# Experimental report

18/01/2024

**Proposal:** DIR-299 **Council:** 4/2023

**Title:** Solving structure of five-layered modulated martensite of Ni-Mn-Ga(-Fe) using single-crystal neutron diffraction

**Research area:** Materials

**This proposal is a continuation of 5-15-626**


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**Samples:** Ni-Mn-Ga

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D19 | 10 | 15 | 07/09/2023 | 18/09/2023 |
| | | | 25/09/2023 | 01/10/2023 |


## Abstract:

The Ni-Mn-Ga is the prototype magnetic shape memory material exhibiting broad range of material functionalities. These functionalities originate from supermobile twin boundaries which occur only in the modulated martensite structures. Despite numerous attempts, the structure of five-layer modulated martensite of Ni-Mn-Ga has still not been fully solved due to the combination of inevitable hierarchical twinning and structural modulation that evolves with temperature. Recently, we discovered sharp hysteretic transition between the commensurate (q=0.400) and incommensurate (0.400<q<0.428) modulation in Ni-Mn-Ga and Ni-Mn-Ga-Fe alloys indicated by the shift in satellite positions and, importantly, unusual number and intensity of high-order satellite reflections. The aim of the current proposal is to collect full single crystal diffraction patterns from the Ni-Mn-Ga and Ni-Mn-Ga-Fe single crystals for both commensurate and incommensurate state and solve the crystal structure in combination with conventional single crystal XRD.

# Experimental report

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| Experimental title: | Solving structure of five-layered modulated martensite of Ni-Mn-Ga(-Fe) using single-crystal neutron diffraction |
| Proposal number: | **DIR-299** |
| Instrument: | **D19** |
| Date of experiment: | 7. – 18.9. 2023 and 25.9. – 1.10. 2023 |
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Abstract:
The Ni-Mn-Ga is the prototype magnetic shape memory material exhibiting broad range of material functionalities. These functionalities originate from supermobile twin boundaries which occur only in the modulated martensite structures. Despite numerous attempts, the structure of five-layer modulated martensite of Ni-Mn-Ga has still not been fully solved due to the combination of inevitable hierarchical twinning and structural modulation that evolves with temperature. Recently, we discovered sharp hysteretic transition between the commensurate ($q$=0.400) and incommensurate (0.400<$q$<0.428) modulation in Ni-Mn-Ga and Ni-Mn-Ga-Fe alloys indicated by the shift in satellite positions and, importantly, unusual number and intensity of high-order satellite reflections. The aim of the current proposal is to collect full single crystal diffraction patterns from the Ni-Mn-Ga and Ni-Mn-Ga-Fe single crystals for both commensurate and incommensurate state and solve the crystal structure in combination with conventional single crystal XRD.

Experiment:
The experiment was intended to collect full single-crystal neutron-diffraction (SC-ND) patterns for the selected Ni-Mn-Ga-based alloys. We used a strong advantage of the neutron diffraction to study larger (approx. 2×2×2 $mm^3$) bulk single crystals, compared to the small (0.2×0.1×0.1 $mm^3$) crystals we previously used for the conventional SC-XRD experiments. Here, in the contrary to the SC-XRD samples, the microstructure of the large bulk single-crystal samples for ND can be easily reoriented by mechanical stress via twin boundary motion to obtain near single-variant state (i.e., to suppress majority of the unwanted twins observed in the XRD data).

Three single crystals, off-stoichiometric $Ni_{50}Mn_{28.7}Ga_{21.3}$, Fe-doped $Ni_{50}Mn_{27}Ga_{22}Fe_1$, and CoCu-doped $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$, were investigated.

The first two crystals were shown to exhibit qualitatively same structural behaviour; however, different macroscopic and microscopic properties have been evidenced, presumably connected with fine details of modulation and/or twins in these materials. The experiment was aimed to reveal and properly understand the subtleties of these materials.

The third crystal, supposedly exhibiting non-modulated martensite was suggested to exhibit unexpected structural modulation discovered by electron diffraction. Our experiment was aimed to prove or disprove this in bulk single crystal.

The neutron diffraction experiment was performed employing D19 diffractometer equipped with an Eulerian cradle, a helium-flow cryostat and an Oxford Cryostream (to access the temperature range of 200 – 370 K). Large position-sensitive detector of D19, which is in a sense equivalent to a conventional X-ray diffractometer setup, enabled us collecting numerous reflections (including satellite reflections) at the same time and a global view of the reciprocal space including diffuse scattering and twinning.

