Experimental report

27/03/2019

Proposal: 5-15-623 **Council:** 4/2018

Title: Site occupancy study of Fe doped Ni45Co5Mn25-xFexGa20Cu5 (x =4 and 5)Heusler single crystals

Research area: Materials

This proposal is a new proposal

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Samples: Ni45Co5Mn21Fe4Ga20Cu5
Ni45Co5Mn20Fe5Ga20Cu5

Instrument	Requested days	Allocated days	From	To
D9	9	7	04/06/2018	12/06/2018

Abstract:

Recently, Ni-Mn-Ga based high temperature magnetic shape memory alloys have become the focus of intense research due to the observation of magnetic-field-induced strain at high temperatures, giving rise to many potential applications as contactless actuators in areas such as aerospace or automotive industries. For these compounds, the martensitic structure and magnetic order are key parameters for the output strain obtained and shown to be extremely sensitive to the composition of the alloys. We propose to carry out a neutron diffraction study in order to clarify experimentally the influence of the Fe addition on the martensitic transformation in two single crystalline samples of composition Ni45Co5Mn25-xFexGa20Cu5 (x= 4 and 5). In these alloys, the effect of the Fe doping promotes a simultaneous increase of Curie temperature and spontaneous magnetization, but a decrease of the martensitic transformation temperatures. The accurate knowledge of the site occupancies will be very important in order to properly analyze the results from polarized neutrons (PN), that will be carried out in the same samples.

EXPERIMENT N°: 5-15-623 **INSTRUMENTS:** D9

DATES OF EXPERIMENT 04/06/2018-11/06/2018

TITLE: Site occupancy study of Fe doped Ni45Co5Mn25-xFexGa20Cu5 (x =4 and 5) Heusler single crystals

REPORT 19/09/2018

Shape memory alloys with a Heusler structure represent new multifunctional materials capable displaying large controllable strains through twin boundary motion in by applying temperature, stress, magnetic field or a combination of them to the alloys in the martensite (tetragona) phase. In particular, Ni-Mn-Ga alloys have shown extremely large field-induced strains up to 10% for modulated martensites and 12% for non-modulated ones at room temperature, giving rise to many potential applications as contactless actuators in areas such as aerospace, automotive industries etc. Recently, multicomponent based on Ni-Mn-Ga alloys with substitutional elements such as Cu, Co and Fe have become the focus of intense research. This is because they have shown magnetic-field-induced martensitic transformation at temperatures higher than the bas ternary alloys. Detailed studies of the magnetic moment's dependence with composition in Ni-Mn-Ga alloys, conclude that the magnetic interactions between the Mn atoms in these alloys are very sensitive to the exact site occupancy of the different atomic species, something that can be determined with high accuracy by neutron diffraction. Thus, in these new alloys, the site occupancy of the substitution atoms is an important issue to understand the alloying effect on the final properties.

The aim of the neutron measurements was to get an accurate determination of the site occupancies, and the nuclear structure to properly analyze the results from polarized neutrons (experiment 1-04-126) for two different single crystals, SCFe4, and SCFe5 with nominal compositions $Ni_{45}Co_5Mn_{21}Fe_4Ga_{20}Cu_5$ and $Ni_{45}Co_5Mn_{20}Fe_5Ga_{20}Cu_5$ respectively.

For the experiment at D9, rectangular prisms ≈3x3x4 mm from the SCFe4 and SCFe5 single crystals was used cut to have <100> directions perpendicular to the crystal faces in the cubic phsase . Previous neutron Laue patterns taken at the ILL (Orient Express) confirm that the SCFe5 single crystal was in a single variant state, while for the SCFe4 there were additional twin variants present. Figure 2 represents the initial pattern taken at room temperature, showing the four axis symmetry characteristic of the tetragonal structure of the martensitic phase for the two single crystals.

