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Institute of Physics of the Jagellonian University, Cracow (a),
Institute "Boris Kidrič", Belgrade-Vinča (b), and
Institute of Physics, University of Belgrade (c)

Atomic and Magnetic Structure of $Mn_{5-x}Fe_xSi_3$

By

H. BIŃCZYCKA (a), Ž. DIMITRIJEVIĆ (b), B. GAJIĆ (c), and A. SZYTUŁA (a)

Information on the mechanism of magnetic interaction in intermetallic compounds may be obtained by studying magnetic properties of the solid solution. Its magnetic properties depend on composition, e.g. a transition from antiferromagnetic to ferromagnetic ordering occurs. An example of such a system may be compounds of the composition $Mn_{5-x}Fe_xSi_3$ in which Mn_5Si_3 is antiferromagnetic (1, 2), while Fe_5Si_3 is ferromagnetic (3 to 6). Compounds with a majority of Mn show antiferromagnetic properties at low temperature, whereas those with prevailing Fe show ferromagnetic properties (7, 8).

Reported in the paper are the results of combined investigations (roentgenographic, neutronographic, and magnetometric methods) of the crystal and magnetic structure of $Mn_{5-x}Fe_xSi_3$ (for $x = 0, 1, 2, 3, 4$).

The specimens of $Mn_{5-x}Fe_xSi_3$ were prepared by a combination of induction melting and solid state diffusion techniques. The purity was 4N for Mn and Fe, and 5N for Si powder. All the samples were melted and annealed for three days at 950 °C and then quenched. Another sample of $x = 2$ was additionally obtained, in such a way that after analogous heat treatment it was cooled together with the furnace.

The X-ray powder diffraction analysis with FeKα radiation showed that the specimens contained only the desired hexagonal phase with the lattice constants given in Table 1.

Magnetic measurements were carried out using a Sucksmith balance (9) for temperatures between 77 and 400 K. From these measurements it follows that Mn_4FeSi_3 and $Mn_3Fe_2Si_3$ are paramagnetic in this temperature range, similarly to Mn_5Si_3. $Mn_2Fe_3Si_3$ and $MnFe_4Si_3$ are ferromagnetic with Curie temperatures of 220 and 330 K, respectively. At 77 K the saturation moment per formula unit is 0.3 μ_B for $Mn_2Fe_3Si_3$ and 1.4 μ_B for $MnFe_4Si_3$.

Table 1

Lattice parameters, the distribution of Mn and Fe atoms in the sublattice, and values of the parameters x_{Me} and x_{Si} in $Mn_{5-x}Fe_xSi_3$

x	lattice parameters		$\frac{c_o}{a_o}$	V(Å^3)	distribution of Mn and Fe atoms in the sublattice (%)				values of the parameters	
					6g		4d			
	a_o(Å)	c_o(Å)			Mn	Fe	Mn	Fe	x_{Me}	x_{Si}
0	6.9077 ± 0.0004	4.8131 ± 0.0004	0.6968	198.90	100	0	100	0	0.2364	0.5957
1	6.8849 ± 0.0009	4.7861 ± 0.0008	0.6952	196.49	94.9	5.1	57.7	32.3	0.2386	0.5945
2Q	6.8572 ± 0.0006	4.7571 ± 0.0006	0.6937	193.72	82.5	17.5	26.2	73.8	0.2231	0.5983
2SC	6.8538 ± 0.0005	4.7579 ± 0.0005	0.6942	193.56	84.8	15.2	22.7	77.3	0.2327	0.5993
3	6.8301 ± 0.0004	4.7390 ± 0.0004	0.6938	191.46	62.7	37.3	6.0	94.0	0.2673	0.5986
4	6.8054 ± 0.0007	4.7290 ± 0.0005	0.6949	189.68	32.8	67.2	0.8	99.2	0.2333	0.5929

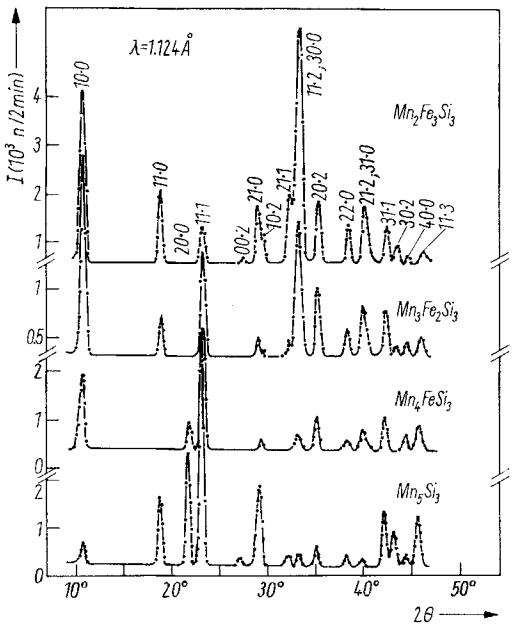

Fig. 1. A fragment of the neutron diffraction patterns in $Mn_{5-x}Fe_xSi_3$ (for x = 0, 1, 2, 3, 4) at 293 K

Powder neutron diffraction measurements were performed at the heavy-water moderated reactor RA in Vinča. The neutron wavelength used was 1.124 Å. The neutron diffractograms of these alloys were obtained at 77 and 293 K. In the case of $MnFe_4Si_3$, in order to separate magnetic contributions to the total scattering, a field of 6 kOe was applied parallel to the scattering vector.

