Chapter 4 Martensite to austenite phase transition in Heusler alloy probed by Ultrafast Electron Diffraction

This chapter is in preparation for publication².

The martensite to austenite phase transition in the magnetic shape memory Heusler alloy Ni-Mn-Ga has been studied using Ultrafast Electron Diffraction. The structural properties of the material were studied in non-equilibrium conditions after excitation with an ultrashort near infrared laser pulse. This study gives new insight into the time scale at which the phase transition can take place. The initial change of the material from the low temperature martensite phase to the high temperature austenite phase takes place in tens of ps, faster than observed before. Subsequently, oscillations are observed, indicating a strong tendency in the lattice to go back to the low-temperature martensite phase.

4.1 Introduction

The discovery of interesting properties of alloys with the general composition $X_2YZ$ dates back to the beginning of the twentieth century and was made by Friedrich Heusler. After him, these materials are called Heusler alloys and nowadays this class of materials includes over 1500 members [1]. Among these compounds a plethora of interesting properties can be found, including multiferroics, shape memory alloys, topological insulators and superconductors [2]. Commercial applications of Heusler alloys include spintronic devices for data storage, as well as thermoelectric materials. There are already commercial applications of Heusler alloys in spintronic devices for data storage. Also thermoelectric materials already found applications [1].

Because of their strong coupling between magnetic and structural degrees of freedom, the sub-class of Ni-Mn-Ga alloys shows magnetic shape memory properties and a structural phase transition that can be magnetically or

temperature-driven. All compounds in this group show a cubic (austenite) phase at higher temperatures whereas at lower temperature the structure gets distorted to form the so-called martensite phase. Within this martensite phase there are several different sub-phases with different geometry, between which intermartensitic phase transitions take place [3].

Although for this class of materials there is no change in volume of the unit cell upon the phase transition [1] like there is in Ni-Mn-Sn and Ni-Mn-In, there are very high magnetic field induced strains (up to 10%), which make this alloy very suitable for technological applications like nanotweezers. There is full shape recovery over $10^8$ cycles.

In the transition from the austenite to martensite phase, the lattice undergoes a transformation, which can be described by a periodic shuffling of (011) planes along the [0-11] direction [4,5]. The martensite phase consists of three crystallographic domains, of which the boundaries (twin planes) can be moved by applying a magnetic field [1]. It has tetragonal or orthorhombic symmetry. The shuffling of the planes in the martensite phase is schematically shown in Figure 4.1. Although very important for the implementation of possible applications, very little is known about the kinetics and the speed of this phase transition and therefore a whole area is open for research.
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The exact chemical composition of the alloy influences the critical temperature for the phase transition between the martensite and austenite phase. In the $\text{Ni}_{50}\text{Mn}_{50-x}\text{Ga}_x$ compounds with $x$ around 20 at%, the transition occurs around 300 K. This temperature increases with decreasing Ga content [1].

The martensite-to-austenite phase transition in this type of compounds has been widely studied. There have been structural studies in equilibrium conditions which unravelled the phase diagram of the austenite phase and several martensite subphases [3]. The resulting phase diagram is shown in Figure 4.2. The 5M and 7M notations refer to different modulations of the lattice in the martensite phase, whereas the $L_x$ notations correspond to tetragonal structures. The solid red line shows the dependence of the transition temperature between the austenite phase and any of the martensite phases on the exact chemical composition (the number on the horizontal axis, $e/a$ indicates the number of valence electrons per atom and is directly related to the $x$ in the chemical composition of the sample).

Figure 4.2: Phase diagram for $\text{Ni}_{50}\text{Mn}_{50-x}\text{Ga}_x$ Heusler alloys. The austenite-to-martensite phase transition temperature as a function of number of valence electrons per atom ($e/a$, directly related to $x$) is shown with the open circles and the solid red line. Image taken from [3].
Another study used ultrafast spectroscopy to learn more about the origin of the martensitic transition [5]. Both in the austenite and in the martensite phase, pump-probe spectroscopy was used to find phonon modes that were resonant with the excitations. In that study also doping with Co was studied because this raises the transition temperature above room temperature and makes the material more suitable for technological applications. The conclusion – based on strong softening of the modes and changes of the mode frequencies in the case of Co doping – was that the phase transition is driven by electronic instability, similar to the CDW mechanism.

