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CHIMICHE, DELLA VITA E DELLA
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February 7th, 2023,Parma

Report on the PhD thesis of Petr Veřtát titled: Characterisation of Martensitic Phases in Ni-Mn-Ga based Heusler Alloys

- how much the topic of the thesis is up to date,

This Phd thesis is addressing an open issue dealing with the formulation of a model encompassing the complex twinning and the structural modulation featuring low symmetry martensites in Ni-Mn-Ga Heusler alloys. The occurrence of hierarchical twinning typical of shape memory alloys coexisting with complex ferromagnetic martensitic structures showing displacive modulations is at the basis of giant strains activated by external magnetic fields. However, the study of the interplay between martensitic crystal structure, twin boundaries mobility and microstructural properties was hampered by the lack of detwinned single crystals and the difficult reproducibility of the crystal growth processes. This work provides valuable insights shading a light onto the correlated structural aspects characterizing the martensitic phases in multifunctional magnetic shape memory Heusler alloys. Hence, this work has a strong level of novelty owing to the presentation of diffraction experiments never attempted with modulated martensites. For some Ni-Mn-Ga-Fe compositional combination it has been reported new structural events such as inter-martensitic transformations involving 10M modulated structures.

- what are the methods applied in the thesis,

The candidate investigated a rich variety of samples namely, single crystals oligocrystalline and polycrystalline materials showing complex Ni-Mn-Ga compositions. The huge experimental work was based on advanced diffraction experiments with conventional and unconventional sources applied, in some cases, for the first time to such class of intermetallics. The experimental protocols used in different diffraction sessions are well described and it demonstrates the expertise of the candidate in performing diffraction experiments with this class of materials. The methods applied encompasses single crystal diffraction from x-ray and neutron sources, reciprocal space mapping, pole figure measurements and a series of scans with different modes involving ω-off set, rocking curves, etc. The whole thesis is well organized and the different issues are clearly illustrated and commented.

I notice that this huge amount of diffraction data could be analyzed by conventional crystallographic tools usually adopted in crystallography for the analysis of crystalline materials (the Rietveld method is applied in a single case). The formulation of a dedicated excel sheet (FitExc) for the calculation of unit cell parameters is redundant considering that there are plenty of software suitable for the analysis of powder diffraction data. Nevertheless, I appreciate the ability of the candidate in formulating his own calculation instrument for the determination of unit cell parameters.

I suggest to change the figure 12 because it is conceptually wrong. The a/b twinning of one-dimensional 5M(10M) modulated Ni-Mn-Ga martensite is not properly described. Otherwise, I recommend to neglect this figure.

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In general the interpretation of the observed diffraction outputs provides a first interesting basis for future investigations.

- whether the goal of the thesis has been achieved,

The goals expressed in the PhD thesis was differentiated and outlined in three points: the individuation of experimental protocols for the application of diffraction experiments investigating martensitic phases; the structural study of Ni-Mn-Ga oligocrystalline samples representing the most frequent condition of synthetized specimens; the search of elements contributing to the origin of commensurate or incommensurate modulation. This work has a strong pioneering character. The diffraction data acquired with different setup was extensively detailed and several valuable results was presented and discussed. In my point of view this PhD thesis represents an important step forward the exploration of the complex interplay between structural modulation and diffuse twinning in multifunctional Ni-Mn-Ga martensitic phases. The scientific debate concerning the origin of the structural modulation in Ni-based Heusler martensitic phases is still ongoing and further theoretical and experimental studies are necessaries. So, in this perspective, this work provides useful but limited information towards the origin of such complex structural distortion.

- what is the scientific value of the results,

The research work of the candidate afforded 8 publications on international peer-reviewed journals with noticeable impact factor and several congress communications. The novelty of the published results is mainly related to the efforts in connecting microstructural aspects with internal commensurate and incommensurate displacive structural modulations. It has been reported diffraction experiments investigating inter-martensitic transitions involving the recombination of lattice distortions and modulation periodicity. In one of the published works it is underlined the anomalous sequence of intense satellites in Ni50Mn27Ga22Fe1 martensite possibly indicating a new form of structural modulation never encountered in Heusler alloys. The reported results brought new important information for the successful solution of the open questions driving the recent scientific research in this field.

- and what is your overall evaluation on the thesis, i.e. whether you recommend it for presentation and defense or not.

My overall evaluation is absolutely positive and I think that the quality of the scientific research is optimal. I suggest that the huge amount of diffraction data gathered in different experimental sessions will be matter of further analysis. I do recommend that this PhD work will access to the final presentation for the defense.

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