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The study of crystal and magnetic properties of $MnNi_{0.85}Fe_{0.15}Ge$

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Abstract. Magnetic and Mössbauer measurements were performed for $MnNi_{0.85}Fe_{0.15}Ge$. The Mössbauer data indicate that Fe atoms in $MnNi_{0.85}Fe_{0.15}Ge$ are randomly distributed over two types of metal sites in hexagonal structure. At 77 K, the hyperfine magnetic fields at Fe located in different crystal sites have similar values of about 12.7 and 12.3 T. The random site distribution of the iron atoms in the non-magnetic hexagonal phase at high temperatures is confirmed by the theoretical calculations in fully relativistic KKR (KKR???) method.

Key words: Mössbauer effect • magnetic interaction • hexagonal structure

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Introduction

The effect of magnetostructural coupling in systems with martensite-like phase transitions plays an important role in magnetoresponsive effects, such as magnetoresistance, magnetocaloric effect, etc. The materials with stable magnetostructural coupling between the structural and the magnetic transition over a broad-temperature region from 70 to 350 K in combination with tunable magnetoresponsive effects are extremely interesting for a practical use. Recently, the possibility to obtain such a combination of properties has been shown for MnNiGe:Fe alloys [1, 2].

The purpose of the work was the magnetometric and Mössbauer studies of structural and magnetic characteristics of two different heat-treated $MnNi_{0.85}Fe_{0.15}Ge$ alloys.

Results and discussion

The $MnNi_{0.85}Fe_{0.15}Ge$ samples were produced by melt spinning in Ar atmosphere at a wheel linear speed of 20 $m \cdot s^{-1}$ from as-cast pellets of nominal composition $MnNi_{0.85}Fe_{0.15}Ge$ previously obtained by arc melting from highly pure elements. Then the samples are (1) quenched and (2) quenched + annealed (6 h, 850°C, in vacuum). X-ray powder analysis at room temperature shows that all samples have a hexagonal Ni_2In-type crystal structure (space group $P6_3/mmc$).

Table 1. Magnetic characteristics of $MnNi_{0.85}Fe_{0.15}Ge$

Composition	Method of treatment	T_C [K]	σ [Gs·cm^3·g^{-1}]
$MnNi_{0.85}Fe_{0.15}Ge$	Quenching	220	62.86
$MnNi_{0.85}Fe_{0.15}Ge$	Quenching + annealing	219	59.61

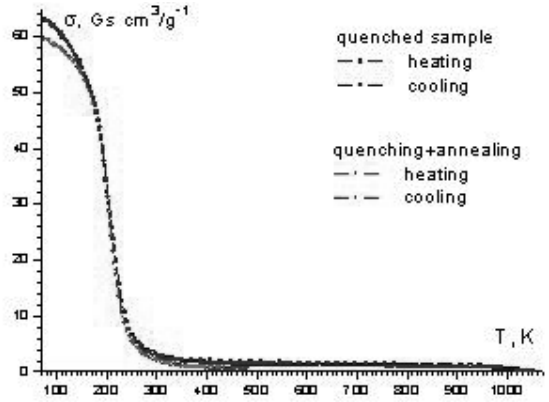

Fig. 1. Temperature dependence of magnetization in H = 0.86 T.

Specific magnetization σ and Curie temperatures T_C were studied by Faraday method in the magnetic field of 0.86 T and temperature range 77 K ≤ T ≤ 500 K. The Curie temperatures were obtained by extrapolation of the linear part of $\sigma^2(T)$ – dependence on T axis. The obtained T_C and σ values show no considerable dependence on the method of sample treatment and on the direction of temperature change (heating or cooling), Table 1 and Fig. 1. The annealing barely leads to an insignificant degradation of magnet characteristics.

Mössbauer experiment was made in usual transmission geometry and constant acceleration regime. ^{57}Fe/Rh was used as a resonance source, the sample temperatures were 77 K ≤ T ≤ 600 K. The Mössbauer spectra are shown in Fig. 2, the spectra fitting results are given in Table 2.

