

SUPERVISOR'S REPORT ON DOCTORAL THESIS

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Title: Characterisation of the Martensitic Phases in Ni-Mn-Ga-based Heusler alloys

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The presented dissertation is a result of Petr Veřtát's work of the FZU - Institute of Physics of the Czech Academy of Sciences in Prague in the group of Magnetic Shape Memory (MSM) and the Department of Solid State Engineering, Faculty of Nuclear Sciences and Physical Engineering CTU in Prague. The work is in the form of traditional monograph even though it is based on the collection of papers in which were written by Petr or he significantly contributed. All together 8 full length papers and several conference proceedings directly related to the thesis are listed apart of 13 other papers unrelated to thesis. This well demonstrated that his working scope was broad and his work indispensable not only for MSM group but also for other research groups in the Institute. On the other hand, perhaps the wideness of the interests contributed to prolonged time (nearly six years) for finishing his thesis. It was not all together negative as it allows Petr to establish himself as real expert in the XRD laboratory.

The doctoral thesis is less traditionally structured to five parts, Introduction, Experimental, Methodology, Results and Conclusion followed by two appendices introducing superspace modulation description and extensive list of analyzed samples of many different forms.

The Introduction brings the brief description of Heusler alloys, martensitic transformation, resulting low symmetry phases and twinning occurring in transformed phases. Then magnetically induced reorientation is described as one of magnetic shape memory effects occurring in twinned low symmetry phase of Ni-Mn-Ga Heusler alloy. The chapter concludes with current state of art description of modulated low symmetry phases. The chapter also introduces the diffraction methods which can be suitable or rather, which are available considering the instrumental limitation in the laboratory. Since the fundamental studies must be done on single crystals the limits of polycrystalline studied are also mentioned. The author quoted large number (129) of bibliography sources, confirming his good orientation in the field.

In chapter Experimental the materials preparation is shortly mentioned but most of the chapter is devoted to various diffraction methods used. One may find this unnecessary, however, it provides method description not usually found in literature. This is quite important considering particularities of twinned phases. As such it can serve as good reference point for future students and other interested parties. He discussed the advantages

and disadvantages and limits of used methods, both for X-ray and neutron diffraction. Moreover, the author also introduces his own program developed for the fitting of overlapped peaks which was used in thesis and is it used also in other laboratories. With the aim to fully characterize the transforming materials other physical methods are shortly mentioned although the firm focus is on the structural analysis of phases and structural evolution with temperature and structural changes over martensitic and intermartensitic transformations.

The third chapter, Methodology is an extension of the Experimental. It describes used methods and the pros and cons of different diffraction approaches are discussed in detail in connection with particularities of twinned microstructure and structural modulation. It is demonstrated on the real examples encountered during the studies. The complex twinning usually found in low symmetry phase of Ni-Mn-Ga can affect the diffraction so that the usual methods may not be used. This is in my opinion well described in the thesis. The author also demonstrates the need for using different approaches for powders, polycrystalline, and oligocrystalline samples prepared in our laboratory. Then he focused on diffraction studies of single crystals using reciprocal space and q-scans. Experiment and Methodology chapters occupy more than one third of the thesis and I value the chapter highly as a reference for future work.

The description, analysis and discussion of the results occupy the last one third of the thesis. This is very rich chapter perhaps sometimes too condensed, but the detailed description can be found in listed papers. The chapter is again divided according the type of material analysed. Provided analyses of powder, polycrystals and oligocrystals unambiguously demonstrate the need to study the single crystal, at first just for crystal quality and then finally to analyse the peculiarities of modulated structures. This is the most important part and the pinnacle of the thesis as proper solving the structure constitutes a crucial step in understanding the unique mechanical properties of modulated phase of Ni-Mn-Ga. The thesis made good, but admittedly just initial step in such understanding. Here the results may feel controversial and the opinion may differ as the author tabled slightly different opinion and pushed against existing literature, but the conclusion is firmly based on his results. I believe that his effort is successful. Although the evolution of modulation with temperature was known previously the main result is a discovery of the thermal hysteresis of the modulation, which affects various physical properties confirmed by other methods. The extensive studies also suggest universal structural evolution of 10M phase in different Ni-Mn-Ga alloys.

Short Conclusion summarizes obtained results and importantly brings the outlook and plan for future research in this field.

In summary the thesis is well written, contains a lot of new results and it satisfies the demands put on doctoral thesis. Considering Petr's diligent work, his skills his willingness and eagerness to try new approaches and his communicativeness, I believe, he can be valuable member of any research team.

I have no doubt and it is my pleasure to recommend the thesis of Petr Veřtát to proceed for public defense.

In Prague 20 of December 2022

Oleg Heczko