Investigation of the crystallographic and magnetic properties of \(Mn_{1+x}Ni_{2-x}Ga\) ferromagnetic shape memory alloys

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Investigation of the Crystallographic and Magnetic Properties of Mn$_{1+x}$Ni$_{2-x}$Ga

Ferromagnetic Shape Memory Alloys

by

Kristin Neumann

A Doctoral Thesis

Submitted in partial fulfillment of the requirements for the award of Doctor of Philosophy of Loughborough University

June, 2012

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Abstract

This thesis work addresses the characterisation of structural and magnetic properties of Ni$_2$MnGa based Heusler alloys. The alloy series Mn$_{1+x}$Ni$_{2-x}$Ga has been investigated experimentally by magnetization measurements, X-ray and neutron scattering. The systematics is established as a function of Mn content of the magnetic and structural properties. Of particular interest is the development of the martensitic phase as a function of Mn content, its hysteresis behaviour and the influence of chemical order as established by a suitable heat treatment. A comprehensive experimental characterisation is given of the alloys series Mn$_{1+x}$Ni$_{2-x}$Ga for 0 ≤ x ≤ 1.

The experimental investigation is complemented by modelling of domains in pure Ni$_2$MnGa. Based on a detailed experimental determination of transformation matrices for the austenite – martensite transformation a characterisation is given of domain walls and their crystallographic orientation. The descriptions and models which exist in the literature are extended to enable the modelling of individual domain walls within a single crystal of Ni$_2$MnGa and its extension to several domain walls. The framework for this modelling is extended to enable the description of domain wall networks. Particular domain wall network configurations are identified and described.

Within the topic of shape memory materials in general, and of the ferromagnetic shape memory Ni$_2$MnGa based alloys in particular, this thesis work offers insight into some important aspects of their physical properties. A range of approaches is used to address some of the characterisation issues for these compounds.
The LORD is the everlasting GOD
   the creator of the ends of the earth.
He will not grow tired or weary,
   and his understanding no one can fathom.
He gives strength to the weary
   and increases the power of the weak.
Even youths grow tired and weary,
   and young men stumble and fall;
but those who hope in the LORD
   will renew their strength.
They will soar on wings like eagles;
   they will run and not grow weary,
they will walk and not be faint.

Isaiah 40, 28-31
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1 Introduction

Shape memory alloys have the ability to remember their shape and to return to that shape after having undergone a substantial deformation.

The key to that behaviour is a martensitic phase transformation. This is a diffusionless transition of first order, and it is also fully reversible. The crystallographic unit cell undergoes large distortions amounting to huge changes of the lattice parameters of up to several percent. In the martensitic phase distortions of \( \frac{c-a}{a} = 21.3\% \) for Mn\(_2\)NiGa [Liu05], of 6\% for Ni\(_2\)MnGa [Brown02] and 18.2\% for Ni\(_{2.17}\)Mn\(_{0.83}\)Ga [Fröhlich04] have been reported. This relates to lattice parameters changes of up to 13.5\% for Mn\(_2\)NiGa, 4.6\% for Ni\(_2\)MnGa and almost 12\% for Ni\(_{2.17}\)Mn\(_{0.83}\)Ga.

Above the martensitic transition temperature the shape memory alloy is in the highly symmetric austenitic phase which for many alloys is the L\(_2\)\(_1\) Heusler structure. It is the shape of the high temperature phase that the alloy will be able to remember. Later it will return to this shape if the deformation has been imposed on the material in the low temperature martensitic phase.

On cooling the martensitic transition takes place between the martensitic start temperature \( M_s \) and the martensitic finish temperature \( M_F \). Below \( M_F \) the alloy is fully transformed into a structure of lower symmetry. In the martensite there are a number of different crystallographic domains (variants) present which enable the alloy to self-accommodate stresses within the structure, because great length changes take place on an atomic level during the transformation. However, the macroscopic shape and the volume of the alloy (also the volume of the unit cell) do not change. It is in the martensitic phase that the alloy may be macroscopically deformed. The variants and the interfaces between variants are
highly mobile and rearrange themselves easily according to the imposed conditions, such as external stresses. This rearrangement of domains and the ease of transformation between different domains ensures that the alloy does not break or degrade in quality. Thus even a single crystal can undergo repeated transformations and deformations without a reduction in sample quality or the sharpness of Bragg reflections in neutron scattering experiments. In fact, the shape memory material in its martensitic state is quite soft and easily deformed. On reheating the reverse transformation from martensite to austenite takes place between the reverse transformation start temperature $A_S$ and the reverse transformation finish temperature $A_F$. At temperatures above $A_F$ the alloy has fully resumed the atomic structure of the austenite phase and completely recovered any strains. Thus it has regained the former macroscopic shape [Otsuka98], [Brown04].

The discovery of the shape memory effect can be traced back to 1932 when A. Ölander [Ölander32] found a rubber-like behaviour in an AuCd alloy. In 1963 the shape memory effect was discovered in NiTi by W. Buehler et al. [Buehler63]. More shape memory alloys have been discovered and a great number of applications have been identified for these materials, especially in the field of medicine and dentistry (e.g. dental arch wire, dental implants, stents, bone plates and joint replacements and artificial organs) and in engineering (e.g. morphine wings and antennae) [Otsuka98], [Humbeeck99], [Morgan04], [Chau06] and [Huang10].

However, ferromagnetic shape memory alloys such as the Ni$_2$MnGa Heusler alloy have an even greater potential for applications due to the possibility to control the shape memory effect through the application of an external magnetic field. This is much faster than a thermally induced transition [Brown07]. Ni$_2$MnGa was
discovered as a shape memory alloy by Webster et al. in 1984 [Webster84]. Since then many investigations were conducted on its atomic and magnetic structure [Webster84], [Brown02], the identification of the driving mechanism of the martensitic transformation [Brown99], [Brown04], [Blum11] and the optimization of its ferromagnetic shape memory properties such as the transition temperature, strain response and ductility for better applicability [Matsumoto99], [Matsumoto02], [Kreissl03], [Fröhlich05].

Recently, the new ferromagnetic shape memory compound Mn₂NiGa was discovered [Liu05]. Several publications appeared addressing its characterization, its structure and magnetic properties [Liu05], [Liu06], [Barman07], [Zhang08] and [Brown10].

1.a **Illustration of the shape memory effect**

Figure 1.1 illustrates how the shape memory effect is being used in satellite based telecommunication. Here shape memory Ni-Ti wires have been formed into an antenna. The shape training is done at high temperatures in the austenite phase (see sections a) and b) in figure 1.1). For the transport into space it is desirable that the antenna is packed into a small volume (see section c) in figure 1.1). This is achieved in the low temperature martensitic phase by simple compression. In outer space the unfolding is initiated by heating. Once the temperature of the antenna has reached the reverse transformation temperature as shown in sections d) to f) of figure 1.1 the shape memory effect ensures that the material adopts the trained form, i.e. an antenna. External motors are not required for the unfolding. Figure 1.1 has been taken from [Otsuka98].
Figure 1.1: Illustration of the behaviour of a shape memory alloy in a practical application. Here the use of a shape memory alloy is being considered as an antenna for a satellite. It has the particular advantage of allowing transport in a compact form and then, in outer space, it enables a form change without the need for motors. [Otsuka98].

1.b Explaining the shape memory effect

The symmetry of the high temperature austenite phase (also called parent phase) of a shape memory alloy is cubic. In the case of Ni$_2$MnGa it is the highly...
symmetric Heusler structure as shown in figure 1.2. It is also known as the L2₁ structure. Upon transformation the cubic structure deforms into a structure of lower symmetry. The structure of the martensite is related to the structure of the austenite by a volume preserving symmetry transformation. In fact, the symmetry group of the martensite is a subgroup of the austenite’s symmetry group. This separates a shape memory alloy from other compounds like iron which also exhibit martensitic transformations [Bhattacharya03].

Many different variants can form from the same parent phase. They are also called martensitic domains. However, all these variants have the same crystallographic structure because they are produced by the same symmetry transformation.

Figure 1.2: The L2₁ Heusler structure of Ni₃MnGa is presented. The space group is \( \text{Fm\hspace{1pt}3m} \). Atoms are located at the following lattice sites: Mn, depicted in large grey circles, at \((0, \, 0, \, 0)\); Ga, depicted in large open circles, at \((\frac{1}{2}, \, \frac{1}{2}, \, \frac{1}{2})\); and Ni, depicted in small black circles, occupies the lattice sites at \((\frac{1}{4}, \, \frac{3}{4}, \, \frac{3}{4})\). The body centred tetragonal (bct) cell which can be described by space group \( \text{I4/mmm} \) is indicated by the broken lines.
Figure 1.2 shows the face centred cubic (fcc) unit cell of the Heusler structure. Its symmetry is fully described by space group $Fm\bar{3}m$. It also shows the related bct unit cell as indicated by the broken lines which is described by space group $I4/mmm$. The latter is a subgroup of the former with tetragonal symmetry. It serves as a starting point for investigations into the low temperature structure for $\text{Ni}_2\text{MnGa}$ and related off-stoichiometric compounds [Brown02], [Fröhlich04].

Upon transformation the symmetry of the alloy is reduced and as a result many different martensitic structural domains (variants) appear. In a simplified manner the concept of variant building is shown in figure 1.3 using a two dimensional unit cell. Here, the unit cell of the cubic parent phase is depicted as a square. As the temperature is lowered below the martensitic transformation temperature $M$ the crystallographic structure changes assuming a related tetragonal symmetry. Accordingly, in figure 1.3b the unit cell of the martensite is depicted as a rectangle. The rectangular unit cell forms either due to shrinking at the top and bottom and simultaneous elongation at the sides of the square, or vice versa. Thus, there are two different variants present in the martensite as shown in figure 1.3b.

![Figure 1.3: Highly simplified illustration of variant building in martensite structure. a) shows the two dimensional ‘square’ unit cell of the parent phase. b) shows the low temperature ‘rectangular’ unit cell of the martensite. The ‘rectangular’ unit cell is formed by either elongating the ‘square’ unit cell to the left and right (dashed rectangle) or, alternatively, to the top and bottom (dotted rectangle). The illustration is taken from [Fröhlich04].](image-url)
For Ni$_2$MnGa a total of 36 different domains are possible, although usually not all of these are realised in an experiment using a single crystal [Brown04].

In the low temperature martensitic phase an applied force is able to change the crystallographic domain distribution. This yields a macroscopic change in shape. This shape change is permanent as long as the temperature of the alloy is kept below the reverse martensitic transition temperature A. However, if the temperature of the alloy is increased above A the martensitic transition is reversed. The alloy assumes its high temperature cubic structure which is independent of the orientation of the low temperature phase. Thus it ‘remembers’ the shape it had before and reverts back to its original form.

The material can undergo such changes repeatedly as the process does not involve the creation of dislocations. Rather it relies on the ease of transforming different crystallographic domains into one another in the low temperature martensitic phase. This process is illustrated in figure 1.4 [Neumann03], [Fröhlich04].