It has been shown that the MnFeGe alloy crystallizes in the Ni_2In-type structure (Fig. 3a) in the whole temperature range [3]. Magnetic moments are localized on both Mn and Fe sites. Neutron diffraction study of a powdered $Fe_{1.0}Mn_{0.95}Ge$ sample below 240 K has shown that the Mn magnetic moments are ordered in antiferromagnetic way whereas the Fe moments are ordered ferromagnetically [4]. Stoichiometric MnNiGe alloy at room temperature has the orthorhombic (TiNiSi-type) crystal structure

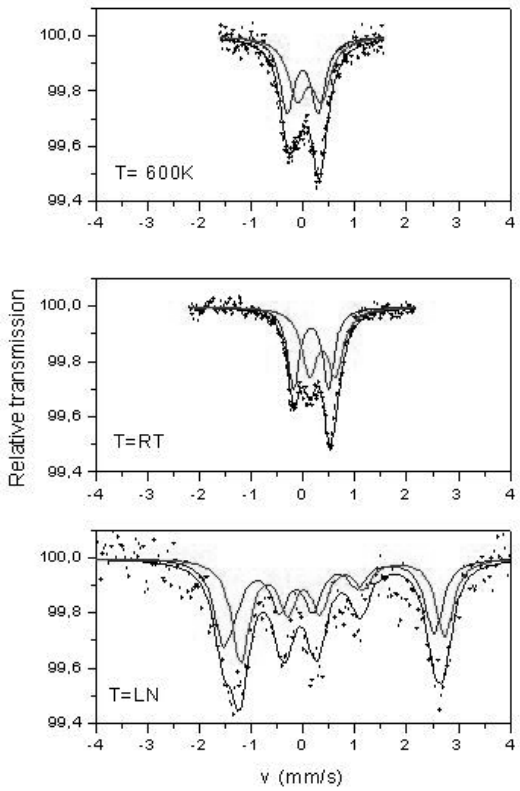

Fig. 2. ^{57}Fe Mössbauer spectra of $MnNi_{0.85}Fe_{0.15}Ge$ (quenched) at different temperatures.

(Fig. 3b) (space group P_{nma}) and shows a spiral antiferromagnet (AFM) state below the Neel temperature T_N = 346 K. At about 470 K, it undergoes a crystallographic structural transition from the low-temperature orthorhombic phase to the high-temperature hexagonal phase [5]. In the case of Fe-doped MnNiGe alloys, the Ni_2In-type instead of the TiNiSi-type structure is observed at room temperature (RT), suggesting a remarkable reduction of transconformation temperature (T_t). It was reported that the Ni atoms in MnNiGe alloy are non-magnetic, leaving the moments of Mn atoms aligning in the spiral AFM ordering [6].

In [7] the ^{57}Fe Mössbauer spectrum of MnFeGe ternary alloy at room temperature (290 K) was fitted

Table 2. ^{57}Fe Mössbauer parameters of $MnNi_{0.85}Fe_{0.15}Ge$ (quenched) spectra

T [K]	1 subspectrum					2 subspectrum				
	IS_1 [mm/s]	QS_1 [mm/s]	H_1 [T]	G_1 [mm/s]	C_1	IS_2 [mm/s]	QS_2 [mm/s]	H_2 [T]	G_2 [mm/s]	C_2
77	0.264	−0.312	12.70	0.210	0.479	0,470	−0.370	12.30	0.200	0.521
290	0.241	0.679	–	0.135	0.479	0.462	0.498	–	0.183	0.521
500	0.095	0.300	–	0.148	0.479	0.321	0.261	–	0.158	0.521
600	0.077	0.300	–	0.168	0.479	0.206	0.236	–	0.200	0.521

IS – isomer shift value relative to metallic Fe (error ±0.005). QS – quadrupole splitting value (error ±0.008). H – hyperfine magnetic field at Fe atom (error ±0.05). G – line width (error ± 0.005). C – relative contribution of the subspectrum area to the total spectrum area.

