Experimental report

25/10/2022

Proposal:	**5-31-2707**	**Council:**	10/2019

Title: Influence of Cu addition on structural and magnetic properties of Ni50Mn25-xGa25Cux (x = 3, 6 and 9) metamagnetic shape memory alloys

Research area: Materials

This proposal is a new proposal

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Samples: NiMnGaCu

Instrument	Requested days	Allocated days	From	To
D2B	2	2	25/09/2020	27/09/2020
D1B	2	0		

Abstract:

Heusler shape memory alloys represent new multifunctional materials capable of controllable activated twin boundary motion. NiMnGa alloys have shown extremely large field-induced strains (12% at RT). Studies of the dependence of the magnetic moment with composition conclude that the magnetic interactions of the Mn atoms are very sensitive to the exact lattice site occupancy of the different atoms. Cu-doping of Ni2MnGa alloys allows smooth adjustment of the magnetic and structural transition temperatures. The doped compounds show a metamagnetic phase transformation, resulting in a large magnetization difference across the transformation. These doped alloys are excellent candidates for technical applications due to the large magnetocaloric and giant magnetoresistance effects they present. Here we present a series of metamagnetic shape memory alloys with varying Mn and Cu content, where the relative compositions of both elements in the alloy affect their transition temperatures. 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 in the magnetic and structural behavior of the alloy series.

EXPERIMENT N°: 5-31-2707 **INSTRUMENTS:** D2B

DATES OF EXPERIMENT: 25/09/2020 – 27/09/2022

TITLE: Influence of Cu addition on structural and magnetic properties of $Ni_{50}Mn_{25-x}Ga_{25}Cux$ (x = 3, 6 and 9) metamagnetic shape memory alloys

REPORT 04/10/2022

Shape Memory Alloys, SMAs, are a type of multifunctional materials that undergo phase transitions induced by changing the temperature and/or applying a stress on them, what result in large recoverable mechanical deformations. In particular, magnetic SMAs, MSMAs, consist in alloys in which the actuation of the material can be induced not only by temperature or stress, but also upon the application of a magnetic field. Ni-Mn-Ga are MSMAs known for showing extremely large field-induced strains (up to 12%) at room temperature. The martensitic structure, magnetic order and magnetic moment per formula unit are key parameters for the motion of twin boundaries, affecting the output strain obtained, and shown to be extremely sensitive to the composition of the alloys. Detailed studies of the structural and magnetic properties with composition, in Ni-Mn-Ga alloys, conclude that they are very sensitive to the lattice site occupancy of the different atomic species. Cu substituting Mn enhances Ni covalency, strengthening the Ni-Ga chemical bonds resulting in increase of the MT temperatures. In addition to that, Cu weakens the magnetic interactions leading to a decrease of Curie temperature. As a result, the structural and magnetic transitions can be tuned in such a way that it is possible to find different structures and magnetic behaviors across the MT, and as in case of the Ni-Mn-Ga the atomic distribution can play a key role on them. Therefore, a neutron powder diffraction study was performed with the goal of elucidating the role of Mn substitution with Cu in the martensitic structures and atomic site occupancies. The results of this experiment are expected to contribute to an article in the next months.

The main goal of the proposal was to obtain the crystalline phases and atomic site occupancies of a series of $Ni_{50}Mn_{25-x}Cu_xGa_{25}$ alloys, with x=3, 6 and 9. These three samples, with the compositions and diffractogram temperatures included in the following table, were measured at the powder neutron diffractometer D2B (ILL), making a total of 48h experiment. We observed that the addition of Cu in substitution of Mn influences the crystal structure of the martensitic phases and the atomic site occupancies in both the martensite and austenite phases of the alloy.

Composition	Name	T1	T2	T3	T4
$Ni_{50}Mn_{22}Ga_{25}Cu_3$	x3	230K	265K	280K	315K
$Ni_{50}Mn_{19}Ga_{25}Cu_6$	x6	205K	240K	300K	335K
$Ni_{50}Mn_{16}Ga_{25}Cu_9$	x9	359K	394K	466K	501K

Table 1: Names and compositions of the six samples measured at D2B during the experiment, with the temperatures at which diffractograms were acquired.

The diffractograms obtained in this experiment were measured at a wavelength of λ=1.59 Å with the following experimental procedure: after inserting the sample in the cryofurnace, neutron diffraction data was continuously acquired until removing the sample. Four different temperatures were set up, and a diffractogram was acquired per specified temperature and alloy.

The aforementioned four different temperatures were chosen so that we could measure a ferromagnetic martensite phase (T1), a paramagnetic austenite (T4) and intermediate temperatures just below and above the structural transformation temperatures (T2 and T3, respectively). always measured at the same temperature distance from the transformation temperature of each sample. For the x=3 alloy the magnetic phase transition (ferromagnetic to paramagnetic) happens in the austenite phase, while for the x=9 sample it takes place in the martensite phase. For the x=6 alloy, the structural and magnetic transitions coincide at the same temperature regions. Besides these standard diffractograms obtained at the set temperatures, we also recorded thermodiffractograms during the temperature ramps from T1 to T2, from T2 to T3, and from T3 to T4.