For our study the family member with $x = 19.5$ at% was chosen. From the data in reference [3] at this composition the transition temperature was expected above 340 K but we observed a lower transition temperature (close to room temperature) due to depletion of the martensite phase in thin films.

Our experiment with Ultrafast Electron Diffraction (UED) is the first one to study this phase transition in non-equilibrium conditions. Whereas in the ultrafast spectroscopic study [5] phonons are excited and probed while the sample stays in one phase, we probe the structural properties of the sample while it undergoes the transition from the martensite to the austenite phase. This will give us directly the speed at which this phase transition occurs and insight into what exactly happens in the several instances of the phase transition.

4.2 Experimental procedure

The samples were prepared by Niclas Teichert at the University of Bielefeld, Germany [6]. The Ni-Mn-Ga films were deposited by magnetron co-sputtering from a Ni$_{55}$Mn$_{19}$Ga$_{26}$ alloy target and elemental Ni and Mn targets. The films were grown on single crystalline MgO(001) substrates. Before the deposition of the 60 nm thick Ni-Mn-Ga layer a 30 nm thick V layer was deposited. The substrate temperature during deposition was 500 °C. The sputtering pressure was set to $2.3 \times 10^{-3}$ mbar and the deposition rate was 0.22 nm/s.

X-ray diffraction measurements confirmed that the V layer and the Ni-Mn-Ga layer grow epitaxially in the (001) direction on the MgO substrate with the in-plane relation MgO(110) // V(100) // Ni-Mn-Ga(100). The film thickness and composition were checked by X-ray reflectivity measurements and X-ray fluorescence measurements, respectively.
In order to obtain freestanding films, the V layer was removed by selective wet etching with Cr ETCH No.1 by Microchemicals and the obtained freestanding Ni-Mn-Ga films were carefully placed on 400 mesh copper grids.

The Ni-Mn-Ga film on the Cu grid was mounted in the UED system, as described in Chapter 2 of this thesis. A metal disk with an aperture of diameter 200 μm was mounted on top of the sample to reduce the probed sample volume and to improve the diffraction pattern by reducing the electron beam size.

The UED pump-probe experiment was carried out in transmission geometry. The pump beam (λ=780 nm, τ=50 fs, F=10±2 mJ/cm², FWHM = 400 µm, P=s-polarized) was aligned to pass through the sample by direct observation of the transmitted light on the wall of the UHV chamber.

4.3 Results
A typical diffraction pattern is shown in Figure 4.3, large image. To calculate the relative intensity changes of the diffraction spots in a correct manner, the background intensity of the laser light and dark current on the CCD detector were subtracted. Subsequently, the central beam was subtracted because otherwise it adds background to the intensity of the diffraction spots. The procedure for this background subtraction is discussed in Section 2.7.3 of this thesis.

The qualitative results of the laser light are most clearly seen in the insets of Figure 4.3. In the left inset, the region of a Bragg spot is shown when the laser is off. The satellites due to the modulation in the martensite phase are clearly visible. In the right inset, the same region is shown at a time after time zero with the laser on, and the satellites are clearly gone, indicating that the martensite phase is destroyed and only the Bragg spots of the cubic lattice are remaining.

For the intensity changes of the satellites that are the signature of the martensite phase, also the background from the main Bragg spots was subtracted. This procedure is discussed in more detail in Section 2.7.4 of this thesis. The results of the analysed data for selected diffraction peaks are shown in Figure 4.4. In the upper panel, the average of the relative intensity differences for the first four Bragg spots ((01), (10), (0-1) and (-10)) is presented. In the lower panel, the average of the relative intensity differences is shown for three selected satellite
peaks, which are a signature of the martensite phase. The differences are plotted as a function of delay time between the pump and the probe.

The intensity of the satellite peaks drops about 70% in the first 15 ps after time zero. This corresponds to a significant yet not complete destruction of the martensite phase in favour of the austenite phase. At the same time, the intensity of the main Bragg spots of the cubic lattice goes up by 3%, mirroring a stronger cubic symmetry in the austenite phase than in the martensite phase.