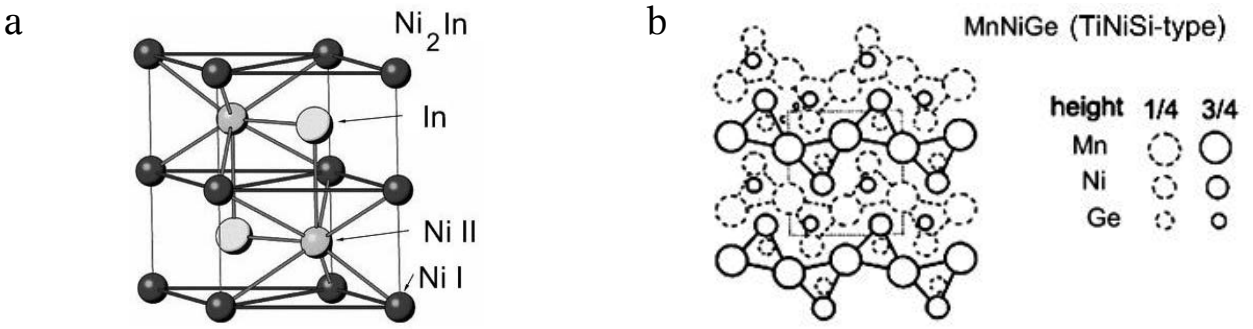

Fig. 3. Crystal structures types: (a) Ni_2In, (b) TiNiSi.

in one doublet model with the doublet parameters: quadrupole splitting (QS) = 0.70 mm/s and isomer shift (IS) = 0.30 mm/s. However, elsewhere [3] the Mössbauer spectra of MnFeGe and NiFeGe were fitted in a two subspectra model. In the present work, each spectrum of $MnNi_{0.85}Fe_{0.15}Ge$ at each temperature was presented as superposition of two subspectra.

In the paramagnetic region, the $MnNi_{0.85}Fe_{0.15}Ge$ spectra were presented by superposition of two doublets as there are two different types of sites for the metal atoms in the hexagonal structure – with octahedral and trigonal–bipyramidal anionic environment, Fig. 3a. So the presence of two doublets in each Mössbauer spectrum corresponds to the essentialities of crystal structure. The parameters of one doublet are close to those of the only doublet in [7]. A conspicuous experimental fact is that the IS and QS values in paramagnetic $MnNi_{0.85}Fe_{0.15}Ge$ state at room temperature significantly differ from those at 500 and 600 K (Table 2).

The spectrum of $MnNi_{0.85}Fe_{0.15}Ge$ (quenched) at T = 77 K is magnetically split and it also fitted in a two subspectra model as there are two types of metal sites in the inherent orthorhombic structure. There are two magnet sextets in the spectrum with similar values of hyperfine magnetic fields at Fe of approximately 12.7 T and 12.3 T and broadened line width. The orthorhombic structure at T = 77 K is not ideal and the electric field gradient axis is not uniquely oriented with respect to the magnetization direction. In such cases, the occurrence of the complex set of Zeeman patterns attributed to one sublattice can be observed [8] or it could give rise to appreciable line width broadening.

It is accepted [3, 9] that the (1) Mn and (2) Ni or Fe atoms are located in different structural positions in MnNiGe or MnFeGe three-component systems. Namely, Mn atoms are located in MeI, and Fe or Ni – in MeII. But the presence of two subspectra in each Mössbauer spectrum testifies to the substitution of Fe atoms for either Mn or Ni in $MnNi_{0.85}Fe_{0.15}Ge$. The relative contributions of corresponding subspectra to the total spectrum are almost equal. So the important conclusion is that the Fe atoms in $MnNi_{0.85}Fe_{0.15}Ge$ at small concentration (notably 15 at.%) are randomly distributed over the two types of metal sites in the orthorhombic or hexagonal structure. At 77 K, the hyperfine magnetic fields at Fe atoms located in different metal sites in $MnNi_{0.85}Fe_{0.15}Ge$ have similar values.

The experimental fact of similarity of magnetic field values at Fe in different crystal positions does not correspond to the calculated results obtained in the work. The hyperfine field values have been calculated by the fully relativistic KKR method [10] in LDA (VWN) [11] and GGA (PBE) [12] approximations for exchange-correlation energy and atomic sphere approximation for crystal potential. According to the calculations in both LDA and GGA approximations (Table 3), the iron atoms in the non-magnetic hexagonal phase at high temperatures are almost randomly distributed over positions of Ni and Mn.

$$\Delta E_{NM,hex} = E[(Mn_{0.99}Fe_{0.01})_{2a}(Ni_{0.85}Fe_{0.14}Mn_{0.01})_{2c}Ge] - [(Mn_{0.86}Fe_{0.14})_{2a}(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{2c}Ge] = -132 \text{ Cal/f.u. (Calories per formula unit)}.$$