As explained above, when a shape memory alloy undergoes the phase transformation the crystallographic structure of the alloy changes and different martensitic variants form. This is shown in figure 1.4b. However, the volume of the unit cell does not change upon transformation, and no macroscopic shape change occurs. This is achieved by the forming of different variants which arrange themselves in such a way that the outer shape of the sample is not affected. This process is called self-accommodation. Figure 1.4b illustrates this process in a simplified manner. However, a typical microstructure appears on the surface of the martensite which may be observed under an optical microscope. This is a result of the self-accommodation of the martensite. Two examples of a microstructure are displayed in figure 1.5.
Figure 1.4: Illustration of one possible transformation mechanism for shape memory alloys. The high temperature phase is shown in a). Within the low temperature (martensitic) phase, as shown b), a force is applied which is able to change the crystallographic domain distribution. As the change of the unit cell axis can be large in a martensitic phase transition the redistribution of domains can yield a macroscopic change of shape, as in c). If the deformed material is warmed up again above the martensitic phase transition and the material reverts back to the square shape the length of the sample is changed back to its original form, see d). The illustration is taken from [Fröhlich04].

Figure 1.5: Optical micrographs of typical martensitic microstructure. On the left hand side a partly transformed Cu-Al-Ni shape memory alloy is shown. The white areas represent the parent phase of the alloy which has not yet transformed. The darker regions in the image show two different variants. A surface relief appears where they form. The picture on the right hand side shows a micrograph of a Ni-Al alloy. The images have been taken from [Murakami94] and [Otsuka98].
The white parts in the micrograph on the left hand side in figure 1.5 represent the parent phase which has not transformed yet. The darker spear-like regions are two different variants of the martensite which have twinned in such a way that the enormous length changes are accommodated as best as possible. The other micrograph on the right hand side in figure 1.5 shows the martensitic microstructure of a Ni-Al alloy.

Clearly visible are differently shaded areas which represent martensitic variants. A surface relief shows that martensitic variants are elevated from the surface in a wedge like manner. These wedges testify to the self-accommodation process of the martensite in order that the large length changes in unit cell parameters are mutually compensated and no macroscopic shape change occurs.

1.c Aim of this thesis

The work of this thesis is concerned with the investigation into the magnetic and structural properties of alloys in the series Mn$_{1+x}$Ni$_{2-x}$Ga with $0 < x \leq 1$. The experimental activity is centred on the structural and the magnetic characterisation of Mn$_{1+x}$Ni$_{2-x}$Ga. The experimental investigation is complemented by a more theoretical analysis which addresses the question of how different domains, i.e. variants, build up the martensite and how the variants fit together. This includes the question of self-accommodation i.e. the fitting together of variants which originate from different parts of the crystal and meet in the process of martensite growth. This thesis also aims to obtain information on how domain walls are oriented with respect to the crystallographic lattice and to one another. The investigation into the microstructure is based upon high resolution neutron scattering experiments on
a single crystal of Ni$_2$MnGa. These investigations have been carried out by Brown et al. [Brown04].

The thesis is organised as follows. First, a review is given of the present status of understanding and investigations as reflected in published works. This is presented in chapter 2. The sample preparation process is addressed in 2.b. Chapter 3 reports on the characterisation of various alloys by magnetization measurements using a SQUID magnetometer. Chapter 4 addresses the experimental investigation of the nuclear structure. Both neutron as well as X-ray scattering has been used to investigate the structure and magnetic order on an atomic level. Chapter 5 concentrates on the question of martensitic domain walls in Ni$_2$MnGa starting from the experimental observation of the transformation matrices of the austenite – martensite transformation. The conditions for the formation of domain walls are given, and the description is extended towards a picture of a domain wall network. The thesis is concluded with a final discussion and an outlook of further work.
2 Framework

Chapter 2.a presents a literature review into the current research on Mn$_{1+x}$Ni$_{2-x}$Ga alloys as reflected in published works. Chapter 2.b comments on the preparation process of samples that were employed in the experimental investigations of this thesis.

2.a Literature review

Ni$_2$MnGa is a well known ferromagnetic shape memory alloy. When quenched from 800°C it undergoes a martensitic phase transition between 200 K and 196 K on cooling, and between 198 K and 202 K on heating. The parent phase exhibits the highly symmetric L2$_1$ Heusler structure which was described in paragraph 1.b. In particular, the cubic lattice parameters of Ni$_2$MnGa at 300 K and 400 K are $a_{300K}$ = (5.8229 ± 0.0002) Å and $a_{400K}$ = (5.8636 ± 0.0002) Å, respectively. The space group $Fm\bar{3}m$ fully describes the symmetry of the high temperature parent phase. The structure of the martensite is a related orthorhombic superstructure with the unit cell oriented along the broken lines as shown in figure 1.2, but with a seven-fold increase along one of the <110> directions and considerable change in the lattice parameters. At 20 K the volume of the unit cell has reduced by just under 0.7% with respect to the volume at 300 K. The symmetry of the martensitic phase is fully accounted for by space group $Pnmm$. The lattice parameters of the martensitic phase at 20 K are as follows: $a_{20K}$ = 29.3016 Å, $b_{20K}$ = 4.2152 Å and $c_{20K}$ = 5.5570 Å. These values can be related to the cubic unit cell. With $a_{20K}$ = $7 \cdot \frac{1}{\sqrt{2}} \tilde{a}_{20K}$, $b_{20K}$ = $\frac{1}{\sqrt{2}} \tilde{b}$ and $c = \tilde{c}$ the following equivalent cubic parameters are obtained: $\tilde{a}$ = 5.9198 Å, $\tilde{b}$ = 5.9612 Å.
and $\tilde{c} = 5.5570 \, \text{Å}$. These indicate a strain of 1.7%, 2.4% and -4.6% for each of the lattice parameters, respectively.

Between 260 K and 200 K the high temperature cubic phase is unstable and a pre-martensitic phase forms which is characterized by a 3-fold increase of the cubic unit cell along one of the $<110>$ directions. Thus the bct description of the unit cell, as indicated by the broken lines in figure 2.1.a, is the more appropriate approach to describing the symmetry of this phase. However, the lattice parameters remain largely unchanged with respect to the parent phase above 260 K. As for the martensitic phase, and due to the increase of the unit cell, space group $Pnma$ is able to adequately account for all peaks emerging in a neutron powder diffraction pattern at 220 K.

The relationship between the high and low temperature structures is illustrated in figure 2.1. This figure shows a (001) plane of the Heusler structure as realised in Ni$_2$MnGa. Mn (grey full circles) and Ga (empty white circles) atoms are shown. The fcc unit cell of the parent phase is indicated in a) by the broad solid line. A rotation of the fcc unit cell by $45^\circ$ and an adjustment of the lattice parameters $a$ and $b$ by a factor of $\frac{1}{\sqrt{2}}$ yields the bct unit cell as indicated by the broken lines in a). The unit cells of the orthorhombic superstructures of the martensitic and pre-martensitic phases are shown in b) and c). Neutron powder diffraction patterns of Ni$_2$MnGa at 400 K, 300 K, 220 K, and 20 K are shown in figure 2.2. The $c/a$ ratio for Ni$_2$MnGa is 0.95.
Figure 2.1: A (001) plane of Ni$_2$MnGa. It is shown: a) f.c.c (fat solid line) and related bct (broken line) unit cell, b) 7-fold increased unit cell of the martensite, c) 3-fold increased unit cell of the pre-martensitic phase.

Figure 2.2: Neutron diffraction pattern of Ni$_2$MnGa at 300 K (top left), 220 K (top right) and 20 K (bottom right). A superposition of the diffraction patterns at 400 K and 220 K is shown on an expanded scale (bottom left).
Ni$_2$MnGa orders ferromagnetically below $T_C \approx 375$ K. At 300 K the moment per Mn atom is 2.4 $\mu_B$. The magnetic moment of the ground state is 4.17 $\mu_B$ per Mn atom. The magnetic moment is confined to Mn atoms and oriented along the c-axis. [Webster84], [Brown02], [Neumann03], [Brown08]

Mn$_2$NiGa is reported to exhibit the shape memory effect with a martensitic transition temperature of $\approx 275$ K and a large hysteresis of 50 K which renders the alloy less useful for applications. Investigations on its structure by Liu et al. suggest a cubic structure with lattice parameter 5.9072 Å at 300 K and a tetragonal structure with lattice parameters 5.5 Å and 6.7 Å [Liu05], [Liu06]. On cooling through the martensitic transition the a-parameter shrinks whilst the c-parameter elongates with an $c/a$ ratio of 1.2 [Liu05].

Liu et al. propose a site occupation as given in table 2.1 and illustrated in figure 2.3 [Liu06]. Figure 2.3 also shows the site occupation in Ni$_2$MnGa as a reference.

Figure 2.3: Atomic structure of Ni$_2$MnGa (left), and of Mn$_2$NiGa (right) as suggested by [Liu06].
<table>
<thead>
<tr>
<th>$\overline{Fm\bar{3}m}$</th>
<th>(000) 4a</th>
<th>($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) 4b</th>
<th>($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) 8c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$NiGa</td>
<td>Mn</td>
<td>Ni</td>
<td>½ Mn, ½ Ga</td>
</tr>
</tbody>
</table>

Table 2.1: Site occupation of Mn$_2$NiGa of the cubic phase as proposed by [Liu06].

However, whilst it is plausible that the surplus Mn atoms occupy depleted Ni positions, it is less plausible that Ga atoms should swap their positions with the remaining Ni atoms as proposed by [Liu06]. In [Brown10] a neutron scattering experiment was undertaken in order to determine the atomic structure of Mn$_2$NiGa. Neutron scattering is a well suited tool for the determination of the atomic positions in Mn$_2$NiGa because the nuclear coherent scattering amplitudes of Ni (10.3 fm), Mn (−3.73 fm) and Ga (7.23 fm) are very different. This study has shown that Mn and Ni atoms are randomly distributed over the ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) site in the L2$_1$ Heusler structure. Thus, surplus Mn atoms indeed take up depleted Ni positions. However, the remaining Ni atoms do not swap their position with Ga atoms. Rather, the positions (000) and ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) remain occupied by Mn and Ga atoms, respectively, as is the case also in Ni$_2$MnGa.

With a $T_C = 588$ K the Curie temperature of Mn$_2$NiGa is high [Liu05]. Ferrimagnetic ordering has been suggested for the austenitic phase with antiparallel, unbalanced moments on Mn atoms on different crystallographic sites. For the martensitic phase ferromagnetism is suggested. Barman et al. refute the results of Liu et al. and argue that Mn$_2$NiGa is ferrimagnetic in both, the austenitic and martensitic phases [Barman07], [Barman08].

Findings by Liu et al. are largely consistent with a study published by Blum et al. who obtained a Curie temperature of 600 K for Mn$_2$NiGa, and a slightly higher martensitic transformation temperature around 320 K with a smaller hysteresis of about 25 K [Blum11].
For shape memory alloys related to Ni$_2$MnGa the stoichiometry and the atomic order of the sample is of high importance for the martensitic transition temperatures. Matsumoto et al. investigated the influence of the stoichiometry on the transition temperatures for Ni-rich compounds of the Ni$_{2+x}$Mn$_{1-x}$Ga [Matsumoto99]. They found that with increasing Ni content the martensitic transition temperatures monotonically increase, whilst the Curie temperatures monotonically decrease.

![Transformation temperatures versus Ni content in Mn$_{1-x}$Ni$_{2+x}$Ga](image)

**Figure 2.4:** Transformation temperatures versus Ni content in Mn$_{1-x}$Ni$_{2+x}$Ga [Matsumoto99].

They mapped the transition temperatures for compounds between Ni$_2$MnGa and Ni$_{2.19}$Mn$_{0.81}$Ga and found that the martensitic and magnetic transition temperatures merge for $x = 0.17$. Figure 2.4 shows the dependence of the transition temperatures as a function of Ni content as published by [Matsumoto99].