Results of X-ray and neutron diffraction investigations indicate that $Mn_{5-x}Fe_xSi_3$ alloys belong to the hexagonal system (the space group is $D8_8$; $P6_3/mcm$; No. 193 (10)). The metal atoms (Mn, Fe) occupy two sublattices

$$4(d): \frac{1}{3}, \frac{2}{3}, 0;\ \frac{2}{3}, \frac{1}{3}, 0;\ \frac{1}{3}, \frac{2}{3}, \frac{1}{2};\ \frac{2}{3}, \frac{1}{3}, \frac{1}{2};$$

$$6(g): x, 0, \frac{1}{4};\ 0, x, \frac{1}{4};\ \bar{x}, \bar{x}, \frac{1}{4};\ \bar{x}, 0, \frac{3}{4};\ 0, \bar{x}, \frac{3}{4};\ x, x, \frac{3}{4};$$

while the Si atoms are at positions 6(g). The distribution of metal atoms within the sublattice 4(d) and 6(g), as well as the parameters x_{Me} and x_{Si}, were determined from the nuclear component of diffraction data performed at 293 K (see Fig. 1). The minimum value of the disagreement factor R was obtained for distribution of atoms and for values of parameters x_{Me} and x_{Si} given in Table 1. The distribution of Mn and Fe atoms in the sublattice is in fair agreement with the distributions suggested on the basis of investigations by means of the Mössbauer effect (8).

There is no difference between the diffraction patterns of Mn_4FeSi_3 and $Mn_3Fe_2Si_3$ made at the temperatures 77 and 293 K. This confirms the results of magnetic investigations indicating the absence of ordering of magnetic moments at

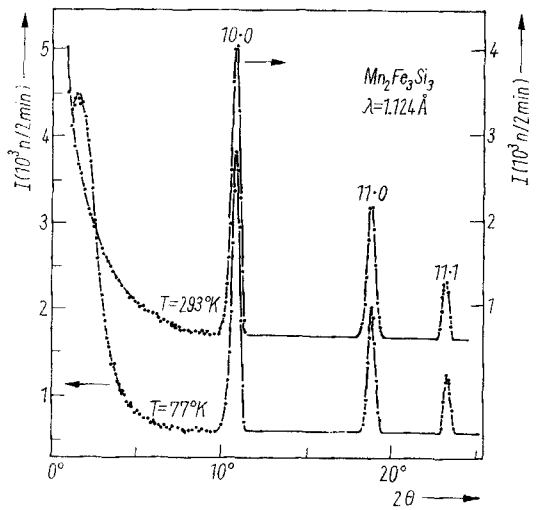

Fig. 2. Neutron diffraction patterns of $Mn_2Fe_3Si_3$ at 77 and 293 K

77 K. In the neutron diffraction pattern of $Mn_2Fe_3Si_3$ (see Fig. 2) we can see an additional reflection for $\sin\theta/\lambda = 164\times10^{-4}$ Å^{-1} at 77 K. Its existence at such a small angle is typical for helical spin configuration. It is impossible to obtain an unambiguous model of magnetic structure for this compound on account of the absence of additional reflections of $(hkl)^{\pm}$ type. Assuming that the reflection $(000)^{\pm}$ is observed, we get a spiral period of 6.5 c_0. Now we begin neutron diffraction investigations at 4.2 K for the compounds mentioned above. In the case of the $MnFe_4Si_3$ specimen (see Fig. 3) we observed the magnetic contributions for several Bragg reflections. This can be explained, assuming the ferromagnetic ordering of magnetic moments of atoms. The magnetic contributions to Bragg reflections were of use in defining the magnetic moments of atoms in respective sublattices. The best consistency with experimental results was obtained

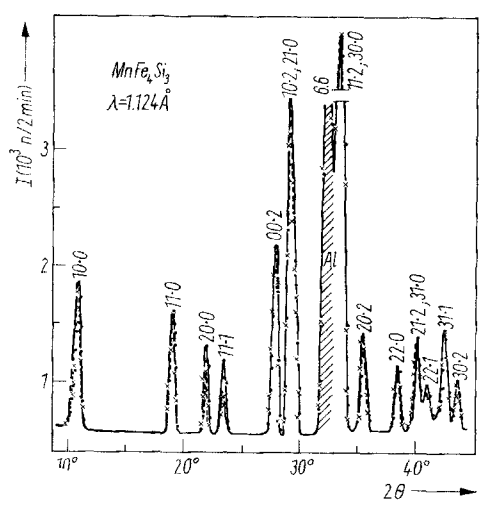

Fig. 3. Neutron diffraction patterns of $MnFe_4Si_3$ at the temperature 77 K; × H = 6 kOe, ● H = O

when assuming the following values of magnetic moments: $\mu(Fe_{4d}) = (1.0 \pm 0.1)\mu_B$, $\mu(Fe_{6g}) = (1.5 \pm 0.1)\mu_B$, $\mu(Mn_{6g}) = (1.2 \pm 0.1)\mu_B$ directed parallel to the c_o-axis.

The structure of the $Mn_{5-x}Fe_xSi_3$ solid solution series belongs to the space group $P6_3/mcm$ with metal atoms in two inequivalent sites (4 Me_I in 4(d); 6 Me_{II} in 6(g)). It was found that Mn and Fe atoms occupy preferably the 6(g) and 4(d) positions respectively. The choice of the site is apparently related to the fact that the less electropositive Fe atom forms more stable metal-metal bonds in the 4(d) position than does the Mn atom. This problem was extensively discussed by Johnson et al. (8).

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