Experimental report

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Council: 4/2017

Title: Intermartensitic transformations and search for the ground state in Ni-Mn-Ga single crystals exhibiting the magnetic shape memory effect

Research area: Physics

This proposal is a new proposal

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Samples: Ni50Mn25+xGa25-x

Instrument	Requested days	Allocated days	From	To
D9	9	9	16/04/2018	23/04/2018
			13/06/2018	15/06/2018

Abstract:

Stoichiometric Ni2MnGa and sligthly off-stoichiometric Ni-Mn-Ga Heusler systems are prototype magnetic shape memory materials with parent cubic L21 structure and extraordinary magnetomechanical properties in lower-symmetry martensitic phases. Upon cooling from cubic parent, a wide range of transformations occur with typical sequence cubic L21->10M->14M->NM, where 10M and 14M denote modulated martensite phases and NM non-modulated tetragonal martensite phase. Ab initio calculations suggest the true ground state to be 4O, i.e. orthorhombic structure with modulation period of 4O atomic planes. We will study the transformation sequence in order to determine structural relation between transforming phases in whole crystal, the nucleation of the phases and their coexistence and changes with magnetic structure as well as the atomic arrangement. We aim to resolve the dilemma whether the intermartensite transitions are true phase transformation or detwinning process and additionally we will search for the newly predicted 4O ground state at low temperatures.

Investigation of the intermartensitic transformations and search for the ground state in Ni-Mn-Ga single crystals exhibiting the magnetic shape memory effect

We performed an experiment on intermartensitic transformations in Ni-Mn-Ga and Ni-Mn-Ga-Fe single crystals of various compositions employing CYCLOPS and D9 diffractometers.
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→14M→NM martensite. Previous experiments have shown that different types of martensite pose different physical properties.
In the first step, we performed Laue neutron diffraction experiment using CYCLOPS diffractometer. Laue diffraction confirmed good quality of investigated single crystals, their orientation and provided first information on structural and microstructural changes at different temperatures. Based on CYCLOPS experiment, six single crystals were chosen for further study, four of which were subsequently measured on D9.
The main part of experimental time (D9) was dedicated to the study of thermal evolution of the modulation satellites. We measured q-scans between nuclear reflections of interest, i.e. (220)-(400) and (2-20)-(400). The example of temperature evolution of modulation satellites is presented in Fig. 1 for the $Ni_{50}Mn_{27}Ga_{22}Fe_1$ single crystal.

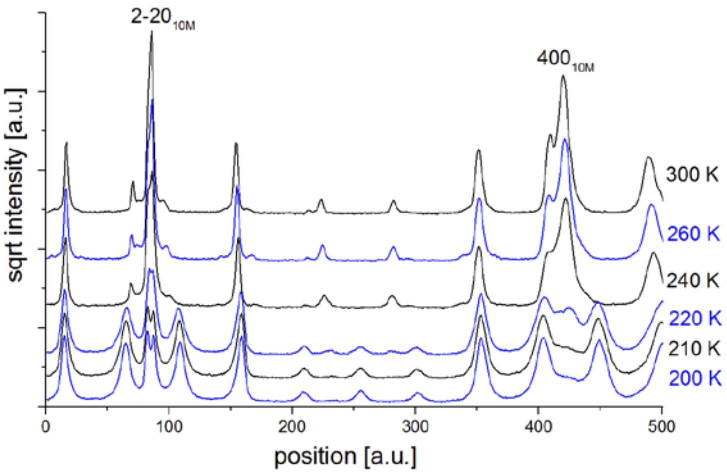

Fig. 1.: Thermal evolution of the modulated martensite of $Ni_{50}Mn_{27}Ga_{22}Fe_1$ single crystal during cooling. At 220 K the structure undergoes the intermartensitic transformation 10M→14M.

$Ni_{50}Mn_{28.2}Ga_{21.8}$ sample was investigated in order to detect possible IMT 10M→14M, transformation to possible 4O martensite recently proposed in literature and to study the thermal evolution of modulation satellites. For this, the sample was cooled down to 2 K in appropriate temperature steps. However, no IMTs were found in the temperature region 2–330 K. The minor change of the positions of the modulation satellites suggested possible slight changes of modulation vector. To explore those small changes in the modulation vector a better resolution experimental setup should be used.

