

Structure and magnetic properties of $Mn_{1-x}Fe_xNiGe$ ($0,05 \leq x \leq 0,60$) solid solutions

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Abstract: Intermetallic alloys and solid solutions having magnetostructural phase transitions are of interest for theory and practice due to the presence of magnetoresistance, magnetocaloric and magnetostriction effects. $MnNiGe$ -based alloys and solid solutions are convenient model objects for studying static and dynamic distortions of the crystal lattice, since magnetostructural transformations of both the first and second kind realized in them. The features of the relationship of magnetic properties and changes in the crystalline structure of $Mn_{1-x}Fe_xNiGe$ ($0,05 \leq x \leq 0,60$) solid solutions are studied. It has been established that $MnNiGe$ is an antiferromagnet with a Néel temperature $T_N \approx 346$ K. Substitution of Mn ions with iron ones causing a decrease in the parameters of the $MnNiGe$ unit cell leads to the emergence of a ferrimagnetic state and in some cases to a manifestation of ferromagnetic ordering of magnetic moments.

Keywords: INTERMETALLIC ALLOYS, SOLID SOLUTIONS, MAGNETIZATION, FERRIMAGNETS

1. Introduction

It is known that the crystalline, magnetic and electronic subsystems of materials are closely related. A striking manifestation of this relationship is the phase transformations induced by external influences in various solid-state objects, which are now being actively investigated. In particular, magnetic phase transformations in magnets lead not only to changes in the magnetic order, but are also accompanied by changes in the symmetry of the crystal lattice and local electronic splitting of magnetoactive bands. This can lead, in particular, to a colossal magnetocaloric effect, which turns out to be important for practical use in cooling devices - magnetic refrigerators operating at room temperature. Multicomponent alloys of 3d-transition elements, including Heusler alloys, in which phase transformations induced by external influences (electric and magnetic fields, pressure, temperature) are observed with manifestation of special physical properties (spin rearrangement of the system, its electronic instability, a giant magnetocaloric effect, etc.), have recently caused increased interest in connection with the revealed prospects of their practical use.

Alloys based on ternary compounds $MnNiGe$, $MnCoGe$, $MnZnSb$, due to the presence of magnetic and structural phase transformations in a wide temperature range, have properties and effects that are in demand in the development of new microelectronic devices. Among them are such as the giant magnetocaloric effect, magnetoresistance, magnetostriction, shape memory effect induced by a magnetic field [1-13]. By selecting the elements of substitution or alloying in ternary alloys $MnNiGe$, $MnCoGe$, one can control the properties, creating new states with spontaneous magnetization, form conditions for changes in magnetoelastic interactions [14-16]. From the point of view of fundamental science, alloys and solid solutions based on $MnNiGe$ are interesting model objects for determining the values of static and dynamic distortions of the crystal structure, since phase transformations of both the first and second kind are realized in them.

The aim of this work is to synthesize $Mn_{1-x}Fe_xNiGe$ solid solutions, study the features of the crystal structure, and determine the values of fundamental magnetic characteristics.

2. Experimental part

Polycrystalline samples of $Mn_{1-x}Fe_xNiGe$ ($0,05 \leq x \leq 0,60$) solid solutions were synthesized by solid-phase reaction method. The mixture with the required ratio of the powders of the initial elements in evacuated quartz ampoules was heated to a temperature of 1323 K. The resulting sintered samples were subjected to homogenizing annealing at 1223 K, followed by quenching. For the studies, the compositions $Mn_{1-x}Fe_xNiGe$ were synthesized with a concentration step of 5 (before $x = 0,30$) and 10 mol.% (after $x = 0,30$). The crystal structure and phase composition studies of the samples after each stage of the synthesis was carried out at room temperature by X-ray diffraction in $Cu K\alpha$ - radiation.

The temperature dependences of the specific magnetization $\sigma = f(T)$ and the reciprocal of the magnetic susceptibility $1/\chi = f(T)$ were

studied in a magnetic field with an induction $B = 0,86$ T by the ponderomotive method [17] in the temperature range of $\sim 80 - 800$ K.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of $Mn_{1-x}Fe_xNiGe$ solid solution powders obtained at 300 K in the range of angles $20^\circ \leq 2\theta \leq 95^\circ$ after all stages of the synthesis by the method of solid-phase reactions in evacuated quartz ampoules.

