Experimental report

25/10/2022

Proposal: 5-31-2804 **Council:** 4/2020

Title: Magnetic, structural and atomic ordering insight of metamagnetic shape memory alloys

Research area: Materials

This proposal is a new proposal

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Samples: Ni40Mn42.5Co8Sn9.5

Instrument	Requested days	Allocated days	From	To
D1B	4	0		
D20	4	2	02/03/2021	04/03/2021
D2B	0	0		

Abstract:

Ni-Mn-Co-X-based Heusler alloys (X=Sn, Ga), a family of metamagentic MSMAs(MetaMSMAs), have been reported to have martensitic transformation (MT) close to room temperature affected by slight changes in the composition. Previous works done in our laboratory on Ni-Mn-Sn alloys have shown that it undergoes a paramagnetic-ferromagnetic phase transition in the MT. Precisely, Ni-Mn-Co-Sn Heusler alloys have been reported to have MT around room temperature, which is promising for solid-state refrigeration applications. For a full understanding of the underlying mechanisms leading to the optimized properties of MetaMSMAs maximizing the MCE on them, the study of the influence of post-spun heat treatments on the structure and atomic order in MetaMSMAs is crucial. Physical properties as magnetization, value of the transformation temperature and hysteresis are atomic ordering dependent, which can be tuned via adequate heat treatments. 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 heat treatments in the magnetic and structural behaviour of the alloy series.

EXPERIMENT N°: 5-31-2804 **INSTRUMENTS:** D20

DATES OF EXPERIMENT 02/03/2021-04/03/2021

TITLE: Neutron diffraction experiment on magnetic, structural and atomic ordering insight of metamagnetic shape memory alloys

REPORT 04/10/2022

Metamagnetic Shape Memory Alloys, MetaMSMAs, have been gaining prominence as an alternative for the rare-earth refrigerators, since they display giant inverse magnetocaloric effect, IMCE. Ni-Mn-Co-Sn MetaMSMAs, in the presence of a magnetic field, undergo a ferromagnetic austenite – weak magnetic martensite transition at around room temperature, leading to a field induced reverse martensitic transformation. Being this transformation key part of the IMCE, a full understanding of the underlying mechanism and the factors that play a role in it is crucial. Among these factors, atomic ordering outstands as one of the most critical ones, due to several physical properties as magnetization, value of the transformation temperature and hysteresis being atomic ordering dependent. Atomic site occupancies are adjustable via adequate heat treatment, so a neutron powder diffraction study was performed with the goal of elucidating the role of different heat treatments in the atomic site occupancies. An article including the results of this experiment is currently in preparation.

In this regard, the aim of the proposal was to obtain the crystalline phases and atomic site occupancies of a series of alloys of $Ni_{40}Co_8Mn_{42.5}Sn_{9.5}$ and $Ni_{45}Co_5Mn_{30}Ga_{20}$, each of them without heat treatment and with three heat treatments, collecting high-resolution diffractograms for each sample. However, only the alloys showing the most interesting properties were measured. $Ni_{43.3}Mn_{39.2}Co_{7.4}Sn_{10.1}$ (both differently heat-treated and non-treated samples) and heat-treated $Ni_{43.1}Mn_{39.5}Co_{7.2}Sn_{10.4}$ alloys, where we observed the influence of different heat-treatments on atomic ordering.

During the 48h experiment performed at the powder neutron diffractometer D20 at ILL, we managed to measure a total of four samples with the composition, heat treatments and diffractogram temperatures included in the following table:

Composition	Treatment	Name	T1	T2	T3	T4
$Ni_{43.3}Mn_{39.2}Co_{7.4}Sn_{10.1}$	24 h at 1223 K + 4 h at 723 K	S1	123K	203K	323K	423K
$Ni_{43.3}Mn_{39.2}Co_{7.4}Sn_{10.1}$	24 h at 1223 K	S2	123K	203K	323K	423K
$Ni_{43.3}Mn_{39.2}Co_{7.4}Sn_{10.1}$	-	S3	123K	203K	323K	423K
$Ni_{43.1}Mn_{39.5}Co_{7.2}Sn_{10.4}$	24 h at 1223 K + 4 h at 723 K	S4	123K	203K	323K	423K

Table 1: Names, compositions and heat treatments of the four samples measured at D20 during the experiment, with the temperatures at which diffractograms were acquired.