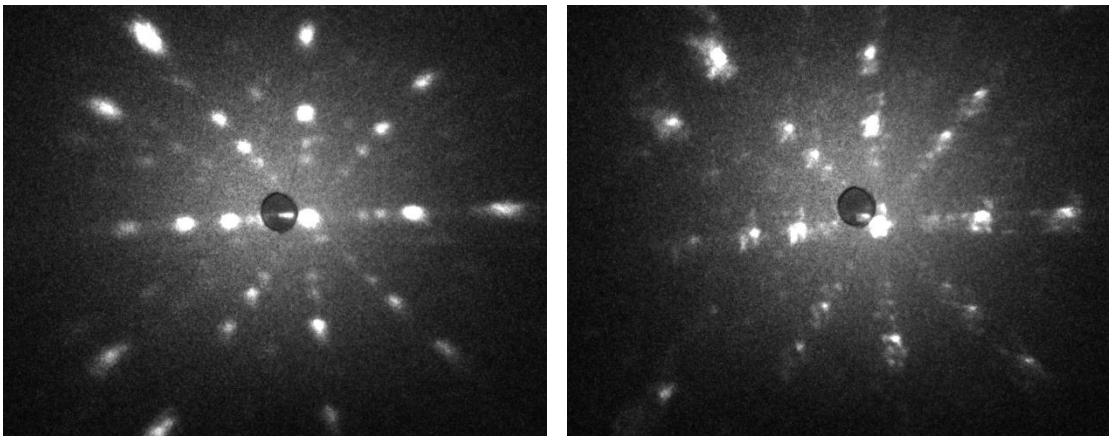

Figure 2. Laue pattern for single crystal a) SCFe5 and b) SCFe4

The structure for SCFe5 was refined from the measured integrated intensities, corrected for absorption, including extinction corrections and isotropic temperature factors.
The results for the paramagnetic and ferromagnetic austenite phases are shown in Figure 3. Both results show a good agreement between the observed and calculated intensities, with agreement factors of R_{bragg} = 2.88% (540 K) and 4.56% (400 K); and R_F = 4.35% (540 K) and 4.32% (400 K).

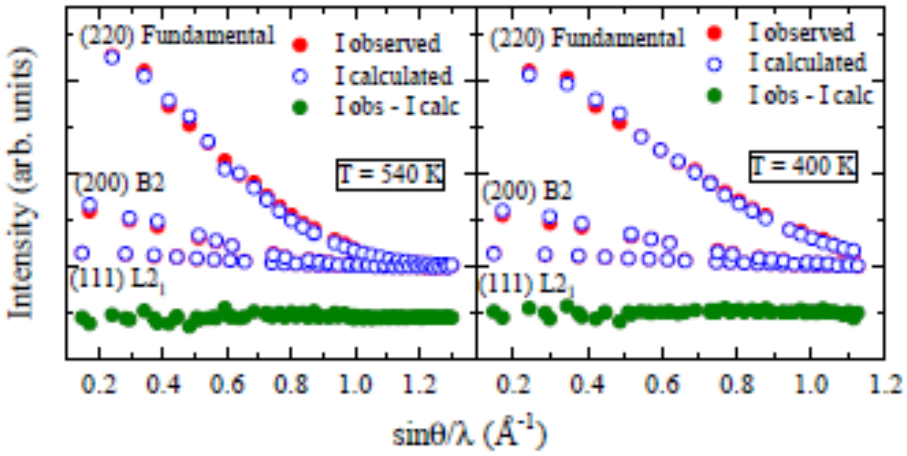

Figure 3. Integrated intensity for the calculated and observed reflections and their difference for Fe5 single crystal in the austenite phase at two different temperatures, 540 K (left) and 400 K (right)

The structures obtained have an Fm-3m space group with lattice parameters of 5.8406 Å (540 K) and 5.8036 Å (400 K). Moreover, the atomic distribution was obtained based on the composition measured by EDX. The results are summarized in Table 1. As was observed from the powder measurements, the additional elements' distribution follows the same behavior. Fe occupies mainly Ni and Mn sites, Co is located in the Ga positions, and Cu remains at the Mn sites.

In the case of the martensite phase, the results are shown in Figure 4.10. The occupancies are assumed to be the same as in the austenitic phase because of the diffusion-less character of the transformation. The phase was determined as an I4/mmm space symmetry group with lattice parameters of a = b = 3.887 and c = 6.486 Å, in agreement to the powder measurements.

Table 1. Site occupancies for Alloy 3 with the L21 structure obtained by Rietveld method. Errors are indicated in brackets.

Alloy	Site (Wyckoff)	Ni	Mn	Ga	Fe	Co	Cu	Total
Alloy 3	Ni (8c)	1.81(2)	0.12(0)	0	0.06(8)	0	0	2
	Mn (4a)	0	0.64(9)	0	0.13(5)	0	0.21(6)	1
	Ga (4b)	0	0.02(7)	0.76(0)	0.02(1)	0.19(2)	0	1

Further analysis of the sample Fe4 to properly determine its atomic order must be performed.