After the first drop/rise, an intensity oscillation is seen to occur for both the main Bragg spots and the satellites. These oscillations of the Bragg spot intensities are...
in antiphase with those of the satellites and have a period of 28 ps (corresponding to a frequency of 36 GHz).

In Figure 4.5 the times traces for the second order Bragg spots ((11), (1-1), (-11), (-1-1)) are shown. The first rise of the diffraction is similar to the one of the first order Bragg spots. The timing, the time duration and the size of the change are all
similar to the case of the first order Bragg spots. However, in contrast to the latter, after reaching the first maximum, the intensity of the second order Bragg spots drops and starts oscillating around a new value of about half the difference reached at the first maximum.

4.4 Discussion

The initial large drop of the intensity of the satellite peaks corresponds to what is expected: a destruction of the martensite phase due to local heating of the sample above the transition temperature. The speed at which the satellite intensity drops, however, is faster than ever observed or predicted in Heusler alloy research. It is also remarkable that the phase transition happened more than $10^8$ times in the course of this experiment, and the pumped sample area is still not destroyed. This very robust property shows the usefulness of the material for possible applications.

The drop in satellite intensity coincides with a rise in the intensity of the main Bragg spots because the cubic symmetry of the lattice becomes stronger. This trend is present for all Bragg spots and for all satellites.
Thereafter, an unexpected behaviour is observed: both the first order Bragg spots and the satellites start oscillating at a very low frequency: 30 GHz, when a normal frequency for phonons would be in the THz frequency regime, as also shown in the ultrafast spectroscopy study [5]. Another reason why these oscillation are not likely the signature of energy transfer from hot electrons to strongly coupled phonons, is that such a process would take place on a faster time scale (a few 10-100 fs) while here the onset of the oscillating intensity is delayed until after the first clear rise/drop (a few ps). Therefore we interpret this oscillation rather as the result of a “restoring” force towards the martensite phase. As discussed before and shown in Figure 4.1, the martensite phase can be interpreted as a periodic shuffling of (011) planes along the [0-11] direction [4] with respect to the austenite phase. We interpret the oscillations as the effect of the atoms moving around the new equilibrium position (namely their position in the austenite, cubic lattice).

The reason why the second order peaks fall back after the first rise is much more complicated. We speculate that it has to do with the other symmetry and therefore they react differently on the coherent oscillation of the atoms around their new equilibrium position than the first order peaks.

The last aspect of the response of the diffraction to the light excitation that needs to be discussed is the observed absence of the Debye Waller effect. To a certain extent, this study is comparable to the study of CDW dynamics by Erasmus et al. [7], the main results of which are shown in Figure 4.6. As seen in the inset of the upper panel, the main Bragg spots first increase in intensity due to the transition to the higher symmetry phase (suppplanation of the periodic lattice displacement, PLD supp.) but shortly afterwards this intensity rise is more or less cancelled by the larger disorder in the system caused by the anharmonic decay of excited electrons (the Debye Waller effect, DW). Qualitatively it seems that the same behaviour is present in our second order Bragg spots but the time scale of the process is crucial and the drop in our diffraction takes place on a much longer time scale than in their case. Therefore it cannot be the same effect.
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4.5 Conclusion

We presented a first Ultrafast Electron Diffraction study of the martensite-to-austenite phase transition in a member of the family of Ni-Mn-Ga Heusler alloys. Whereas other studies so far investigated the material in equilibrium conditions in the martensite or austenite phase, we followed the structural properties of the material during the phase transition.

The expected rise and drop of the diffraction peaks that are a signature of the two phases respectively, take place in about 10 ps; a time scale that is faster than ever observed or predicted in Heusler alloy research. After this initial change, oscillations are observed which indicate that there is a strong force opposing the transition from the martensite towards the austenite phase.

We shed new light on the transition dynamics from the martensite to the austenite phase. Further research into the nature of the restoring forces would give more insight in the physics of the phase transition.

Figure 4.6: Results of the UED experiment on 4Hb-TaSe$_2$ from the study of Erasmus et al. [7]. In the upper panel the intensity of the Bragg peaks is shown as a function of delay time; in the lower panel the corresponding CDW peak intensity is shown. Image taken from [7].
References
