Experimental report

02/10/2023

Proposal: **5-23-784** **Council:** 10/2022

Title: Magnetostrictive behaviour and crystal structure of Fe-doped Ni-Mn-Ga-Co-In-Fe Metamagnetic Shape MemoryAlloys

Research area: Materials

This proposal is a new proposal

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Samples: Ni43Mn28Ga14Co9In3Fe3
Ni43Mn27Ga14Co9In3Fe4
Ni43Mn26Ga14Co9In3Fe5
Ni43Mn30Ga14Co9In3Fe1
Ni43Mn31Ga14Co9In3
Ni43Mn29Ga14Co9In3Fe2

Instrument	Requested days	Allocated days	From	To
D1B	4	3	03/03/2023	06/03/2023
D20	4	0		

Abstract:

Ni-Mn-based magnetic shape memory alloys (MSMAs) are active materials that undergo martensitic transformations induced by temperature, stress and/or magnetic fields, leading to large recoverable mechanical transformations. As a result of the strong magnetoelastic coupling they show, these alloys can present large magnetostrains, due to either a reorientation of martensitic twin-variants or a magnetic-field induced martensitic transformation. Ni-Mn-Ga-Co-In alloys present a metamagnetic behaviour in their martensite phase, where stoichiometry controls the critical transformation temperatures: structural, TM, and magnetic, TC. When doped with Fe, these critical temperatures are affected, together with the magnetic properties of the alloys. It is well assessed that the cyclability of the magnetostriction depends on the hysteretic character (sharpness and temperature) of the structural transformation, that is highly influenced by the atomic positions. Within this context, we propose to carry out a neutron powder diffraction study with the goal of elucidating the role of the atomic site occupancies and the effect of Fe-doping in the magnetic and structural behaviour of the alloy series.

EXPERIMENT N°: 5-23-784 **INSTRUMENTS:** D1B

DATES OF EXPERIMENT: 03/03/2023 - 06/03/2023

TITLE: Magnetostrictive behavior and crystal structure of Fe-doped Ni-Mn-Ga-Co-In-Fe Metamagnetic Shape Memory Alloys

REPORT 28/09/2023

Magnetostrictive materials have been gaining prominence due to their potential applications in many fields, such as sensors and actuators. These applications are a consequence of the deformation they suffer from the action of external magnetic fields, and of the subsequent regaining of the original shape after the removal of that field. In Magnetic Shape Memory Alloys, MSMAs, this process arises from a first order solid-state phase transformation that involves a change in both structural and magnetic properties, known as martensitic transformation. For some Meta-MSMAs, such as Ni-Mn-Ga-based compounds, this magnetostrictive deformation process can be controlled by tuning the hysteresis character and the structural and magnetic transition temperatures, that depend strongly on the composition, structure and atomic order.

In this regard, the aim of the proposal was to obtain the crystalline phases and atomic site occupancies of a series of Ni-Mn-Ga-Co-In-Fe alloys, with the goal of elucidating the effect a 0 to 5 at.% Mn substitution with Fe has on both the hysteresis and structural and magnetic transition temperatures.

During the 72h experiment performed at the powder neutron diffractometer D1B at ILL, we managed to collect diffractograms of six samples, whose composition and measurement temperatures are shown in the following table

Name	Composition	T1	T2	T3	T4
M1	$Ni_{40.9}Mn_{30.7}Ga_{17.0}Co_{8.8}In_{2.6}$	50	300	425	500
M2	$Ni_{40.5}Mn_{30.8}Ga_{16.2}Co_{8.5}In_{3.1}Fe_{0.9}$	50	250	425	500
M3	$Ni_{41.8}Mn_{30.8}Ga_{14.6}Co_{9.1}In_{2.9}Fe_{1.4}$	–	250	300	500
M4	$Ni_{40.8}Mn_{29.7}Ga_{14.9}Co_{8.6}In_{3}Fe_{3.3}$	–	–	300	500
M5	$Ni_{41.3}Mn_{26.8}Ga_{15.4}Co_{8.9}In_{3}Fe_{4.6}$	–	–	300	500
M6	$Ni_{41.8}Mn_{27.9}Ga_{13.5}Co_{8.9}In_{3}Fe_{4.6}$	–	–	–	500

Table 1. Names and compositions of the four samples measured at D1B during the experiment, with the temperatures (in Kelvin) at which diffractograms were acquired.