All the diffractograms obtained in this experiment were measured working at a wavelength of λ=1.54 Å. The experimental procedure was the following: the sample was inserted in the cryofurnace at D20 and a routine was configured to continuously acquire neutron diffraction data until removing the sample. For each sample, four diffractograms were acquired for 1 hour each at four different temperatures.

The four different temperatures were chosen so that we could measure a ferromagnetic martensite phase (T1), an intermediate paramagnetic martensite (T2), a weak magnetic austenite (T3), and a high

temperature paramagnetic austenite (T4). All the samples were measured at the same temperatures so that the atomic ordering could be compared. Besides these standard diffractograms obtained at the aforementioned stable temperatures, we also recorded thermodiffractograms during the temperature ramps from T1 to T2, from T2 to T3, and from T3 to T4.

A Le Bail analysis was performed via FULLPROF in the experimental diffractograms obtained at 423K. It was concluded that the paramagnetic austenite phases of all the alloys studied presented a cubic (Fm3m space group) structure, with similar lattice parameters in the treated samples (S1, S2, S4) and slightly different ones in the non-treated sample (S3). It can be observed in the diffractograms attached to this report (*Fig.1*) the difference between the diffractograms. A more detailed analysis of the obtained diffractograms, by means of Rietveld FULLPROF refinements, allowed us to unravel the atomic site occupancies of the paramagnetic austenite phase at each alloy. These results, along with the lattice parameters, are shown in *Fig.2*. Finally, a further analysis will give us the lattice parameters and atomic site occupancies in the martensite phase of each alloy. By the comparison of the ferromagnetic phase and the paramagnetic martensite phases (below and above T_C), we will try to obtain the magnetic moments at each atomic site.

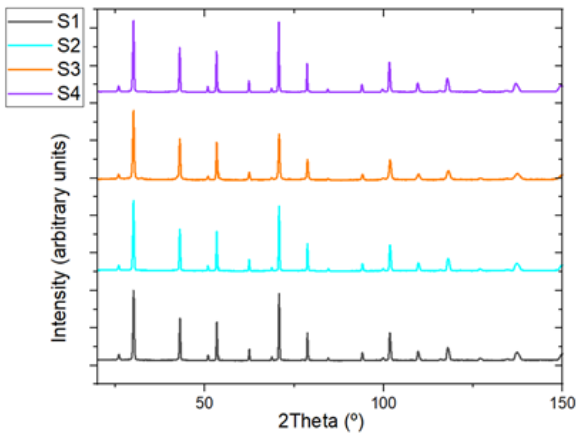

Fig.1: Neutron thermodiffractograms obtained by powder neutron diffraction of the paramagnetic austenite phases, at 423 K, of the alloys studied.

	Structure	Atomic sites occupancy				
Alloy	a (Å)	Site	Ni	Mn	Sn	Co
S1	5.774	(0.25, 0.25, 0.25)	43.3	–	–	6.7
		(0.5, 0.5, 0.5)	–	14.0	10.5	0.5
		(0, 0, 0)	–	25.0	–	–
S2	5.730	(0.25, 0.25, 0.25)	43.3	0.3	–	6.4
		(0.5, 0.5, 0.5)	–	13.6	10.5	0.9
		(0, 0, 0)	–	24.7	–	0.3
S3	5.972	(0.25, 0.25, 0.25)	43.3	0.2	–	6.5
		(0.5, 0.5, 0.5)	–	14.4	10.7	–
		(0, 0, 0)	–	24.1	–	0.9
S4	5.774	(0.25, 0.25, 0.25)	43.3	1.5	–	5.2
		(0.5, 0.5, 0.5)	–	13.6	10.3	1.1
		(0, 0, 0)	–	24.7	–	0.3

Fig.1: Atomic site occupancies and lattice parameters of the paramagnetic austenite phases (Cubic, Fm3m space group), at 423 K, of the alloys studied.