The variation of transition temperature and magnetization curves was also investigated for off-stoichiometric alloys Mn$_{1+x}$Ni$_{2-x}$Ga with Mn excess [Liu05].
Liu et al. found that the Curie temperature of $\text{Mn}_{1+x}\text{Ni}_{1-x}\text{Ga}$ increases linearly with rising Mn content $x$. This is in agreement with the results by [Matsumoto99]. However, the martensitic transition temperature is reported to vary quadratically with the lowest value of under 50 K obtained for $\text{Mn}_{1.5}\text{Ni}_{1.5}\text{Ga}$.

The temperatures at which shape memory compounds are annealed influence the transition temperatures. $\text{Ni}_2\text{MnGa}$ melts at $1109^\circ\text{C}$ and it undergoes a phase transition from the cubic B2 to the highly symmetric Heusler $\text{L}_2_1$ structure at $798^\circ\text{C}$ [Overholser99]. Samples annealed at and quenched from temperatures above and below that critical value differ substantially in the transition temperatures [Kreissl03]. The martensitic phase transition temperature is reduced from ~200 K for samples annealed at $800^\circ\text{C}$ to 101 K for samples quenched from $1000^\circ\text{C}$. [Zhang08] reported for Ga deficient alloys $\text{Mn}_{2+x}\text{NiGa}_{1-x}$ that annealing at $850^\circ\text{C}$ for 24 h is required for a single martensitic phase to form.

The transformation process and its driving forces have also been intensively studied by Brown et al. A band Jahn-Teller effect with a redistribution of electrons associated with a high density of states at the Fermi level has been established as the driving force behind the martensitic transformation [Brown99] and [Brown08].

2.b Sample Preparation

Metals of at least 3N purity (99.9%) have been used for the preparation of the alloys. The constituent metals were weighed using a high precision electronic balance with an accuracy of at least ± 0.0001 g. Manganese was cleaned from oxidisations by washing it in diluted nitric acid. Afterwards it was melted in an
argon arc furnace in order to reduce the surface area and hence minimise future contamination. Subsequently, the constituent materials were melted under a reduced argon atmosphere in an argon arc furnace. During the melting process the samples experienced some weight loss. Its magnitude depends on various factors, many of which are difficult to determine or predict. However, the way in which the ingredients are melted together does significantly influence the weight loss. This includes the arrangement of constituents in the crucible, the employed power, but also the order in which the alloys were molten, and the duration of the melting process.

Due to a low vapour pressure, molten manganese evaporates quickly. The rising of blue vapour is an indicator for evaporation which can be minimised to a large extent if the manganese is enclosed by nickel as soon as the manganese is molten. This is possible because the melting point of nickel (~1726 K) is higher than the melting point of manganese (~1517 K) [Gerthsen04].

In order to achieve good and homogenous samples the ingot was molten at least four times and turned over in between melts.

After melting, the ingots were powdered using a mortar and hardened steel pestle and sifted through a mesh with a hole size of 250 μm. Some powder samples were annealed for 3 days at T = 800°C or 900°C (after having been enclosed in a sealed quartz ampoule under a reduced argon atmosphere) followed by a quench in cold water.
3 Report on the investigation into magnetic properties of $\text{Mn}_{1+x}\text{Ni}_{2-x}\text{Ga}$ alloys

The investigation into the magnetic properties of alloys is presented with the composition $\text{Mn}_{1+x}\text{Ni}_{2-x}\text{Ga}$, with $x$ assuming values between 0 and 1. Magnetization data have been obtained using a SQUID magnetometer (Quantum Design) at temperatures between 5 K and 350 K. A list of the used samples and some of their characteristics is given in table 3.1.

For some compositions different samples have been employed. In this case they are distinguished by the extension (A), (B) or (C). Samples of the same composition originate from the same ingot and differ by heat treatment and mass only.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Heat treatment</th>
<th>weight loss [%]</th>
<th>Mass [mg]</th>
<th>Molar Weight [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}<em>{1.05}\text{Ni}</em>{1.95}\text{Ga}$ (A)</td>
<td>untreated</td>
<td>1.3</td>
<td>1.22</td>
<td>241.859</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.05}\text{Ni}</em>{1.95}\text{Ga}$ (B)*</td>
<td>untreated</td>
<td>0.7</td>
<td>2.3</td>
<td>241.672</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.1}\text{Ni}</em>{1.9}\text{Ga}$</td>
<td>untreated</td>
<td>0.8</td>
<td>1.45</td>
<td>241.296</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.15}\text{Ni}</em>{1.85}\text{Ga}$ (A)</td>
<td>3d at 800°C</td>
<td>1.5</td>
<td>1.85</td>
<td>240.170</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.15}\text{Ni}</em>{1.85}\text{Ga}$ (B)</td>
<td>3d at 800°C</td>
<td>0.7</td>
<td>2.43</td>
<td>240.545</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.15}\text{Ni}</em>{1.85}\text{Ga}$ (C)</td>
<td>untreated</td>
<td>0.3</td>
<td>2.93</td>
<td>241.484</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.2}\text{Ni}</em>{1.8}\text{Ga}$</td>
<td>untreated</td>
<td>0.3</td>
<td>3.92</td>
<td>239.794</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.2}\text{Ni}</em>{1.8}\text{Ga}$ (B)</td>
<td>3d at 800°C</td>
<td>0.8</td>
<td>2.4</td>
<td>238.292</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.8}\text{Ni}</em>{1.2}\text{Ga}$ (A)</td>
<td>3d at 900°C</td>
<td>0.9</td>
<td>2.5</td>
<td>239.043</td>
</tr>
<tr>
<td>$\text{Mn}<em>{1.8}\text{Ni}</em>{1.2}\text{Ga}$ (B)</td>
<td>untreated</td>
<td>0.3</td>
<td>4.24</td>
<td>238.292</td>
</tr>
</tbody>
</table>

Table 3.1: Specification of samples used in magnetization measurements. (*) Measurements on sample (B) were obtained one year after measurements on sample (A).
The investigation is based on measurements of the magnetization as a function of both temperature and applied magnetic field. Scans of the thermal variation of the magnetization were conducted with small external magnetic fields. Martensitic transitions of first order usually manifest themselves in temperature scans at low applied fields as a sudden change in magnetization.

The field dependency was measured for isotherms at several temperatures. Arrott plots ($M^2$ versus $B/M$) were determined. According to [Arrott54] the intersection of the linear high field sections of the Arrott plots with the $M^2$-axis yields a value for the spontaneous magnetization $M_0$ which is defined at zero applied magnetic field. Thus, the high field sections of the Arrott plots were fitted by a straight line. The coefficients of the linear equations used in the linear fits at each temperature are listed in appendix A. The thermal variation of the spontaneous magnetization allows the Curie temperature $T_C$ to be estimated [Ziebeck01]. The spontaneous magnetization $M_0$ of the ground state (at $T = 0$ K) is determined by plotting the spontaneous magnetization versus $T^{3/2}$ and fitting low temperature data as a straight line. This procedure is in accordance with the model of spin waves [Kittel64], [Crangle91] which predicts that the spontaneous magnetization of a ferromagnet varies linearly as a function of $T^{3/2}$ at low temperatures.

In the sections below, the various alloys have been analysed as sketched above. If applicable, the martensitic and magnetic transition temperatures, as well as the ground state magnetic moment, were obtained. Results of the analysis for each compound are given in tabular form following to the presentation of the experimental data. A summary for all compounds is given in appendix B.
3.a  \( \text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga} \)

The magnetization of \( \text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga} \), sample (A), as a function of temperature in an applied magnetic field of 0.1 T is shown in figure 3.1 for first heating and then cooling. Prior to the measurements, the sample was cooled down to 5 K in zero applied magnetic field.

![Graph](image)

**Figure 3.1**: Thermal variation of the magnetization of \( \text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga} \), sample (A), using an applied magnetic field of 0.1 T.

When heating from low temperatures the magnetization remains constant until \( \sim 250 \) K whereupon it starts to fall. At 300 K it drops quickly towards zero, indicating the approach of the ferromagnetic to paramagnetic transition. At 350 K the magnetization reaches its lowest value. Thereafter the sample was cooled down again. Initially, the magnetization rises and follows the same curve as the heating data until about 300 K. On further cooling the magnetization assumes higher readings. The magnetization levels off at about 250 K and remains approximately constant at lower temperatures. A first order martensitic phase transition is not evident in the thermal variation of the magnetization.
The field dependence of the magnetization $M$ and Arrott plots for various temperatures between 350 K and 5 K are shown in figure 3.2.

**Figure 3.2:** Magnetization against applied magnetic field (left) and Arrott plots (right) for $\text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga}$, sample (A). Isotherms, presented between 5 K and 350 K, were obtained whilst cooling. Linear fits to the high field sections of the Arrott plots are indicated. Fit coefficients are listed in appendix A.

**Figure 3.3:** Spontaneous magnetization of $\text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga}$, sample (A) is shown as a function of $T$ (left) and $T^{3/2}$ (right). A linear fit for temperatures up to 100 K is indicated. The equation used in the fit is given. Units of $M$ and $T$ are as on the axes.
The spontaneous magnetization of $\text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga}$ which is plotted as a function of temperature in figure 3.3 (left) has the form expected for a ferromagnet. Error bars are not shown due to their small size. The right hand side of figure 3.3 shows a plot of the spontaneous magnetization as a function of $T^{3/2}$. A linear fit for temperatures up to 100 K is included. It achieves an $R^2$-value of 0.99 which shows that the model of spin waves gives a good description of the deviation from the ground state at low temperatures. The ground state magnetization $M_0$ of $\text{Mn}_{1.05}\text{Ni}_{1.95}\text{Ga}$ is obtained as $M_0 = (70.90 \pm 0.06)$ J/kg/T. This corresponds to $m = (2.92 \pm 0.01) \mu_B$ as the magnetic moment $m$ of the ground state per Mn atom.

The magnetic moment $m$ of the ground state per manganese atom is determined using $m = \frac{M_0 \cdot m_w}{1000 \cdot N_A \cdot \mu_B \cdot C_{Mn}}$, where $M_0$ is the spontaneous magnetization at $T = 0$ K in units of [J/kg/T], $m_w$ is the molar weight of the sample in units of [g/mol], $N_A = 6.022 \times 10^{23}$ is the number of formula units (f.u.) per mole, $\mu_B = 9.27 \times 10^{-24}$ is the Bohr magneton in units of [J/T] and $C_{Mn}$ is the content of Mn per formula unit.

The spin $S_z$ can be obtained using the relationship $m = g \cdot S_z$ and taking the Landé-factor $g = 2$. It follows that $S_z = 1.46$. The effective magnetization, as defined by $p_{eff}^2 = 4S(S+1)$, is calculated to be $p_{eff} = 3.79 \mu_B$. These results are summarized in table 3.2.

Five isotherms between 250 K and 350 K were obtained using sample (B), a year after the measurements on sample (A). The measurements on sample (B) and the respective Arrott plots are shown in figure 3.4. The spontaneous magnetization is shown in figure 3.5 for both, sample (B) and sample (A). The inset of figure 3.5 shows a plot of the square of the spontaneous magnetization.
versus temperature. A linear fit for temperatures between 250 K and 350 K is included for the determination of the Curie temperature. It yields $T_C = (356 \pm 4) K$ for Mn$_{1.05}$Ni$_{1.95}$Ga.

Figure 3.4: Magnetization against applied magnetic field (left) and Arrott plots (right) for Mn$_{1.05}$Ni$_{1.95}$Ga, sample (B). Isotherms between 250 K and 350 K were obtained whilst heating. Linear fits to the high field sections of the Arrott plots are indicated. Coefficients of the equations used in the linear fits are listed in appendix A.