The different temperatures were chosen so that different structural and magnetic states could be measured in each sample. A high temperature paramagnetic austenite (T4) and a ferromagnetic austenite (T3) were measured in every sample, and, for those samples showing martensitic transformation, a paramagnetic martensite phase (T2) and a weak magnetic martensite (T1) were measured as well.

All the diffractograms obtained in this experiment were measured working at a wavelength of λ=1.28 Å. The experimental procedure was the following: the sample was inserted in the cryofurnace at D1B and a routine was configured to continuously acquire neutron diffraction data until removing the sample. Therefore, besides the standard diffractograms obtained at the aforementioned stable temperatures, thermodiffractograms were also acquired during the temperature sweeping process.

A LeBail analysis was performed via FULLPROF in every experimental diffractogram obtained at a stable temperature. It was concluded that the paramagnetic austenite phases of all the alloys studied presented a cubic (Fm3m space group) structure, with smaller lattice parameter as Fe content increase. The refinements performed in the diffractograms corresponding to the martensitic phases show a non-modulated tetragonal structure (I4/mmm space group). An increase in the a/c relation is observed with the increasing Fe content. The results are shown in Table 2 and the atomic sited occupancies unraveled by means of Rietveld refinements are shown in Table 3.

	Structure		
Sample	**a_C**	**a_T**	**c_T**
M1	5.845	5.409	6.652
M2	5.839	5.414	6.631
M3	5.837	5.459	6.805
M4	5.837	–	–
M5	5.841	–	–
M6	5.836	–	–

Table 2. Atomic site occupancies and lattice parameters of the martensitic (I4/mmm tetragonal structure) and austenitic (Fm3m cubic structure) phases of the measured alloys

	Atomic sites occupancies						
Sample	**Sites**	**Ni**	**Mn**	**Ga**	**Co**	**In**	**Fe**
M1	(0.25, 0.25, 0.25)	40.7	0.6	–	8.7	–	–
	(0, 0, 0)	–	22.3	–	–	2.7	–
	(0.5, 0.5, 0.5)	–	8.3	16.7	–	–	–
M2	(0.25, 0.25, 0.25)	40.5	0.1	–	8.5	–	0.9
	(0, 0, 0)	–	21.9	–	–	3.1	–
	(0.5, 0.5, 0.5)	–	8.8	16.2	–	–	–
M3	(0.25, 0.25, 0.25)	41.8	6	–	2	–	0.2
	(0, 0, 0)	–	20.9			2.9	1.2
	(0.5, 0.5, 0.5)	–	3.3	14.6	7.1		–
M4	(0.25, 0.25, 0.25)	40.8	0.9	–	7.1	–	1.2
	(0, 0, 0)	–	20.2	–	–	2.7	2.1
	(0.5, 0.5, 0.5)	–	8.6	14.9	1.5	–	–
M5	(0.25, 0.25, 0.25)	41.3	1.2	–	5.6	–	1.9
	(0, 0, 0)	–	19.3	–	–	3	2.7
	(0.5, 0.5, 0.5)	–	6.3	15.4	3.3	–	–
M6	(0.25, 0.25, 0.25)	41.8	6.1	–	0.5	–	1.6
	(0, 0, 0)	–	18.3	–	–	2.4	4.3
	(0.5, 0.5, 0.5)	–	3.5	13.5	8	–	–

Table 3. Atomic site occupancies and lattice parameters of the paramagnetic austenite phases (Cubic, Fm3m space group), at 500 K, of the alloys studied.