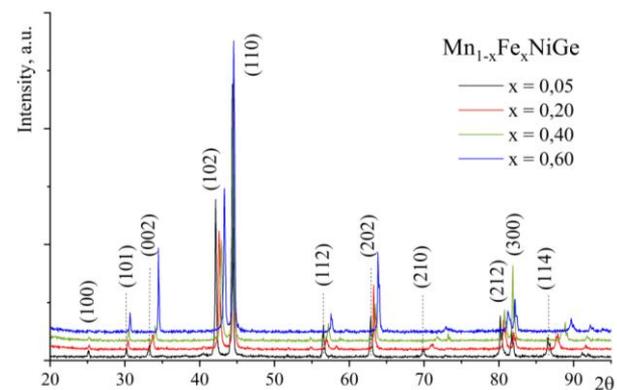


Fig. 1 X-ray diffraction patterns of obtained after all stages of the synthesis $Mn_{1-x}Fe_xNiGe$ solid solution powders.

It was found that at a room temperature the $Mn_{1-x}Fe_xNiGe$ ($0,05 \leq x \leq 0,60$) solid solutions have a hexagonal crystallographic Ni_2In ($B8_2$) type structure of the $P6_3/mmc$ space group. There is a fairly smooth variation in the angular positions of diffraction reflections and redistribution of their intensities in the concentration range $0,05 \leq x \leq 0,60$, which is typical for solid solutions with cationic substitution. The concentration dependences of parameters a , c and unit cell volume V of $Mn_{1-x}Fe_xNiGe$ solid solutions are shown in Figure 2.

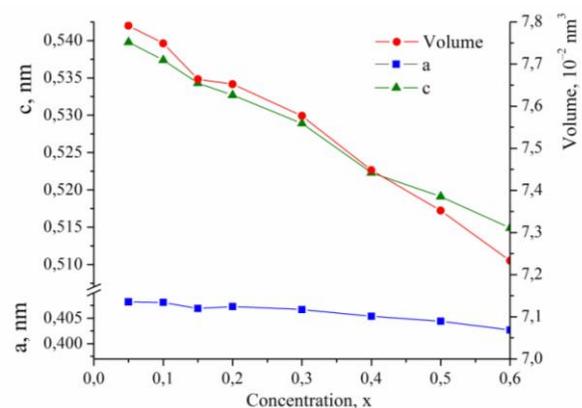


Fig. 2 Concentration dependences of parameters $a = f(x)$, $c = f(x)$, $V = f(x)$ change of the hexagonal unit crystal cell of $Mn_{1-x}Fe_xNiGe$ solid solutions.

The numerical values of the quantities characterizing the sizes of the hexagonal unitary crystal cells a and c , the ratio of the c/a axes, the values of the unit cell volumes V and the X-ray density ρ_{ren} of powders of $Mn_{1-x}Fe_xNiGe$ solid solutions at $T \sim 300$ K are given in Table 1.

Table 1: Values of a and c , c/a ratio, values of unit cell volumes V and X-ray density ρ_{ren} of $Mn_{1-x}Fe_xNiGe$ solid solutions.

x	a , nm	c , nm	c/a	V , 10^{-2} nm ³	ρ_{ren} , g/cm ³
0.05	0,408 ₁	0,539 ₁	1,32	7,78	7,95
0.10	0,407 ₈	0,536 ₂	1,31	7,72	8,01
0.15	0,407 ₆	0,533 ₇	1,31	7,68	8,06
0.20	0,407 ₁	0,530 ₉	1,30	7,62	8,12
0.25	0,407 ₂	0,529 ₇	1,30	7,61	8,14
0.30	0,406 ₅	0,527 ₄	1,30	7,55	8,21
0.40	0,407 ₄	0,525 ₇	1,29	7,56	8,22
0.50	0,407 ₄	0,521 ₉	1,28	7,50	8,27
0.60	0,406 ₅	0,519 ₅	1,28	7,43	8,35

The variation of the $a = f(x)$, $c = f(x)$, $V = f(x)$ dependences in Fig. 2 demonstrates that the change in the unit crystal cells parameters at ~ 300 K with a change in the concentration x of the Fe content in the synthesized samples agrees with the Vegard rule for continuous series of solid solutions. A decrease in the parameters a and c upon cationic substitution is most likely a consequence of the difference in the ionic radii of the divalent manganese cations (0.91-0.80) Å and iron (0.82-0.74) Å.