Figure 3.5: Thermal variation of the spontaneous magnetization for Mn$_{1.05}$Ni$_{1.95}$Ga. Measurements of samples (A) (black diamonds) and (B) (red circles) are shown. The inset shows a linear fit of the data of sample (B) with $M^2$ as the ordinate. The linear equation used in the fit is given in the figure. $M$ and $T$ are measured in the same units as given on the axes.
<table>
<thead>
<tr>
<th>Sample Mn&lt;sub&gt;1+x&lt;/sub&gt;Ni&lt;sub&gt;2-x&lt;/sub&gt;Ga</th>
<th>M&lt;sub&gt;0&lt;/sub&gt; [J/kg/T]</th>
<th>m [μA]</th>
<th>S&lt;sub&gt;z&lt;/sub&gt;</th>
<th>p&lt;sub&gt;eff&lt;/sub&gt; [μA]</th>
<th>T&lt;sub&gt;C&lt;/sub&gt; [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.05 (A)</td>
<td>70.90 ± 0.06</td>
<td>2.92 ± 0.01</td>
<td>1.46</td>
<td>3.79</td>
<td>356 ± 4</td>
</tr>
</tbody>
</table>

Table 3.2: Spontaneous magnetization and magnetic moment of Mn<sub>1.05</sub>Ni<sub>1.95</sub>Ga at T = 0 K per Mn-atom, spin and effective magnetization per Mn-atom are summarized. The g value is taken to be g = 2. T<sub>C</sub> is also given.

**3.b Mn<sub>1.1</sub>Ni<sub>1.9</sub>Ga**

The thermal variation of the magnetization of Mn<sub>1.1</sub>Ni<sub>1.9</sub>Ga in fields of 0.1 T and 1 T is shown in figure 3.6. At low temperatures, the magnetization is independent of temperature for both fields, 0.1 T and 1 T. A sudden rise as normally associated with a martensitic phase transition in shape memory alloys appears around 140 K. The size of the increase is small (~1%) when a field of 1 T is applied; however, it is large (~40%) for an applied field of 0.1. The transition region is broader when the smaller field is applied.

![Figure 3.6: Magnetization as a function of temperature for Mn<sub>1.1</sub>Ni<sub>1.9</sub>Ga in applied magnetic fields of 0.1 T and 1 T for first heating and then cooling.](image)
Figure 3.7 shows the detail around the transition for all scans. Linear regions around the anomaly have been identified (green triangles) and fitted. The equations obtained in the fitting process are given. The indices ‘low’, ‘middle’ and ‘high’ correspond to the respective temperature ranges. The martensitic transition temperatures have been determined and are listed in table 3.3.

\[
\begin{align*}
M_{\text{low}} &= (0.0020 \pm 0.0001) T + (9.311 \pm 0.005) \\
M_{\text{middle}} &= (0.137 \pm 0.001) T + (-7.8 \pm 0.1) \\
M_{\text{high}} &= (-0.0033 \pm 0.0012) T + (14.11 \pm 0.25)
\end{align*}
\]

Figure 3.7: The temperature dependence of the magnetization is displayed for Mn$_{1.1}$Ni$_{1.9}$Ga. A magnetic field of 0.1 T (1 T) is applied and is shown at the top (bottom) of the figure. On the left (right) hand side the heating (cooling) curves are shown. Linear regions have been identified (green triangles) and fitted. Fitting equations are displayed. $M_{\text{low}}$, $M_{\text{middle}}$ and $M_{\text{high}}$ denote linear fits for low, middle and high temperature ranges, respectively. Intersection points yield martensitic transition temperatures for start and finish of the martensitic transition.
Table 3.3: Start and finish temperatures of the martensitic transformation for Mn$_{1.1}$Ni$_{1.9}$Ga as obtained from linear fits in figure 3.7. $M_s$ ($A_s$) and $M_f$ ($A_f$) are the martensitic start and finish temperatures on cooling (heating), respectively. Hysteresis, as given in the 6th column, refers to the relative displacement of the interval centres $(M_s + M_f)/2$ and $(A_s + A_f)/2$.

Table 3.3 also shows that the size of the transition intervals depends on the external field. In particular, when the larger field is applied the transition region is much narrower, especially for the cooling measurement. However, the transition mean is not affected by the size of the external field. This is also illustrated by figure 3.8 which shows the temperature derivative of the heating curves for 0.1 T and 1 T applied fields.

Figure 3.8: Derivative of the heating scans as shown in figure 3.7 for Ni$_{1.1}$Mn$_{1.9}$Ga. Red squares (black dots) show the data with 0.1 T (1 T) applied field.

Figure 3.6 also shows a sharp drop at 340 K in the heating curve where a field of 0.1 T is applied. Between 340 K and 350 K the magnetization changes its magnitude by a factor of 2. At 350 K the temperature direction of the
measurement is reversed and the sample is cooled down again. On cooling, the magnetization stays constant until 315 K whereupon it suddenly rises and recovers the magnitude from before the drop. This process has a hysteresis of about 25 K.

Figure 3.9: Magnetization against applied magnetic field for Mn$_{1.1}$Ni$_{1.9}$Ga. On the left (right) isotherms are presented between 200 K and 350 K (5 K and 175 K).

Figure 3.10: Arrott plots for Mn$_{1.1}$Ni$_{1.9}$Ga. On the left (right) isotherms are presented between 200 K and 350 K (5 K and 175 K). Linear fits of the high field section are indicated. Fit coefficients are listed in appendix A.
The field dependence of the magnetization of Mn$_{1.1}$Ni$_{1.9}$Ga was measured for temperatures between 5 K and 350 K. Arrott plots were produced from these measurements and evaluated. Figures 3.9 to 3.12 show the measurements and deduced plots. The results of these measurements are summarized in table 3.4.

![Figure 3.11: Spontaneous magnetization of Mn$_{1.1}$Ni$_{1.9}$Ga as a function of temperature.](image)

![Figure 3.12: Spontaneous magnetization of Mn$_{1.1}$Ni$_{1.9}$Ga versus T$^{3/2}$ (left) and the square of the spontaneous magnetization versus T. Linear fits at low (up to 110 K) and high temperatures are shown. The equations used in the linear fit are included with units of M and T as given on the axes.](image)

<table>
<thead>
<tr>
<th>Sample Mn$<em>{1+x}$Ni$</em>{2-x}$Ga</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.1$</td>
<td>34.41 ± 0.26</td>
<td>1.35 ± 0.01</td>
<td>0.68</td>
<td>2.13</td>
<td>407 ± 9</td>
</tr>
</tbody>
</table>

Table 3.4: Spontaneous magnetization and magnetic moment per Mn-atom at $T = 0$ K in units of one Bohr magneton, spin and effective magnetization per Mn-atom are summarized. $g$ is taken to be $g = 2$. $T_C$ is also given.
3.c \( \text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga} \)

The thermal variation of the magnetization of \( \text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga} \), in an applied magnetic field of 0.1 T, is shown in figure 3.13 whilst cooling for all three samples. The signatures of a typical martensitic transition can be identified in the graphs of samples (B) and (C) which were annealed at 800°C and 900°C, respectively. A sudden rise in the magnetization appears between 50 K and 100 K for sample (B) and between 100 K and 200 K for sample (C). This shows that the martensitic transition temperature depends strongly on the annealing temperature. The graph of sample (A) hardly shows any variation in the magnetization. Thus, no martensitic transition is evident in the untreated sample.

![Figure 3.13: Thermal variation of the magnetization for \( \text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga} \) in a field of 0.1 T for samples of different heat treatment.](image)

In the following the field dependence and Arrott plots of \( \text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga} \), sample (B), are presented in figure 3.14. The spontaneous magnetization as a function of temperature is shown in figure 3.15. Plots and linear fits which facilitate the determination of the ground state magnetization \( M_0 \) and \( T_C \) are shown in figure 3.16. Accordingly, \( M_0 \) and \( T_C \) of \( \text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga} \), sample (B), are summarized in table 3.5.
Figure 3.14: Field dependence of the magnetization (left) and Arrott plots (right) of Mn$_{1.15}$Ni$_{1.85}$Ga, sample (B). Isotherms are presented for temperatures between 350 K and 5 K which were measured whilst cooling. Linear fits of the high field sections of Arrott plots are included. Fit coefficients of the equations used in the fits are listed in appendix A.

Figure 3.15: Spontaneous magnetization as a function of temperature for Mn$_{1.15}$Ni$_{1.85}$Ga, sample (B).

Figure 3.16: Spontaneous magnetization versus $T^{3/2}$ (left) and square of the spontaneous magnetization versus $T$ for Mn$_{1.15}$Ni$_{1.85}$Ga, sample (B). Linear fits at low (up to 100 K) and high temperatures are included. The equations used in the fits are given. Units of $M$ and $T$ are the same as the units on the axes.
Data of the field dependence of the magnetization are also presented for sample (A) (untreated) and sample (C) (annealed at 900°C). A plot of the spontaneous magnetization versus temperature is shown for all three samples in figure 3.17.

**Figure 3.17:** Spontaneous magnetization as a function of temperature for samples of Mn$_{1.15}$Ni$_{1.85}$Ga with different heat treatments.

**Figure 3.18:** Spontaneous magnetization versus $T^{3/2}$ (left) and square of the spontaneous magnetization versus $T$ for Mn$_{1.15}$Ni$_{1.85}$Ga, sample (A). Linear fits at low (up to 100 K) and high temperatures are included. The equations used in the fits are given. Units of $M$ and $T$ are the same as the units of the axes.
The annealing at either, 800°C or 900°C, has a marked effect on the spontaneous magnetization of the sample amounting to differences of ~30%. By contrast, there is no variation in the spontaneous magnetization obtained from the samples annealed at 800°C and 900°C.

Graphs of $M$ versus $T^{3/2}$, and $M^2$ versus $T$, respectively, for $\text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga}$, sample (A), are shown in figure 3.18. Linear fits at low and high temperatures are displayed. Values of the Curie temperature and the ground state magnetization are derived and listed in table 3.5. The Curie temperature also depends on whether or not the sample was heat treated by a margin which is slightly larger than the error bars.

<table>
<thead>
<tr>
<th>Sample $\text{Mn}<em>{1+x}\text{Ni}</em>{2-x}\text{Ga}$</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.15$ (A)</td>
<td>62.38 ± 0.08</td>
<td>2.35 ± 0.01</td>
<td>1.17</td>
<td>3.19</td>
<td>401 ± 4</td>
</tr>
<tr>
<td>$x = 0.15$ (B)</td>
<td>92.53 ± 0.20</td>
<td>3.48 ± 0.01</td>
<td>1.74</td>
<td>4.37</td>
<td>413 ± 2</td>
</tr>
</tbody>
</table>

Table 3.5: Spontaneous magnetization and magnetic moment per Mn atom of $\text{Mn}_{1.15}\text{Ni}_{1.85}\text{Ga}$ at $T = 0$ K, spin and effective magnetization per Mn-atom are summarized. $g$ is taken to be $g = 2$. Values for the untreated sample (A) and the annealed sample (B) are given. The Curie temperatures for both samples are also given.

3.d $\text{Mn}_{1.2}\text{Ni}_{1.8}\text{Ga}$

The thermal variation of the magnetization of $\text{Mn}_{1.2}\text{Ni}_{1.8}\text{Ga}$ in fields of 0.1 T and 1 T is shown in figure 3.19 for first heating and then cooling. A martensitic phase transition appears as a sudden rise around 100 K in all graphs. It is more pronounced when a smaller field is applied. Amplified plots around the anomaly are shown in figure 3.20 for each graph.
Figure 3.19: The thermal variation of the magnetization of Mn$_{1.2}$Ni$_{1.8}$Ga in fields of 0.1 T (circles) and 1 T (squares) for first heating and then cooling.