An initial Le Bail FULLPROF analysis of the diffractograms obtained in the experiment shows that the x=5 sample seems to present a modulated martensite phase while the martensite phase in x=9 is a tetragonal, non-modulated one. Nevertheless, x=6 alloy has a non-modulated tetragonal martensite phase. Also, it can be stated that no diffractogram show a pure austenite phase for x=6 and x=9 alloys, but just a mixture of martensite and austenite phases. More specifically, x=9 diffractograms are all four a mixture of martensite and austenite phases, while x=6 sample show a martensite phase diffractogram at 359K, and three mixed phases diffractograms. This can be observed in the diffractogram figures attached to the report (*Fig.1*). Lattice parameters of every alloy in their low-symmetry martensite and cubic austenite phases were also obtained via Le Bail refinements. A further analysis of the obtained diffractograms at the different temperatures measured will be performed by means of Rietveld FULLPROF refinements, in order to unravel the specific site occupancies of each phase in the three alloys measured at each temperature.

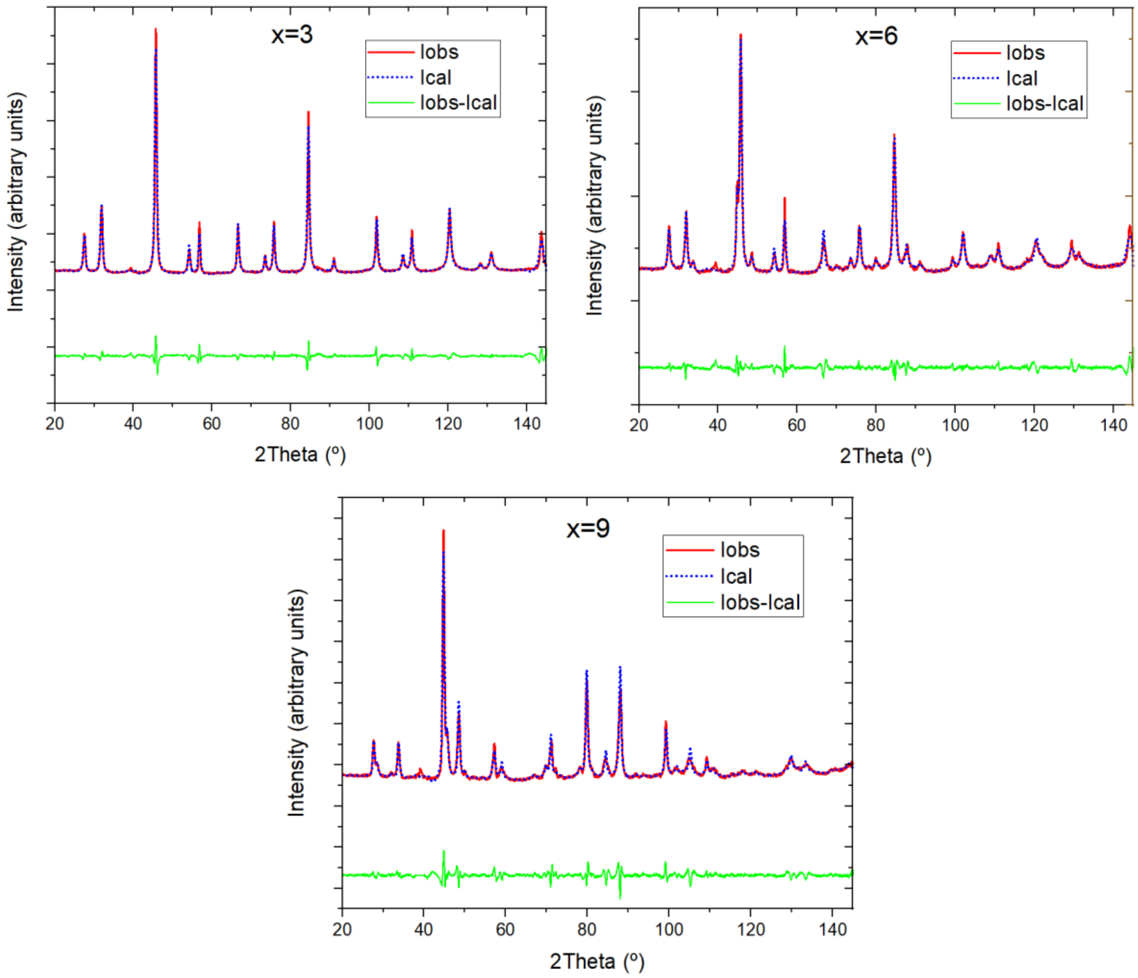

Fig.1: Neutron diffractograms obtained by powder neutron diffraction at the higher measured temperature of each of the alloys studied.