$Ni_{50}Mn_{27}Ga_{22}Fe_1$ alloy was investigated to prove the presence of the newly discovered nanotwinned 10M martensite and to study the intermartensitic transformations. The nanotwinning was not detected, possibly due to the instrumental resolution. However, the measurements indicated the changes in the nature of the modulation of 10M martensite phase. The comparison of the q-scans at the room temperature after two different thermal treatments (after cooling the sample to 250 K and after heating to 330 K using heat blower) revealed the appearance of additional sattelites in the diffraction patterns, Fig. 2. The analysis of the data explained this effect as the transition between commensurate 10M modulated martensite and incommensurate close-to-10M martensite with modulation vector slightly varying from that of 10M. Thermal cycling indicated hysterisis of such behaviour. Furthermore, the size of the modulation vector continuously increased from commensurate value q=0.4 to q~0.428, detected just above the IMT 10M→14M at 220 K. These unprecedented results might contribute to the ongoing discussion on the true character of structural modulations in martensitic phases of Ni-Mn-Ga based magnetic shape memory alloys and their proper study requires additional experimental time.

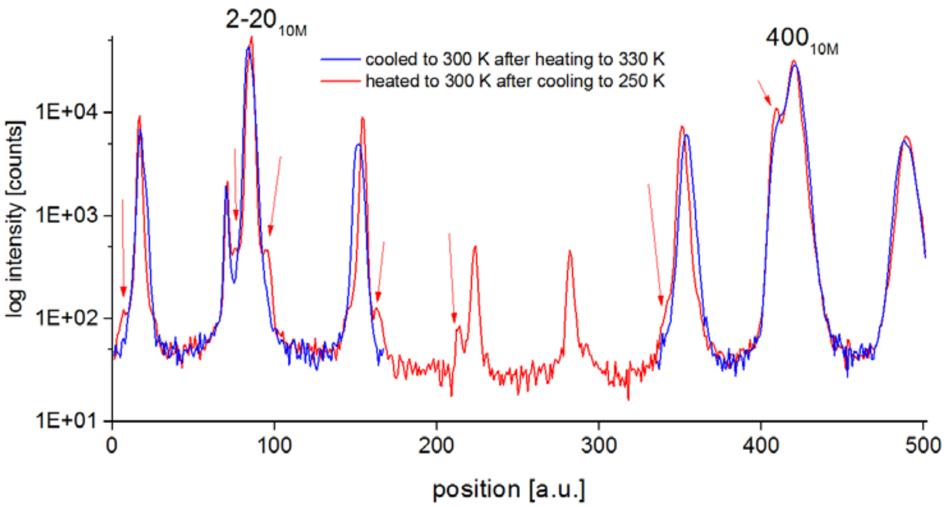

Fig 2. Comparison of the q-scans measured at the room temperature. Additional satellite peaks (marked by red arrows) appear after cooling the sample down to 250 K. This effect indicates the transition from commensurate 10M to slightly incommensurate modulated structure.

$Ni_{50}Mn_{28.5}Ga_{21.5}$ sample was investigated in order to detect the IMT 10M→14M (predicted at 90 K by AC susceptibility measurements) and identify possible 4O modulated martensite predicted by literature. None of these was confirmed, the sample remained stable in 10M martensite phase during cooling down to 2 K. Additional detected satellites indicate slightly incommensurate nature of 10M modulation of this sample, similarly to that of aforementioned $Ni_{50}Mn_{27}Ga_{22}Fe_1$.

In $Ni_{50}Mn_{28.9}Ga_{21.1}$, the IMT 10M→14M was detected at 220 K. Here, the diffraction pattern changed significantly. Probably due to the mosaicity of the crystal the peaks are twinned. At 140 K, the structure started to transform to NM martensite. The sample transformed back to 10M martensite during heating to the room temperature. Comparison of the positions of the modulation satellites before and after the cooling-heating cycle indicated the possible transformation from commensurate 10M to incommensurate 10M structure. However, the data collection with better statistics and mainly better resolution is required to prove such conclusion.

In the summary, our measurements provided valuable data on the thermal evolution of different martensites of the Ni-Mn-Ga(-Fe) alloys of different compositions. The changes in the nature of modulation were confirmed to be the bulk effects (so far, only the surface methods were employed). The measurements provided the base for the ongoing research on the nature of modulation in martensites of MSM alloys and the particular results represent crucial points in our understanding of the material.