Figure 3.20: Amplified plots of the thermal variation of Mn$_{1.2}$Ni$_{1.8}$Ga at 0.1 T and 1 T. The top left (right) hand side shows the heating (cooling) curve with 0.1 T applied field. The bottom left (right) hand side shows the heating (cooling) curve with 1 T applied field. Points used for linear fitting are marked with green/red triangles. Equations used in the fits are listed in the diagrams. The indices ‘low’, ‘middle’ and ‘high’ indicate the temperature range of the respective fit.
Linear sections were fitted and intersections of the lines were determined. The intersections correspond to the martensitic transition temperatures which are listed in table 3.6. Similar to the anomaly, which was observed at high temperatures in the thermal variation of the magnetization in Mn$_{1.1}$Ni$_{1.9}$Ga, there is also a jump in the magnetization of this composition, when a magnetic field of 0.1 T is applied. It appears at 350 K where the magnetization reduces abruptly by a factor of 2. The reduction is not recovered on subsequent cooling.

The magnetization as a function of the applied magnetic field and Arrott plots are shown in figure 3.21 for isotherms between 5 K and 350 K. Linear fits of the saturated sections of the Arrott plots have been based on selected data points only such that a high R$^2$ value was achieved. The spontaneous magnetization is plotted in figures 3.22 and 3.24, and linear fits at low and high temperature ranges are included. The ground state magnetization and Curie temperature are determined and summarized in table 3.7.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>106.3 ± 0.3</td>
<td>49.1 ± 0.2</td>
<td>90.5 ± 0.2</td>
<td>123.9 ± 0.1</td>
<td>30</td>
</tr>
<tr>
<td>1</td>
<td>102.6 ± 0.9</td>
<td>49.1 ± 1.4</td>
<td>80.2 ± 1.0</td>
<td>120.0 ± 0.7</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 3.6: Martensitic transition temperatures of Mn$_{1.2}$Ni$_{1.8}$Ga as obtained from linear fits in figure 3.20. $M_S$ ($A_S$) and $M_F$ ($A_F$) are the martensitic start and finish temperatures on cooling (heating), respectively. Hysteresis, as given in the 6th column, refers to the relative displacement of the interval centres $(M_S + M_F)/2$ and $(A_S + A_F)/2$. 
Figure 3.21: Magnetization against applied magnetic field (top) and Arrott plots (bottom) for Mn$_{1.2}$Ni$_{1.8}$Ga. Isotherms, which were measured whilst heating, are presented between 5 K and 350 K. Diagrams on the right hand side show isotherms between 5 K and 150 K on an amplified scale. Coefficients of linear equations used in Arrott plot fits are listed in appendix A.

Figure 3.22: The spontaneous magnetization of Mn$_{1.2}$Ni$_{1.8}$Ga as a function of temperature.
Figure 3.23: Spontaneous magnetization $M$ of Mn$_{1.2}$Ni$_{1.8}$Ga. On the left (right) a plot of $M$ versus $T^{3/2}$ ($M^2$ versus $T$) is shown. Linear fits at low (up 100 K) and high temperatures and the respective equations used in the fits are included. $M$ and $T$ are measured in the same units as given on the axes.

<table>
<thead>
<tr>
<th>Sample Mn$<em>{1+x}$Ni$</em>{2-x}$Ga</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.2$</td>
<td>86.53 ± 0.12</td>
<td>3.12 ± 0.01</td>
<td>1.56</td>
<td>3.99</td>
<td>453 ± 3</td>
</tr>
</tbody>
</table>

Table 3.7: Spontaneous magnetization and magnetic moment of Mn$_{1.2}$Ni$_{1.8}$Ga per Mn-atom at $T = 0$ K. Spin, effective magnetization and $T_C$ are also summarized. $g$ taken to be $g = 2$.

3.e Mn$_{1.4}$Ni$_{1.6}$Ga

Figure 3.24 shows the thermal variation of the magnetization in a field of 0.1 T of Mn$_{1.4}$Ni$_{1.6}$Ga, sample (A), for first heating and then cooling. A sudden change appears in the magnetization around 90 K which is linked to the martensitic phase transition. The reverse transition on heating takes place in several stages as there are also two minor steps around 200 K and 250 K. The transition temperatures are summarized in table 3.8.
Figure 3.24: Thermal variation of the magnetization of \( \text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga} \) (A) in a field of 0.1 T for first heating and then cooling. The magnetization is not normalized due to some ambiguity regarding the sample mass.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>92.0 ± 0.2</td>
<td>61.1 ± 0.2</td>
<td>92.9 ± 0.4</td>
<td>118.4 ± 0.6</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 3.8: Martensitic transition temperatures of \( \text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga} \), sample (A). \( M_S \) \((A_S)\) and \( M_F \) \((A_F)\) are the (reverse) martensitic start and finish temperatures on cooling (heating), respectively. Hysteresis, as given in the 6th column, refers to the relative displacement of the interval centres \( (M_S + M_F)/2 \) and \( (A_S + A_F)/2 \).

Isotherms of the field dependence of the magnetization and Arrott plots for \( \text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga} \) sample (B) are shown in figure 3.25. Plots of the spontaneous magnetization are shown in figures 3.26 and 3.27. Values of the ground state magnetization and the Curie temperature are listed in table 3.9.
Figure 3.25: Magnetization against applied field (top) and Arrott plots (bottom) for Mn$_{1.4}$Ni$_{1.6}$Ga, sample (B). Diagrams on the right show isotherms between 5 K and 150 K on an amplified scale. Coefficients of linear equations used in Arrott plot fits are listed in appendix A.
**Figure 3.26:** The spontaneous magnetization of $\text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga}$, sample (B), as a function of temperature.

**Figure 3.27:** Plot of the squared spontaneous magnetization against temperature (left) and the spontaneous magnetization against $T^{3/2}$ for $\text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga}$, sample (B). Linear fits at low (up to 100 K) and high temperatures and the equations used in the fits are indicated, with units of $M$ and $T$ as given for the axes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.4$ (B)</td>
<td>75.75 ± 0.07</td>
<td>2.33 ± 0.01</td>
<td>1.17</td>
<td>3.18</td>
<td>439 ± 3</td>
</tr>
</tbody>
</table>

**Table 3.9:** Spontaneous magnetization and magnetic moment per Mn-atom of $\text{Mn}_{1.4}\text{Ni}_{1.6}\text{Ga}$, sample (B), at $T = 0$ K. Spin, effective magnetization and $T_C$ are also given. $g$ taken to be $g = 2$. 

$M(T^{3/2}) = (-1.68 \pm 0.13) \times 10^{-3} T^{3/2} + (75.75 \pm 0.07)$

$R^2 = 0.98$

$M^2(T) = (-19.54 \pm 0.09) T + (8575 \pm 27)$

$R^2 = 1.00$
3.f  Mn$_{1.5}$Ni$_{1.5}$Ga

The thermal variation of the magnetization is shown in figure 3.28. The graph obtained for sample (A) in a field of 0.1 T is shown on the left. Graphs obtained for sample (B) in different fields not higher than 1 T are shown on the right. At 0.1 T, the heating and cooling curves are approximately temperature independent for both samples. However, a discontinuous drop of about a third of its magnitude appears in the magnetization of sample (A) between 344 K and 350 K, where the measurement was reversed. The drop is not recovered as the sample is subsequently cooled down. A similar observation had been made in the thermal variation of the magnetization of Ni$_{1.2}$Mn$_{1.8}$Ga in a field of 0.1 T. The signatures of a martensitic transformation are not present in figure 3.28.

![Thermal variation of magnetization](image)

Figure 3.28: Thermal variation of the magnetization of Mn$_{1.5}$Ni$_{1.5}$Ga is shown for sample (A) for first heating and then cooling in a field of 0.1 T (left) and for sample (B) whilst cooling in fields of 0.05 T to 1 T (right).

The magnetization was measured as a function of the applied magnetic field for Mn$_{1.5}$Ni$_{1.5}$Ga, sample (B). The measurements and Arrott plots are shown for various temperatures in figure 3.29. Plots of the spontaneous magnetization are presented in figures 3.30 and 3.31. Results of these measurements are listed in table 3.10.
Figure 3.29: Magnetization against applied magnetic field for $\text{Mn}_{1.5}\text{Ni}_{1.5}\text{Ga} \ (B)$. Isotherms were obtained whilst cooling and are shown between 350 K and 5 K. Linear fits to Arrott plots are indicated. Coefficients of equations used in the fits are given in appendix A.

Figure 3.30: Spontaneous magnetization as a function of temperature for $\text{Mn}_{1.5}\text{Ni}_{1.5}\text{Ga}$, sample (B)

Figure 3.31: Spontaneous magnetization as a function of $T^{3/2}$ (left) and square of spontaneous magnetization as a function of temperature $T$ (right) for $\text{Mn}_{1.5}\text{Ni}_{1.5}\text{Ga}$, sample (B). Linear fits at low (up to 100 K) and high temperatures are included. The equations used in the linear fits are shown, with units of $M$ and $T$ as given for the axes.

$M (T^{3/2}) = (-2.51 \pm 0.14) \times 10^{-3} T^{3/2} + (68.96 \pm 0.07)$

$R^2 = 0.99$

$M^2 = (-14.08 \pm 0.08) T + (6294 \pm 23)$

$R^2 = 1.00$
Table 3.10: Spontaneous magnetization and magnetic moment at T = 0 K per Mn-atom of Mn$_{1.5}$Ni$_{1.5}$Ga, sample (B). Spin, effective magnetization and $T_C$ are summarized. g taken to be g = 2.

<table>
<thead>
<tr>
<th>Sample Mn$<em>{1+x}$Ni$</em>{2-x}$Ga</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.5 (B)</td>
<td>68.96 ± 0.14</td>
<td>1.98 ± 0.01</td>
<td>0.99</td>
<td>2.80</td>
<td>447 ± 4</td>
</tr>
</tbody>
</table>

3.g Mn$_{1.6}$Ni$_{1.4}$Ga

The thermal variation of the magnetization of Mn$_{1.6}$Ni$_{1.4}$Ga is presented. The graph for the annealed sample (B) whilst heating and then cooling is shown on the left. There is no evidence for a first order phase transition. However, graphs in applied fields of 0.05 T, 0.1 T and 1 T of the untreated sample (A), which are shown on the right whilst heating, have a kink below 25 K.

Measurements of the magnetization as a function of the applied magnetic field and Arrott plots for Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A), are shown in figure 3.33. The spontaneous magnetization against temperature, the square of the spontaneous magnetization against temperature and the spontaneous magnetization against $T^{3/2}$ for Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A), are shown in figures 3.34 and 3.35.

Figure 3.32: Thermal variation of the magnetization for Mn$_{1.6}$Ni$_{1.4}$Ga, sample (B), for first heating and then cooling (left), and for sample (A) whilst heating in fields of 0.05 T, 0.1 T and 1 T (right).
Figure 3.33: Magnetization versus applied magnetic field (left) and Arrott plots (right) for Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A). Coefficients of equations used in the fits are given in appendix A.

Figure 3.34: Low temperature Arrott plots on an expanded scale (left). Spontaneous magnetization of Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A), as a function of temperature (right).

