Experimental report

11/02/2020

Proposal: **5-15-626** **Council:** 4/2019

Title: Investigation of commensurate-incommensurate structure modulation transitions in Ni-Mn-Ga-Fe martensite

Research area: Physics

This proposal is a continuation of 5-41-950

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Samples: $Ni_{50}Mn_{27}Ga_{22}Fe_1$
$Ni_{50}Mn_{25}Ga_{21}Fe_4$

Instrument	Requested days	Allocated days	From	To
D10	6	4	10/10/2019	14/10/2019

Abstract:

There is still ongoing discussion on the true character of structural modulations in martensitic phases of Ni-Mn-Ga based magnetic shape memory alloys. Previous reports indicate commensurate ($q=0.400$) or incommensurate ($0.400<q<0.428$) structure modulation with the latter developing with temperature. Recently, we discovered sharp, thermally-induced, transitions between the commensurate and incommensurate modulated structures in Ni-Mn-Ga-Fe alloys. The aim of the current proposal is to investigate these transitions in detail. By combining the measurements with XRD and direct SEM and TEM observations of twins and nanotwins in the material, we expect to obtain some evidence on the true origin of the observed incommensurateness in the material.

Investigation of commensurate-incommensurate structure modulation transitions in Ni-Mn-Ga-Fe martensite

We performed an experiment on modulation changes in five-layered modulated (10M) martensites of the Ni-Mn-Ga-Fe and Ni-Mn-Ga single crystals of three different compositions employing the D10 diffractometer.

The Ni-Mn-Ga system represents the archetype of magnetic shape memory alloy. For this, the martensitic transformation from the high-temperature high-symmetry austenite phase to lower-temperature lower-symmetry martensites and the possible intermartensitic transformations (IMTs) between different martensites are of scientific interest for possible practical applications. With decreasing temperature, the typical transformation sequence is cubic ($L2_1$) → 10M modulated → 14M modulated → non-modulated (NM) martensite. Various experiments have shown that different types of martensite pose different physical properties.

Our previous neutron (D9 instrument, experiment 5-41-950) and X-ray diffraction experiments indicated the transition from commensurate to incommensurate 10M modulated martensite with a thermal hysteresis. During this, the modulation vector **q** gradually increased upon cooling from commensurate $\mathbf{q}=(2/5)\mathbf{g}_{110}$, where $\mathbf{g}_{110}$ is reciprocal lattice vector, to incommensurate one. The pseudo-commensurate $\mathbf{q}=(3/7)\mathbf{g}_{110}$ was reached just above the intermartensitic transformation to seven-layered modulated (14M) martensite. In the current experiment, we examined such a transition in detail in small temperature steps for three different Ni-Mn-Ga-based compositions.

After proving the correct orientation of the single crystals and confirming the modulation direction of [110]*, the main part of experimental time was dedicated to the measurements of q-scans between nuclear reflections (220) and (400) to get the data for the calculation of the modulation vector.

$Ni_{50}Mn_{27}Ga_{22}Fe_1$ alloy, for which the commensurate-incommensurate transition was previously detected, was investigated to further study the hysteresis behaviour of the transition and to obtain the magnitude of modulation vector q (defined following $\mathbf{q} = q\ \mathbf{g}_{110}$) for the previously unexplored temperature region. Before the measurements, sample was heated to 328 K to stabilise the commensurate 10M phase. The q-scan revealed four equidistant satellite peaks between (220) and (400) reflections at 300 K indicating the commensurate 10M martensite with $\mathbf{q} = (2/5)\mathbf{g}_{110}$, Fig. 1 (a).