In the ferromagnetic state, the energy difference between these configurations in the hexagonal phase increases up to $\Delta E_{FM,hex}$ = –623 Cal/f.u., and in the orthorhombic phase – up to $\Delta E_{FM,orth}$ = –846 Cal/f.u. Therefore, quenching can freeze the 'non-equilibrium' distribution of Fe atoms on Ni and Mn sublattices, as well as part of the 'non-equilibrium' of the orthorombic phase. The comparison of calculated hyperfine magnetic fields (Table 3) with experimental values (12.7 T and 12.3 T) shows that the best agreement with the experimental data would be if iron atoms are in the Mn sublattice in the alloy with orthorhombic FM (???) phase. In this case, H_{hf} = 13.5 T, but in fact, the Fe atoms have them in Ni positions of this structure as well.

Conclusions

The Mössbauer data indicate that Fe atoms in $MnNi_{0.85}Fe_{0.15}Ge$ are randomly distributed over two types of metal sites in the orthorhombic or hexagonal structure. At 77 K, the hyperfine magnetic fields at Fe located in different crystal sites have similar values of about 12.7 and 12.3 T. The theoretical calculations also show that the iron atoms in the non-magnetic hexagonal phase at high temperatures are almost randomly distributed over positions of Ni and Mn. The sample quenching can freeze the 'non-equilibrium' distribution of Fe atoms on Ni and Mn sublattices in $MnNi_{0.85}Fe_{0.15}Ge$ as well as the part of the 'non-equilibrium' hexagonal phase.

Table 3. Hyperfine magnetic fields calculated with SPRKKR code [10]

Alloy	$M(Mn_I)$	$M(Fe_I)$	H_{hfI},T	$M(Mn_{II})$	$M(Fe_{II})$	H_{hfII}	$M_{f.u.}$	E_{tot}, Ry/f.u.
Hexagonal Ni_2In-type structure, LDA approximation, non-magnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	–	–	–	–	–	–	–	−9468.06075
$(Mn_{0.99}Fe_{0.01})_I(Ni_{0.85}Fe_{0.14}Mn_{0.01})_{II}Ge$	–	–	–	–	–	–	–	−9468.06159
Hexagonal Ni_2In-type structure, GGA approximation, non-magnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	–	–	–	–	–	–	–	−9482.84201
$(Mn_{0.95}Fe_{0.05})_I(Ni_{0.85}Fe_{0.10}Mn_{0.05})_{II}Ge$	–	–	–	–	–	–	–	−9482.84255
Hexagonal Ni_2In-type structure, LDA approximation, ferromagnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	2.71	2.26	−14.4	0.91	1.19	−15.5	2.78	−9468.08958
$(Mn_{0.99}Fe_{0.01})_I(Ni_{0.85}Fe_{0.14}Mn_{0.01})_{II}Ge$	2.71	2.27	−14.5	0.26	1.00	−15.8	2.83	−9468.09353
Hexagonal Ni_2In-type structure, GGA approximation, ferromagnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	2.98	2.44	−17.1	1.58	1.42	−17.0	3.12	−9482.87981
$(Mn_{0.95}Fe_{0.05})_I(Ni_{0.85}Fe_{0.10}Mn_{0.05})_{II}Ge$	3.00	2.47	−17.2	1.15	1.33	−17.6	3.14	−9482.88268
Orthorhombic TiNiSi-type structure, LDA approximation, ferromagnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	2.84	2.24	−13.5	2.22	1.75	−20.5	3.10	−9468.19401
$(Mn_{0.99}Fe_{0.01})_I(Ni_{0.85}Fe_{0.14}Mn_{0.01})_{II}Ge$	2.84	2.25	−14.1	2.21	1.73	−21.7	3.10	−9468.19938
Orthorhombic TiNiSi-type structure, GGA approximation, ferromagnetic								
$(Mn_{0.86}Fe_{0.14})_I(Ni_{0.85}Fe_{0.01}Mn_{0.14})_{II}Ge$	2.97	2.33	−14.7	2.37	1.82	−22.9	3.18	−9482.98647
$(Mn_{0.95}Fe_{0.05})_I(Ni_{0.85}Fe_{0.10}Mn_{0.05})_{II}Ge$	2.97	2.33	−15.1	2.36	1.81	−23.8	3.17	−9482.99038

M – magnetic moment (atom/position). H_{hf} – calculated hyperfine magnetic field value in I or II type of positions. E_{tot} – exchange-correlation energy.

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