Figure 3.35: The spontaneous magnetization as a function of $T^{3/2}$ (left) and the square of the spontaneous magnetization as a function of $T$ (right) of Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A). A linear fit at high temperatures is indicated and the equation used in the fit is displayed. The units in which $M$ and $T$ of the equations are measured are the same as given for the axes of the diagrams.
At lower temperatures, the spontaneous magnetization of $\text{Mn}_{1.6}\text{Ni}_{1.4}\text{Ga}$ does not behave linearly as a function of $T^{3/2}$. This is in contrast to all of the above compositions. The $T^{3/2}$ law is not valid for the untreated sample of $\text{Mn}_{1.6}\text{Ni}_{1.4}\text{Ga}$. Instead, for low temperatures up to 50 K the spontaneous magnetization increases. A linear fit of the region between 5 K and 50 K has a poor $R^2$ value. The behavior of the thermal variation of the magnetization (figure 3.32) and the spontaneous magnetization below 50 K is an indicator for a martensitic phase transition as reported by [Liu05].

<table>
<thead>
<tr>
<th>Sample $\text{Mn}<em>{x}\text{Ni}</em>{2-x}\text{Ga}$</th>
<th>$M_{5K}$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$\mu_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.6$ (A)</td>
<td>30.27 ± 0.13</td>
<td>0.81 ± 0.01</td>
<td>0.41 ± 0.01</td>
<td>1.51 ± 0.11</td>
<td>372 ± 9</td>
</tr>
</tbody>
</table>

Table 3.20: Spontaneous magnetization and magnetic moment per Mn atom at $T = 5$ K of $\text{Mn}_{1.6}\text{Ni}_{1.4}\text{Ga}$, sample (A). Spin, effective magnetization and $T_C$ are summarized. $g$ taken to be $g = 2$.

3. $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$

The thermal variation of the magnetization in an applied magnetic field of 0.1 T is shown for $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$. Records were taken for sample (A) (first heating and then cooling) and sample (B) (first cooling and then heating), and are shown in figure 3.36.

![Figure 3.36: Thermal variation of the magnetization of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$ in a magnetic field of 0.1 T.](image-url)
A martensitic phase transition is evident in the thermal variation of the magnetization in both samples. It is more pronounced in the graphs of the sample (B). The temperature scan of the annealed sample exhibits the anomaly between 200 K and 270 K with a hysteresis of 40 K. The temperature scan of the untreated sample shows a much broader and flatter anomaly around 125 K, with a hysteresis of 54 K. The characteristic martensitic transition temperatures are summarized in table 3.21.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(A)</td>
<td>132.1 ± 2.2</td>
<td>61.6 ± 2.6</td>
<td>125.5 ± 4.0</td>
<td>176.1 ± 3.0</td>
<td>54</td>
</tr>
<tr>
<td>0.1</td>
<td>(B)</td>
<td>236.2 ± 1.9</td>
<td>197.1 ± 2.1</td>
<td>238.1 ± 2.1</td>
<td>281.0 ± 2.1</td>
<td>40</td>
</tr>
</tbody>
</table>

Table 3.21: Martensitic transformation temperatures of Mn$_{1.8}$Ni$_{1.2}$Ga. $M_S$ ($A_S$) and $M_F$ ($A_F$) are the (reverse) martensitic start and finish temperatures on cooling (heating), respectively. Hysteresis, as given in the 6th column, refers to the relative displacement of the interval centres ($M_S + M_F$)/2 and ($A_S + A_F$)/2.

In the following, the magnetization as a function of the applied magnetic field and Arrott plots are presented in figure 3.37 for the untreated sample (A). Plots of the spontaneous magnetization are presented in figures 3.38 and 3.39. A shift appears in the spontaneous magnetization for temperatures above 50 K. It coincides with the anomaly observed in the cooling curve of the temperature scan of the untreated sample (A) of Mn$_{1.8}$Ni$_{1.2}$Ga.
Figure 3.37: Plot of the magnetization versus applied magnetic field for Mn$_{1.8}$Ni$_{1.2}$Ga (A). Coefficients of equations used in the fits are given in appendix A.

Figure 3.38: Spontaneous magnetization versus temperature of Mn$_{1.8}$Ni$_{1.2}$Ga, sample (A).

Figure 3.39: Spontaneous magnetization versus $T^{3/2}$ (left) and square of spontaneous magnetization versus $T$ (right) of Mn$_{1.8}$Ni$_{1.2}$Ga, sample (A).
The field dependence of the magnetization and Arrott plots of sample (B) which was annealed at 900°C are presented in figure 3.40. Isotherms were recorded whilst cooling. Plots of the spontaneous magnetization are shown in figures 3.41 and 3.42.

**Figure 3.40:** Magnetization $M$ versus applied magnetic field (left) and Arrott plots (right) of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$, sample (B). Coefficients of equations used in the fits are given in appendix A.

**Figure 3.41:** Spontaneous magnetization versus temperature of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$, sample (B).
Figure 3.42: Spontaneous magnetization versus $T^{3/2}$ (left) and the square of the spontaneous magnetization versus $T$ (right) for Mn$_{1.8}$Ni$_{1.2}$Ga, sample (B). Linear fits at low (up to 100 K) and high temperatures are included. The equations used in the fits are displayed; units of $M$ and $T$ are equal to the units of the diagram axes.

Table 3.22: Spontaneous magnetization and magnetic moment per Mn-atom at $T = 0$ K of Mn$_{1+x}$Ni$_{2-x}$Ga. Spin, effective magnetization and $T_C$ are summarized. $g$ taken to be $g = 2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$\mu_{eff}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0.8$ (A)</td>
<td>46.79 ± 0.17</td>
<td>1.11 ± 0.01</td>
<td>0.56 ± 0.01</td>
<td>1.86</td>
<td>475 ± 13</td>
</tr>
<tr>
<td>$x = 0.8$ (B)</td>
<td>52.29 ± 0.15</td>
<td>1.24 ± 0.01</td>
<td>0.62 ± 0.01</td>
<td>2.00</td>
<td>465 ± 10</td>
</tr>
</tbody>
</table>

3.i Mn$_2$NiGa

The magnetization of Mn$_2$NiGa was measured as a function of the applied magnetic field for various temperatures. These measurements and Arrott plots are shown in figure 3.43. Plots of the thermal variation of the spontaneous magnetization are shown in figures 3.44 and 3.45.

Figure 3.46 shows the temperature dependence of the magnetization for different applied fields as obtained from the isotherms in figure 3.43. For increasing temperatures and in small fields the magnetization rises by about 33% between 250 K and 300 K. This is an indicator for a martensitic transformation between these temperatures. A deviation from the expected shape of an
isotropic ferromagnet is also present at high fields at temperatures above 250 K where the spontaneous magnetization levels.

At 350 K the variation of the magnetization shows an increase at high fields according to $M(B) = (0.27 \pm 0.04)B + (23.46 \pm 0.13)$ with an $R^2$ value of 0.98; and $M$ and $B$ are measured in units of J/kg/T and T, respectively. At these applied fields and for a fixed moment system the increase is taken to originate from band electrons. This contribution corresponds to a band electron susceptibility of $\sim 0.27$ J/kg/T$^2$.

![Figure 3.43](image1.png)

**Figure 3.43:** Magnetization versus applied magnetic field and Arrott plots with high field linear fits of Mn$_2$NiGa. Coefficients of equations used in the fits are given in appendix A.

![Figure 3.44](image2.png)

**Figure 3.44:** Spontaneous magnetization as a function of temperature of Mn$_2$NiGa.
Figure 3.45: Spontaneous magnetization versus $T^{3/2}$ (left) and the square of the spontaneous magnetization versus $T$ (right) for Mn$_2$NiGa. A linear fit at low temperatures (up to 100 K) is included. The equation used in the fit is displayed, with the units of $M$ and $T$ equal the units of the diagram axes.

\[ M(T^{3/2}) = (-1.4 \pm 0.3) \times 10^{-3} T^{3/2} + (31.1 \pm 0.2) \]
\[ R^2 = 0.94 \]

Figure 3.46: Temperature dependence of the magnetization of Mn$_2$NiGa in different applied fields.

Table 3.27: Spontaneous magnetization $M_0$ and ground state magnetic moment $m$ per Mn-atom at $T = 0$ K for Mn$_2$NiGa. Spin, effective magnetization and $T_C$ are summarized. $g$ taken to be $g = 2$.

<table>
<thead>
<tr>
<th>Sample Mn$<em>{1+x}$Ni$</em>{2-x}$Ga</th>
<th>$M_0$ [J/kg/T]</th>
<th>$m$ [$\mu_B$]</th>
<th>$S_z$</th>
<th>$p_{\text{eff}}$ [$\mu_B$]</th>
<th>$T_C$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 1$</td>
<td>31.1 ± 0.2</td>
<td>0.66 ± 0.01</td>
<td>0.33 ± 0.01</td>
<td>1.33</td>
<td>&gt; 500</td>
</tr>
</tbody>
</table>

The square of the spontaneous magnetization is shown in figure 3.67. It can be confirmed that the Curie temperature lies above 500 K. The martensitic transformation can be identified by the change in the value of the spontaneous
magnetization as a function of temperature around 250 K. As for Mn$_{1.8}$Ni$_{1.2}$Ga and Mn$_{1.6}$Ni$_{1.4}$Ga the martensitic transformation is evident in the spontaneous magnetization.
3.j Summary of magnetization measurements

In summary, samples annealed at either 800°C or 900°C are well suited for magnetization investigations because there is no significant difference between samples annealed at either temperature. This is particularly supported by measurements on Mn$_{1.15}$Ni$_{1.85}$Ga. The magnetization of annealed samples varies monotonically as a function of Mn content as shown in figure 3.47 which displays the measured magnetization data at 5 K and 300 K, respectively. The magnetization decreases for increasing Mn content. The results for annealed samples are in agreement with data published by Liu (Liu06).

The spontaneous magnetization as obtained from linear fits of the high field portion of the Arrott plots is shown as a function of temperature for all annealed samples in figure 3.48. Again, the curves assume smaller magnitudes with increasing Mn content.

Figure 3.47: The experimentally observed field dependence of the magnetization at 5 K (left) and 300 K (right) for annealed samples of Mn$_{1+x}$Ni$_{2-x}$Ga with x = 0.15, 0.20, 0.40, 0.50, 0.80 and 1.00.
The spontaneous magnetization $M_0$ of the ground state is displayed for annealed samples as a function of Mn content in figure 3.49. It decreases with increasing Mn content. A linear fit is indicated in the figure and the equation used in the fit is given.

$$M_0 (x) = (-64.32 \pm 0.22) x + (101.58 \pm 0.14)$$

$R^2 = 0.99$
An extrapolation of the fit in figure 3.49 toward \( x = 0 \) yields a value of \( M_0 = (101.6 \pm 0.2) \text{ J/kg/T} \) for Ni\(_2\)MnGa. This in turn gives for the magnetic moment per Mn atom at \( T = 0 \text{ K} \) a value of \( m = (4.36 \pm 0.1) \mu_\text{B} \) for Ni\(_2\)MnGa. It is \(~5\%\) larger than the value reported by [Webster84] and [Liu06].

However, Webster derived the magnetic moment of the ground state by extrapolation of the high field magnetization curve at 202 K. The higher value derived in this thesis is therefore in agreement with the one derived by Webster et al. as isotherms were used here at much lower temperatures.