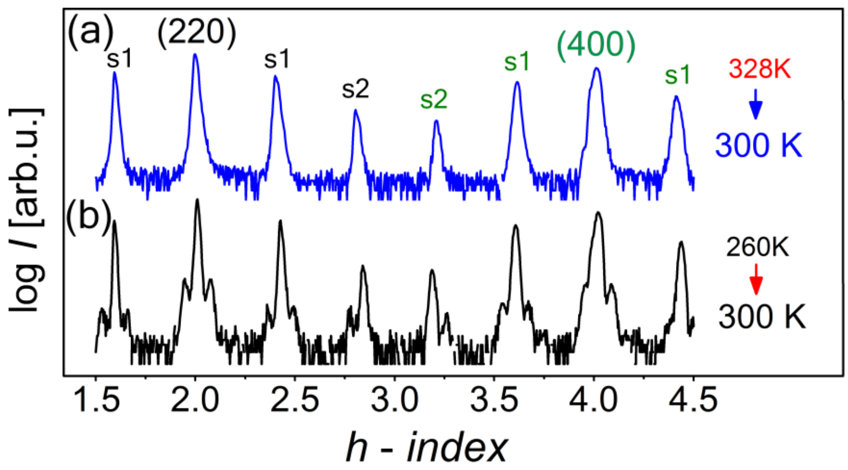

Fig. 1: Contrasting q-scans along the [110]* reciprocal direction at 300 K obtained during thermal cycling in illustrating the *commensurate* 10M modulated martensite after cooling down from 328 K (a) and the *incommensurate* modulated structure after heating up from 260 K (b).

During cooling, additional satellites appeared and the analysis indicated the modulation changes to incommensurate modulation bellow 300 K. The magnitude of the modulation vector *q* continuously increased during cooling. The cooling was stopped at 240 K, where the reasonable agreement with the previously obtained data from the D9 instrument (experiment 5-41-950) and X-ray diffractometer was found.

During heating, *q* decreased, reaching ~ 0.414 at 300 K. Corresponding q-scan is shown in Fig. 1 (b). Temperature evolution of the calculated magnitude of the modulation vector *q* is shown in Fig. 2.

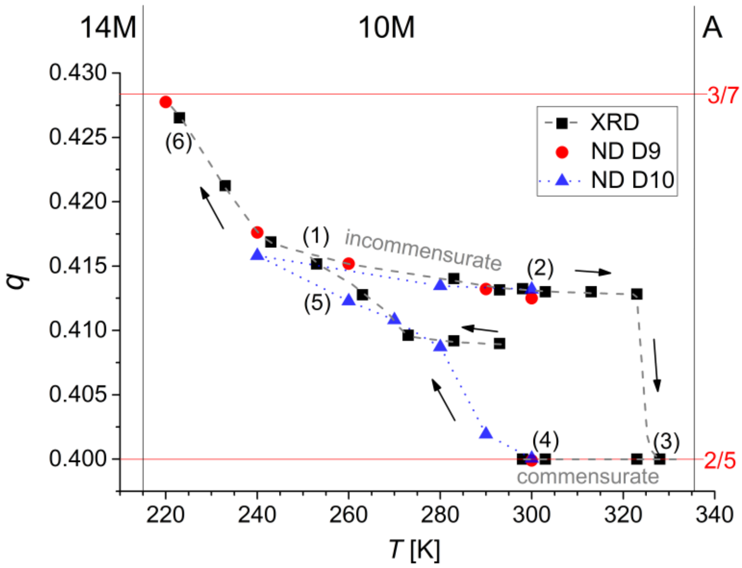

Fig. 2: Temperature evolution of the magnitude of the modulation vector *q* of the $Ni_{50}Mn_{27}Ga_{22}Fe_1$ single crystal within the temperature region of 10M martensite. Current D10 experiment is marked with blue triangles.

<u>$Ni_{50}Mn_{27.7}Ga_{22.3}$</u> alloy was investigated to study the changes in the nature of the modulation of 10M martensite for the pure Ni-Mn-Ga alloy. This sample was chosen after finding out the reachable temperature maximum of the D10 in the current setup because of its lower martensitic transformation temperature. Close to the room temperature, sample appeared to have incommensurate modulation with $q = 0.402$ (very close to commensurate $q = 2/5$). During cooling the incommensurateness increased and stabilised at $q \sim 0.416$ for temperatures lower than 140 K. No intermartensitic transformation was detected. During heating, hysteresis behaviour was observed, Fig. 3.