Thanks to known thermal hysteresis of small crystals' structure and microstructure, the measurement protocol was optimized for the off-stoichiometric and Fe-doped samples to follow the most significant features of the 10M phase: The samples were heated just below martensitic transition temperature and after few minutes of thermal equilibration, they were cooled down by several kelvin. Then, high-statistics diffraction patterns were collected. Subsequently, the samples were cooled down deep to the 10M martensite region and measured again. After that, samples were heated to the temperature of the first measurement and the comparative diffraction patterns were collected. Finally, short measurements above martensitic phase transition (in cubic austenite phase) were done.

For the CoCu-doped sample, only the room-temperature diffraction pattern was collected.

Results:

Measurements for the Fe-doped sample unveiled the presence of two prominent twin domains, commonly referred to as *modulation twins* in the MSM field, confirming a successful reorientation of the microstructure prior the measurement.

In the off-stoichiometric $Ni_{50}Mn_{28.7}Ga_{21.3}$ sample, additional minor contribution (20%) from additional twin domains oriented along the short axis was observed. Despite significant compressive stress, full reorientation was not achieved.

The diffraction patterns of both samples disclosed expected slight temperature-induced alterations, previously associated with changes in the modulation vector from *commensurate* to *incommensurate*. Furthermore, we verified the presence of unusual high-order satellites in the raw data. Unfortunately, due to their extremely low intensity (some peaks were more than three orders weaker than the main peak) and their close proximity to the main peaks, initial attempts at data integration led to their omission. This may necessitate a reintegration of the original data to gain deeper insights into the recently suggested anharmonic nature of the modulation. Our current working model of the incommensurate 10M martensite structure is illustrated in Fig.1.

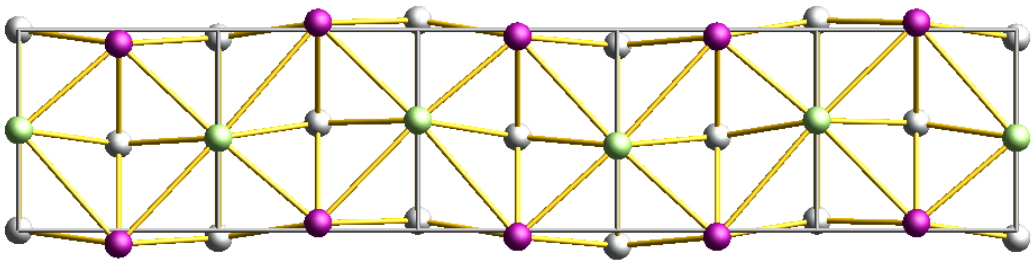

Fig.1: Current working model of the incommensurate $Ni_{50}Mn_{28.7}Ga_{21.3}$ structure with a modulation vector **q** = (0, 0, 0.412).

Short measurements of the cubic austenite phase, conducted to refine atomic occupations in a cubic de-twinned phase, unveiled unexpected reflections "in the middle" of the unit cell for the Fe-doped sample, Fig.2. Despite their low intensity, these additional reflections are anticipated to provide insights into the order/disorder introduced by the 1% Fe doping.

For the $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$ sample, characterized by an unexpected modulation as indicated by electron diffraction, we encountered extremely diffuse diffraction maxima. This prevented us from obtaining a reliable UB matrix and conducting a meaningful indexation. Nevertheless, a closer examination of the raw data revealed additional intensity in the *bc* plane, providing evidence for the presence of structural modulation within its martensite phase.

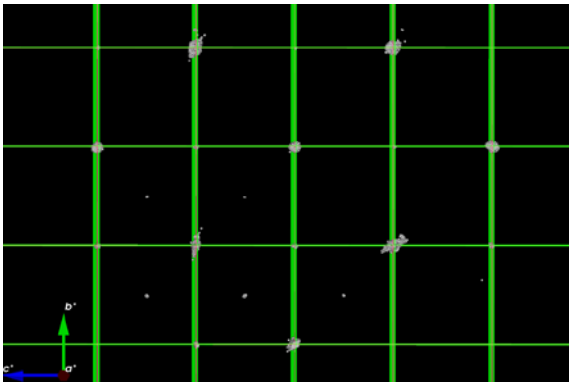

Fig.2: Detail on the reflections in the middle of the cubic austenite unit cell discovered in the diffraction pattern of the Fe-doped sample.

In summary, as the main result, the DIR-299 experiment provided comprehensive neutron diffraction patterns for the 10M modulated Ni-Mn-Ga-based martensites, revealing various complex structural features. To fully benefit from the experiment and not miss any “low-intensity” details, unusually careful approach to the measured data must be employed (e.g. finding the best way to re-integrate the data to preserve extremely weak satellites partially overlapping with the main peaks etc.). Since this poses a genuine crystallographic challenge, our work is still in progress and will not only require combining our SC-ND patterns with our previously acquired conventional SC-XRD data, but probably also additional high-resolution XRD on the bulk samples from our ND experiment to further enhance our understanding.