Figure 3.50 shows the distribution of the ground state magnetic moment for both, annealed and untreated samples, for all compositions measured. The measurements of annealed samples (either at 800°C or 900°C) are shown as black diamonds. The other non-annealed samples are shown as empty black circles. It is noticeable that the measurements on untreated samples are more scattered, and thus measurements on these samples do not provide a reliable indicator to the magnitude of the ground state magnetic moment.

**Figure 3.50:** Magnetization \( M_0 \) at \( T = 0 \text{ K} \) as a function of Mn content for annealed and untreated samples. Best linear fits are indicated for annealed (solid line) and untreated (broken line) samples.
On an atomic level, the bulk magnetic moment is carried by Mn atoms [Brown02]. It is therefore surprising to see that the ferromagnetic moment decreases with increasing Mn content (see figure 3.49). If it is assumed that the magnetic moment of Mn is fixed in magnitude and independent of composition then the trend with alloying can be understood as indicating an antiferromagnetic alignment of the Mn moment on Ni sites (position 8c (¼,¼,¼) in $Fm\overline{3}m$) compared to the pure Mn sites at position 4a (000) within the space group $Fm\overline{3}m$. However, more detailed structural data is required to confirm this model. This point will be discussed more fully at the end of the thesis when combined with the results of the neutron scattering investigation.

Next the Curie temperatures are shown for annealed and untreated samples in figure 3.51. The Curie temperatures rise with increasing Mn content. A linear was fitted to the data of annealed samples with a $R^2$ value of 0.80.

![Figure 3.51: Curie temperatures derived from high field magnetization measurements for both, annealed and untreated samples, as a function of the Mn content. The value for $x = 0$ (Ni$_2$MnGa) was taken from Webster[84]. Linear fits are indicated for annealed (solid line) and untreated (broken line) samples.](image-url)
The martensitic transition temperatures are shown in figure 3.5. Samples either annealed at 800°C or untreated were included. Mean values

\[ M = \frac{M_S + M_F}{2} \]

and

\[ A = \frac{A_S + A_F}{2} \]

for cooling and heating are shown.

Figure 3.5: Martensitic transition temperatures as a function of the Mn content for samples annealed at 800°C or untreated. The pink circles and the blue diamonds show the mean transition temperatures whilst heating and cooling, respectively. No transition was observed for Mn\(_{1.05}\)Ni\(_{1.95}\)Ga, Mn\(_{1.15}\)Ni\(_{1.85}\)Ga (A), Mn\(_{1.15}\)Ni\(_{1.5}\)Ga and Mn\(_{1.6}\)Ni\(_{1.4}\)Ga.

Liu[S] measured a parabola like behavior of the martensitic transition temperatures with increasing Mn content which is confirmed here. However, not all compositions measured showed a typical transformation in the temperature scans of the magnetization. No martensitic transition was detected in thermal variation of the magnetization of Mn\(_{1.05}\)Ni\(_{1.95}\)Ga (untreated), Mn\(_{1.15}\)Ni\(_{1.85}\)Ga (untreated), Mn\(_{1.5}\)Ni\(_{1.5}\)Ga and Mn\(_{1.6}\)Ni\(_{1.4}\)Ga (annealed).

The martensitic transition observed in samples annealed at 900°C takes place at temperatures about 100 K higher than in samples annealed at 800°C.

In some samples with lower Mn content another anomaly at high temperatures is evident in the thermal variation of the magnetization in fields of 0.1 T. There the magnetization suddenly drops by several percent on heating. This happens regardless of the heat treatment, as this feature is present in untreated
Mn$_{1.05}$Ni$_{1.95}$Ga and Mn$_{1.1}$Ni$_{1.9}$Ga but also in annealed Mn$_{1.2}$Ni$_{1.8}$Ga and Mn$_{1.5}$Ni$_{1.5}$Ga. Yet, whilst in Mn$_{1.1}$Ni$_{1.9}$Ga this anomaly is present in both, heating and cooling curves, and exhibits hysteresis, as expected for first order phase transitions, it is different for Mn$_{1.05}$Ni$_{1.95}$Ga where it is only present in the heating, but not in the cooling curve. Yet again, in Mn$_{1.2}$Ni$_{1.8}$Ga and Mn$_{1.5}$Ni$_{1.5}$Ga it happens at 350 K, the highest temperature of the measurement. Here, the transition is not reversible as the decrease in magnetization is not recovered on subsequent cooling.
4 Report on the investigation into the atomic structure of \( \text{Mn}_{1+x} \text{Ni}_{2-x} \text{Ga} \)

Investigations into the atomic structure of \( \text{Mn}_{1+x} \text{Ni}_{2-x} \text{Ga} \) compounds were facilitated by X-ray and neutron scattering experiments. Neutron scattering experiments were conducted at the Institut Laue-Langevin (ILL), Grenoble, France, on powder samples of \( \text{Mn}_{1+x} \text{Ni}_{2-x} \text{Ga} \) alloys and using the instruments D1a (1.91 Å), D2b (1.594 Å) and D1b (2.52 Å). Atomic positions, lattice constants, symmetry and magnetic moments on Mn atoms were investigated. Neutron scattering patterns were obtained at different temperatures including high and low temperature phases. The ‘FullProf’ program, as provided by the ILL, was employed in the analysis of the neutron scattering patterns for the refinement of the various parameters. For the analysis of the neutron scattering patterns it is assumed that magnetic and nuclear scattering are present in the experimental patterns.

4.a \( \text{Mn}_2 \text{NiGa} \)

At 500 K, 400 K and 300 K \( \text{Mn}_2 \text{NiGa} \) (annealed at 800°C for 3 d) exhibits the high temperature cubic parent phase with the L2\(_1\) Heusler structure, space group \( \text{Fm\bar{3}m} \), and Mn and Ni atoms occupying the 8c position in equal parts and at random. Lattice parameters and atomic positions are summarized in table 4.1.

<table>
<thead>
<tr>
<th>( \text{Fm\bar{3}m} )</th>
<th>lattice constant [Å]</th>
<th>(000) 4a</th>
<th>(½, ½, ½) 4b</th>
<th>(¼, ¼, ¼) 8c</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Mn}_2 \text{NiGa} ) (500 K)</td>
<td>5.9362 ± 0.0004</td>
<td></td>
<td>Mn</td>
<td>½ Mn, ½ Ni</td>
</tr>
<tr>
<td>( \text{Mn}_2 \text{NiGa} ) (400 K)</td>
<td>5.9228 ± 0.0002</td>
<td></td>
<td>Ga</td>
<td></td>
</tr>
<tr>
<td>( \text{Mn}_2 \text{NiGa} ) (300 K)</td>
<td>5.9102 ± 0.0003</td>
<td></td>
<td>Mn</td>
<td></td>
</tr>
<tr>
<td>( \text{Ni}_2 \text{MnGa} ) (400 K)</td>
<td>5.8636 ± 0.0002</td>
<td></td>
<td>Ga</td>
<td>Ni</td>
</tr>
<tr>
<td>( \text{Ni}_2 \text{MnGa} ) (300 K)</td>
<td>5.8229 ± 0.0002</td>
<td></td>
<td>Mn</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1: Lattice constant and atomic positions of the cubic parent phase of \( \text{Mn}_2 \text{NiGa} \) at 500 K, 400 K and 300 K. As a reference the parameters of \( \text{Ni}_2 \text{MnGa} \) at 400 K and 300 K are also given [Brown02].
At 300 K, the neutron diffraction pattern of Mn$_2$NiGa indicates the co-existence of both the parent and the martensitic phase of Mn$_2$NiGa. The martensitic phase is tetragonal with the related symmetry of the sub space group $I4/mmm$. This symmetry is prevalent down to 5 K. Lattice parameters of the martensitic phase are summarized in table 4.2.

<table>
<thead>
<tr>
<th>$I4/mmm$</th>
<th>a</th>
<th>c</th>
<th>(000)</th>
<th>(0, 0, ½)</th>
<th>(0, ½, ¼)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$_2$NiGa (300 K)</td>
<td>3.9286 ± 0.0003</td>
<td>6.6962 ± 0.0007</td>
<td>Mn</td>
<td>Ga</td>
<td>½ Mn, ½ Ni</td>
</tr>
<tr>
<td>Mn$_2$NiGa (150 K)</td>
<td>3.9023 ± 0.0003</td>
<td>6.7304 ± 0.0007</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$_2$NiGa (5 K)</td>
<td>3.8874 ± 0.0003</td>
<td>6.7643 ± 0.0008</td>
<td>Mn</td>
<td>Ga</td>
<td>Ni</td>
</tr>
<tr>
<td>Ni$_2$MnGa (5 K)</td>
<td>4.2152</td>
<td>5.5570</td>
<td>Mn</td>
<td>Ga</td>
<td>Ni</td>
</tr>
</tbody>
</table>

*Table 4.2: Lattice parameters and atomic positions of the tetragonal martensitic phase of Mn$_2$NiGa at 300 K, 150 K and 5 K. As a reference the parameters of Ni$_2$MnGa at 5 K are also given [Brown02].

The refinement includes a magnetic contribution to the diffraction pattern. This is treated as a purely magnetic phase including Mn atoms only. There are 2 different Mn positions: MnI position at (0, 0, 0) and MnII position at (¼, ¼, ¼). For the latter position a site occupation of 50% Mn and 50% Ni has been assumed. The magnetic moment arising from that position is a net magnetic moment which is taken to only involve the Mn atom. This does not exclude a contribution from Ni atoms. However, in the experiments such a superposition of magnetic contribution cannot be resolved. Therefore a net magnetic moment of Mn atoms only is refined. Refined magnetic moments are listed in table 4.3. Magnetic moments on sites 4a and 8c are oriented antiparallel to one another.
T [K] | $\chi^2$ | $m_{\text{MnI}}$ [\(\mu_B/\text{Mn}\)] | $m_{\text{MnII}}$ [\(\mu_B/\text{Mn}\)] | $m_{\text{tot}}$ [\(\mu_B/\text{Mn}\)] | $m_{\text{MnI}}$ [\(\mu_B/\text{f.u.}\)] | $m_{\text{MnII}}$ [\(\mu_B/\text{f.u.}\)] | $m_{\text{tot}}$ [\(\mu_B/\text{f.u.}\)]
--- | --- | --- | --- | --- | --- | --- | ---
500 | 2.9 | $2.4 \pm 0.4$ | $-0.7 \pm 0.3$ | $1.7 \pm 0.5$ | 
400 | 4.0 | $2.4 \pm 0.4$ | $-1.2 \pm 0.3$ | $1.2 \pm 0.4$ | 
300 | 4.9 | $2.5 \pm 0.5$ | $-1.0 \pm 0.4$ | $1.5 \pm 0.7$ | $2.9 \pm 0.5$ | $-1.3 \pm 0.4$ | $1.6 \pm 0.7$ | 
150 | 6.0 | 
5 | 5.9 | $3.8 \pm 0.6$ | $-1.9 \pm 0.5$ | $1.9 \pm 0.8$ | 

Table 4.3: Magnetic moments on MnI and MnII atoms as well as total magnetic moments per f.u. At 300 K the magnetic moments of the parent and martensitic phase are summarized. The $\chi^2$ of the refinements are given.

In the refinement, the purely nuclear and magnetic phases have to be linked by a mutual scale factor. However, usually the number of symmetry operators in the nuclear and the magnetic phase is not the same. This requires a scale factor $scale$ to be identified such that

$$scale \cdot (# \text{ of sym. op.}) \cdot (\text{site occup.}) = (\text{multiplicity of lattice site})$$

Here $(# \text{ of sym. op.})$ is the number of symmetry operators in the magnetic or nuclear phase, $(\text{site occup.})$ is the site occupation (which may be fractional) and $(\text{multiplicity of lattice site})$ is the multiplicity of the lattice site as listed in the International Tables of Crystallography [Hahn83].