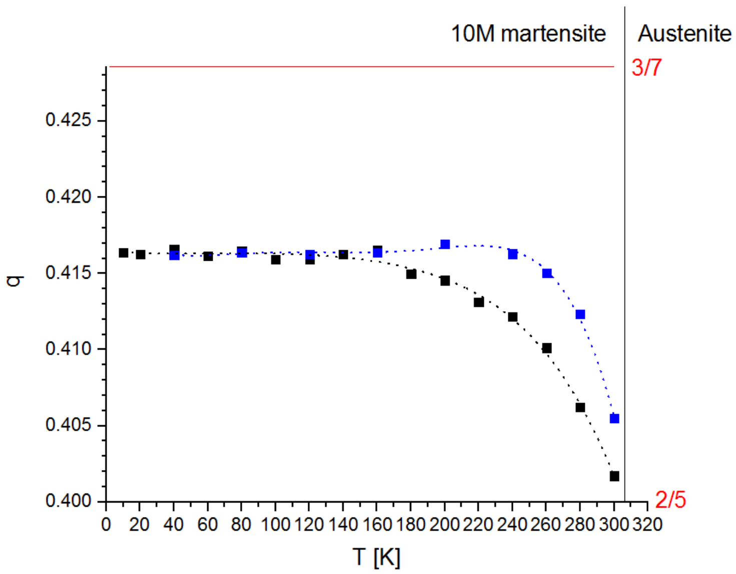

Fig. 3: Temperature evolution of the magnitude of the modulation vector *q* for $Ni_{50}Mn_{27.7}Ga_{22.3}$ single crystal during cooling and heating.

$Ni_{50}Mn_{25}Ga_{21}Fe_4$ alloy was investigated to study the nature of modulation in Ni-Mn-Ga-based composition with higher Fe content. At 300 K, sample was in incommensurate modulated state with $q = 0.421$. During heating to 315 K (maximum temperature reachable with the current D10 experimental setup) q decreased slightly to ~ 0.420. During cooling increase of the q was detected, attaining the value of 3/7 (pseudo-commensurate 10M) just before the intermartensitic transformation to seven-layered (14M) modulated martensite, Fig. 4.

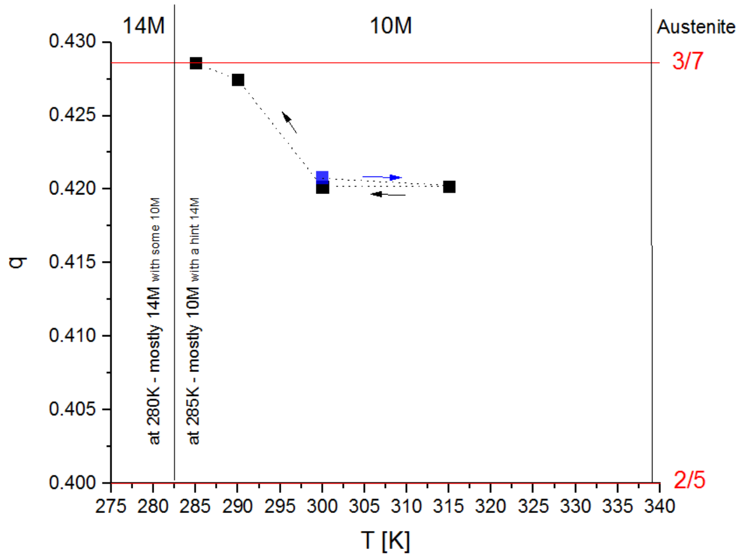

Fig. 4: Temperature evolution of the magnitude of the modulation vector q for $Ni_{50}Mn_{25}Ga_{21}Fe_4$ single crystal during heating and cooling.

In the summary, our measurements provided valuable data on the temperature evolution of the modulation vector **q** in 10M martensite of the Ni-Mn-Ga(-Fe) alloys of different compositions.

We found that in the temperature region of 10M martensite, the **q** continuously changes from $\mathbf{q} = 2/5\ \mathbf{g}_{110}$ (commensurate 10M structure) to $3/7\ \mathbf{g}_{110}$ (pseudo-commensurate 10M, known from stoichiometric Ni_2MnGa) during cooling. The changes exhibit a thermal hysteresis. Further cooling after reaching the pseudo-commensurate 10M martensite results in the transition to 14M martensite with $\mathbf{q} = 2/7\ \mathbf{g}_{110}$. Furthermore, stabilisation of the q on the intermediate value (the average $q \sim 0.417$) was observed for all three compositions.

Based on our studies of three different samples, we propose the changes of **q** might be common for the wide range of Ni-Mn-Ga(-Fe) compositions, where the transition sequence Austenite → 10M → 14M martensite is present.

The changes in the nature of modulation were confirmed to be the bulk effects. The presented measurements represent crucial point in our understanding of the material.