The temperature dependences of the specific magnetization of some $Mn_{1-x}Fe_xNiGe$ solid solutions are shown in Figure 3.

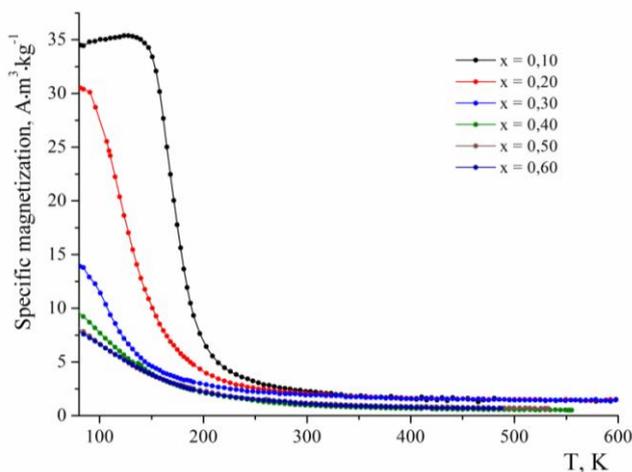


Fig. 3 Temperature dependences of the specific magnetization of $Mn_{1-x}Fe_xNiGe$ solid solutions in a magnetic field of 0.86 T.

Cationic substitution in the $Mn_{1-x}Fe_xNiGe$ system already at 10% substitution of iron for manganese leads to degradation of the antiferromagnetic ordering. The dependences $\sigma = f(T)$ of some compositions indicate the retention of a significant fraction of the antiferromagnetic component at temperatures $T < 150$ K. At concentrations $x > 0.10$, solid solutions exhibit the presence of an uncompensated magnetic moment with a specific magnetization of ~ 8.0 to ~ 36 A·m²·kg⁻¹ at $T = 80$ K. Table 2 shows the values of the magnetic moments of solid solutions calculated from the values of the specific magnetization at 80 K, using formula (1):

$$\mu = \frac{\sigma \cdot M}{N_A} \mu_B, \quad (1)$$

where σ is the value of the specific magnetization at nitrogen temperature, M is the molar mass, μ_B is the value of Bohr's

magneton, N_A is Avogadro's constant. The temperatures of the "magnetic order - magnetic disorder" phase transformation in solid solutions of the $Mn_{1-x}Fe_xNiGe$ system were determined using the dependence of the square of the specific magnetization $\sigma^2 = f(T)$.

Table 2: Specific magnetization at 80 K, Curie temperatures and average magnetic moments of $Mn_{1-x}Fe_xNiGe$ solid solutions.

x	σ_{80K} , A·m ² ·kg ⁻¹	T_C , K	μ_{80K} , μ_B
0.05	13.69	272	0.46
0.10	34.53	183	1.15
0.15	36.07	153	1.20
0.20	30.55	148	1.02
0.25	20.38	143	0.68
0.30	13.90	137	0.46
0.40	9.45	-	0.32
0.50	7.98	-	0.27
0.60	7.85	-	0.26

4. Summary

Solid solutions of $Mn_{1-x}Fe_xNiGe$ system in the concentration range $0.05 \leq x \leq 0.60$ by the solid state reaction method were synthesized. X-ray diffraction studies have shown that the samples are single-phase at room temperature. It was found that an increase in the concentration of iron in solid solutions leads to a decrease in the size of the unit crystal cell. It is revealed that the temperature of the phase transformation "magnetic order - magnetic disorder" of the studied samples decreases with an increase in the concentration x of substitution of manganese by iron ions from 272 K for $Mn_{0.95}Fe_{0.05}NiGe$ to 137 K for the $Mn_{0.70}Fe_{0.30}NiGe$ solid solution.

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