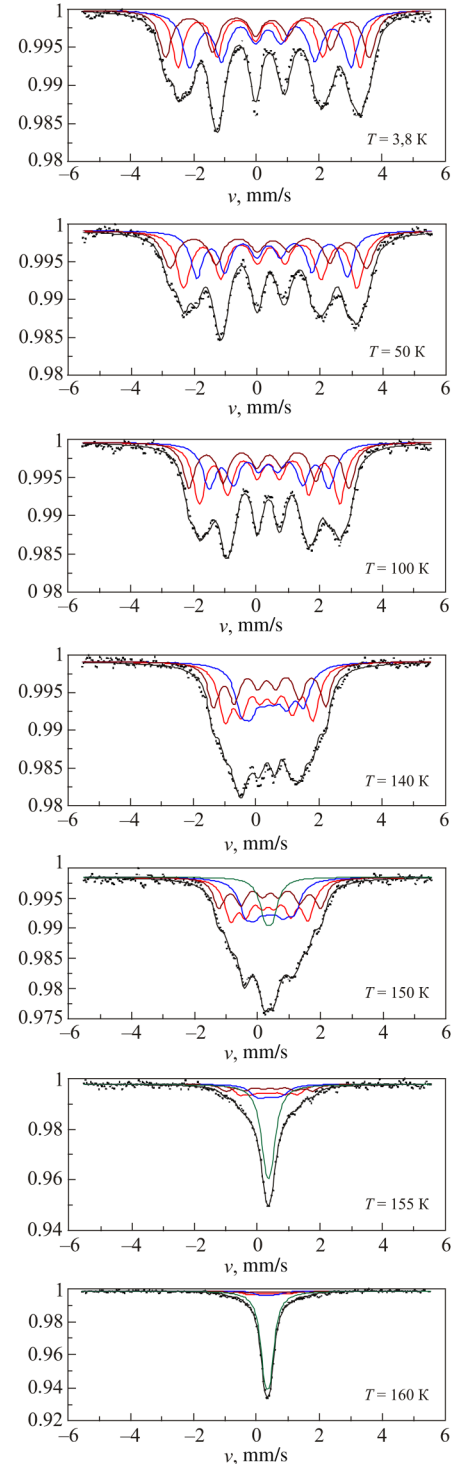

FIG. 2. Mössbauer temperature spectra of the $Mn_{1.4}Fe_{0.6}P_{0.5}As_{0.5}$ sample. Hyperfine spectrum parameters (magnetic and paramagnetic sub-spectra) are provided in Table I.

TABLE I. Hyperfine spectrum parameters of ^{57}Fe in the solid solution $Mn_{1.4}Fe_{0.6}P_{0.5}As_{0.5}$.

T, K	No.	Magnetic sub-spectra					Paramagnetic sub-spectrum		
		IS, mm/s	QS, mm/s	B, T	W, mm/s	A, %	IS, mm/s	QS, mm/s	A, %
3.8	1	0.42	−0.02	17.9	0.48	40.9			
	2	0.41	0.07	15.8	0.46	30.9	–	–	–
	3	0.41	−0.13	20.2	0.47	28.2	–	–	–
50	1	0.42	−0.01	17.12	0.51	40.8			
	2	0.41	0.07	14.84	0.46	30.9			
	3	0.42	−0.13	19.41	0.52	28.3	–	–	–
100	1	0.39	0.03	13.87	0.46	39.5			
	2	0.38	0.03	11.82	0.5	31.7			
	3	0.39	−0.01	15.8	0.44	28.8	–	–	–
110	1	0.38	0.03	12.9	0.44	39.5			
	2	0.37	0.03	10.68	0.49	31.7			
	3	0.4	−0.01	14.91	0.46	28.8	–	–	–
120	1	0.39	0.03	11.81	0.46	39.47			
	2	0.4	0.03	9.56	0.50	31.71			
	3	0.4	−0.01	13.87	0.44	28.82	–	–	–
130	1	0.39	0.03	10.47	0.46	39.47			
	2	0.4	0.03	8.24	0.50	31.71			
	3	0.4	−0.01	12.69	0.44	28.82	–	–	–
140	1	0.38	0.03	8.68	0.47	39.47			
	2	0.39	0.03	6.2	0.53	31.71			
	3	0.4	−0.01	11.1	0.47	28.82	–	–	–
150	1	0.35	0.03	7.69	0.46	34.84	0.35	0.25	11.7
	2	0.36	0.03	4.83	0.50	27.99			
	3	0.39	−0.01	10.04	0.44	25.47	–	–	–
155	1	0.35	0.03	5.75	0.46	19.9	0.35	0.16	49.8
	2	0.36	0.03	2.84	0.50	15.9			
	3	0.39	−0.01	8.56	0.44	14.4	–	–	–
160	1	0.35	0.03	4.47	0.46	8.1	0.35	0.17	79.5
	2	0.36	0.03	2.07	0.50	6.5			
	3	0.39	−0.01	7.57	0.44	5.9	–	–	–

IS is an isomeric chemical shift, QS is a quadrupole splitting at a half-height.

Magnetic and non-magnetic sub-spectra in the spectra have approximately the same values of isomeric shifts, indicating that the iron atoms have chemically identical states under different magnetic states. The refined magnetic phase diagram of $Mn_{2−x}Fe_xAs_{0.5}P_{0.5}$ is shown in Fig. 3.

TABLE II. The Interatomic Distances in $MnFeP_{0.5}As_{0.5}$.

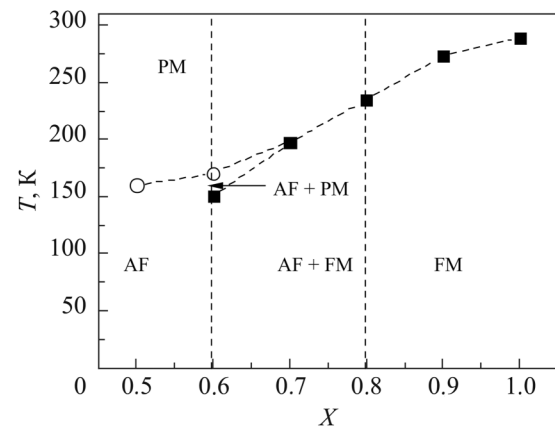| No.	Atom 1	Atom 2	Distance, Å
1	P	Fe	2.3525
2	P	Mn	2.5694
3	Mn	Fe	2.6395
4	Mn	As	2.5339
5	Fe	Fe	2.7231
6	Fe	As	2.3084
7	Mn	Fe	2.6395

FIG. 3. Magnetic phase diagram of $Mn_{2−x}Fe_xAs_{0.5}P_{0.5}$.

CONCLUSION

The Mössbauer studies have clearly shown that magnetic and non-magnetic states of $Mn_{1.4}Fe_{0.6}As_{0.5}P_{0.5}$ coexist in the temperature range 150–160 K, whereas magnetic measurements showed only AFM.

ACKNOWLEDGMENT

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