<table>
<thead>
<tr>
<th>cubic phase</th>
<th>contribution</th>
<th>site occup.</th>
<th># of sym. op.</th>
<th>multiplicity of lattice site</th>
<th>Scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn (4a)</td>
<td>atomic</td>
<td>0.1*</td>
<td>192</td>
<td>4</td>
<td>0.20833</td>
</tr>
<tr>
<td></td>
<td>magnetic</td>
<td>1.2</td>
<td>16</td>
<td>4</td>
<td>0.20833</td>
</tr>
<tr>
<td>Mn (8c)</td>
<td>atomic</td>
<td>0.1†</td>
<td>32</td>
<td>8</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>magnetic</td>
<td>0.4</td>
<td>8</td>
<td>8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 4.4: Site occupation of atomic and magnetic phases is linked by mutual $scale$ factor as described in the text. Here, an example is given for the cubic phase. (*): Full site occupation (= 1) needs to be divided by 10 for practical reasons or the number in the magnetic phase would be greater than 10 which evokes an error in the FullProf routine. (†) Here, the site is half occupied by Mn atoms, but the multiplicity of the site is twice the multiplicity of the 4a site. Thus half the occupation is mirrored by using 0.1 instead of 0.2.
Two impurity phases have been included in the refinement. The first one is Ni$_2$Ga. Pearson [Pearson85] identified the structure of Ni$_2$Ga as a hexagonal NiAs structure type with lattice parameters $a \approx 4.002$ Å and $c \approx 4.988$ Å. The refinement completed here for Ni$_2$Ga at 500 K yields lattice parameters and atomic positions for this phase as given in table 4.5.

<table>
<thead>
<tr>
<th>Ni$_2$Ga $P6_3/mmc$</th>
<th>Lattice constant $a$ [Å]</th>
<th>Lattice constant $c$ [Å]</th>
<th>Atomic positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 K</td>
<td>4.167 ± 0.001</td>
<td>5.341 ± 0.002</td>
<td>Ni (2a) (0, 0, 0)</td>
</tr>
<tr>
<td>400 K</td>
<td>4.159 ± 0.001</td>
<td>5.329 ± 0.002</td>
<td>Ga (2c) ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$)</td>
</tr>
<tr>
<td>300 K</td>
<td>4.152 ± 0.001</td>
<td>5.321 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>150 K</td>
<td>4.147 ± 0.002</td>
<td>5.294 ± 0.004</td>
<td></td>
</tr>
<tr>
<td>5 K</td>
<td>4.142 ± 0.002</td>
<td>5.282 ± 0.004</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.5: Lattice constants and atomic positions of Ni$_2$Ga impurity phase.

Some assumptions have to be made with respect to the properties of this phase. Here it was initially assumed that the atomic positions are randomly occupied by Ga and Ni atoms. This assumption cannot be entirely correct as there must be some additional Mn present in the compound. As the scattering length of Mn is negative, this results in a systematic underestimate of the abundance of this phase.

The refinement, however, requires an unequal occupation of the lattice sites 2a and 2c. Allowing the occupations of Ni and Ga to vary resulted in a better fit. The fit improved considerably by reducing the R-factor of the impurity phase by a factor of 2. The best fit was obtained with a negative occupation factor for some atomic positions. This is taken to indicate that on these sites Mn is present with a negative scattering length. In the absence of the detailed knowledge of the precise composition of this impurity phase it is reasonable to refrain from any further modelling of the occupation parameters. However, the negative
occupation factors are physically sensible given the interpretation put forward above. For this reason it is also not possible to determine the abundance of the impurity phase with respect to the main phase. The abundance may be judged by the size of the first Bragg peak to be of the order of several per cent.

The second impurity phase has been identified as the MnO structure. Its space group is $Fm\overline{3}m$. Pearson lists the lattice parameter as 4.4444 Å. The structural details of this impurity phase are given in table 4.6.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Lattice constant $a$ [Å]</th>
<th>Atomic positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 K</td>
<td>4.598 ± 0.002</td>
<td>Mn (4a) (0, 0, 0)</td>
</tr>
<tr>
<td>400 K</td>
<td>4.588 ± 0.002</td>
<td>O (4b) (½, ½, ½)</td>
</tr>
<tr>
<td>300 K</td>
<td>4.576 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>150 K</td>
<td>4.569 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>5 K</td>
<td>4.566 ± 0.002</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.6: Lattice constants and atomic positions of MnO impurity phase.

In the following the neutron scattering patterns are shown for Mn$_2$NiGa and temperatures between 500 K and 5 K in figures 4.1 to 4.5. A model calculation (black line) is superimposed on the observation (red dots). The blue line at the bottom indicates the difference between model calculation and observation. Beneath the reflection there are a number of lines or green bars which indicate the peak positions according to the model calculation. The contributions from different phases are separated by different lines.
**Figure 4.1:** Neutron scattering pattern (red) and refinement (black) of Mn$_2$NiGa at 500 K. Four phases are included (from top to bottom): Mn$_2$NiGa cubic phase, Mn$_2$NiGa cubic magnetic phase, Ni$_2$Ga, and MnO.

**Figure 4.2:** Neutron scattering pattern (red) and refinement (black) of Mn$_2$NiGa at 400 K. Four phases are included (from top to bottom): Mn$_2$NiGa cubic phase, Mn$_2$NiGa cubic magnetic phase, Ni$_2$Ga, and MnO.

**Figure 4.3:** Neutron scattering pattern (red) and refinement (black) of Mn$_2$NiGa at 300 K. Six phases are included (from top to bottom): Mn$_2$NiGa tetragonal, Mn$_2$NiGa tetragonal magnetic phase, Mn$_2$NiGa cubic, Mn$_2$NiGa cubic magnetic phase, Ni$_2$Ga, MnO.
Figure 4.4: Neutron scattering pattern (red) and refinement (black) of Mn$_2$NiGa at 150 K. Four phases are (from top to bottom): Mn$_2$NiGa tetragonal, Mn$_2$NiGa tetragonal magnetic phase, Ni$_2$Ga, and MnO.

Figure 4.5: Neutron scattering pattern (red) and refinement (black) of Mn$_2$NiGa at 5 K. Six phases are included in the refinement, which are (from top to bottom) Mn$_2$NiGa tetragonal, Mn$_2$NiGa tetragonal magnetic phase, Ni$_2$Ga, and MnO.

The temperature dependence of the lattice parameters of the cubic and the tetragonal phases is plotted in figures 4.6 to 4.8. The thermal expansion coefficients have been determined and are shown in the figures.
Figure 4.6: Evolvement of the a parameter of the cubic phase of Mn$_2$NiGa as a function of temperature. A linear fit is included with $a_{\text{cubic}}$ and T in units of Å and K, respectively. The thermal expansion factor is given.

$$a_{\text{cubic}} (T) = (1.29 \pm 0.03) \times 10^{-4} T + (5.871 \pm 0.001)$$

$$R^2 = 1.00$$

$$\Rightarrow \Delta a/a_0 = (2.20 \pm 0.05) \times 10^{-5} \text{ K}^{-1}$$

Figure 4.7: Evolvement of the a parameter of the tetragonal phase in Mn$_2$NiGa as a function of temperature. A linear fit is included with $a_{\text{cubic}}$ and T in units of Å and K, respectively. The thermal expansion factor is given.

$$a_{\text{tetra}} (T) = (1.40 \pm 0.02) \times 10^{-4} T + (3.8849 \pm 0.0003)$$

$$R^2 = 0.98$$

$$\Rightarrow \Delta a/a_0 = (3.60 \pm 0.04) \times 10^{-5} \text{ K}^{-1}$$

Figure 4.10: Evolvement of the c parameter of the tetragonal phase in Mn$_2$NiGa as a function of temperature. A linear fit is included with $a_{\text{cubic}}$ and T in units of Å and K, respectively. The thermal expansion factor is given.

$$c_{\text{tetra}} (T) = (-2.31 \pm 0.04) \times 10^{-4} T + (6.765 \pm 0.001)$$

$$R^2 = 1.00$$

$$\Rightarrow \Delta c/c_0 = (-3.41 \pm 0.06) \times 10^{-5} \text{ K}^{-1}$$
4.b \textit{Mn}_{1.8}\textit{Ni}_{1.2}\textit{Ga}

Neutron diffraction patterns were obtained on Mn$_{1.8}$Ni$_{1.2}$Ga (annealed at 800$^\circ$C for 3d) whilst heating at temperatures between 6 K and 296 K. Three constituent phases have been identified which are present at all temperatures: the cubic phase, the tetragonal phase and the Ni$_2$Ga impurity phase. The 8c position in the cubic phase, or the 4d position in the tetragonal phase, is 40% occupied by Mn atoms and 60% occupied by Ni atoms. Lattice constants and atomic positions are summarized in table 4.7 for a few selected temperatures. Plots of the evolvement of the lattice parameters, as the temperature changes, are given in figures 4.11 to 4.13. A transition is evident around 150 K where the expansion curves have a kink. Beyond the linear region, the lattice parameters fluctuate a lot and the uncertainty of the length of the lattice constants increases, especially in the tetragonal phase. This arises due to the changes in abundance of the various phases due to the phase transition. Figure 4.14 shows the thermal variation of the electric resistivity of an untreated sample of Mn$_{1.8}$Ni$_{1.2}$Ga whilst cooling and heating. It also shows a transition around 150 K whilst heating, and around 100 K whilst cooling. A superposition of the neutron diffraction patterns and model calculations at 6 K and 296 K are shown in figures 4.15 and 4.16.

![Figure 4.11](image_url)

\textit{Figure 4.11:} The thermal variation of the lattice parameter $a$ of the cubic phase of Mn$_{1.8}$Ni$_{1.2}$Ga. A linear fit for temperatures above 153 K and the equation used in the fit as well as the thermal expansion coefficient are given.
Figure 4.12: The thermal variation of the lattice parameter $a$ of the tetragonal phase of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$. A linear fit for temperatures below 145 K, the equation used in the fit as well as the thermal expansion coefficient are given.

\[
a(T) = (7.2 \pm 0.9) \times 10^{-5} T + (3.896 \pm 0.001)
\]

\[R^2 = 0.89\]

$\Rightarrow \Delta a/a_0 = (1.8 \pm 0.3) \times 10^{-5} \text{K}^{-1}$

Figure 4.13: The thermal variation of the lattice parameter $c$ of the tetragonal phase of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$. A linear fit for temperatures below 145 K, the equation used in the fit as well as the thermal expansion coefficient are given.

\[
c(T) = (-1.2 \pm 0.2) \times 10^{-4} + (6.653 \pm 0.002)
\]

\[R^2 = 0.82\]

$\Rightarrow \Delta a/a_0 = (-1.8 \pm 0.3) \times 10^{-5} \text{K}^{-1}$

Figure 4.14: The electric resistivity of $\text{Mn}_{1.8}\text{Ni}_{1.2}\text{Ga}$ (untreated) whilst cooling and heating.
Table 4.7: Summary of the lattice constants of the cubic and tetragonal phases in Mn\textsubscript{1.8}Ni\textsubscript{1.2}Ga for a few selected temperatures.

<table>
<thead>
<tr>
<th>( T ) [K]</th>
<th>( Fm\bar{3}m )</th>
<th>( 14/mmm )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>lattice constant ( a ) [Å]</td>
<td>Volume of the unit cell [Å(^3)]</td>
</tr>
<tr>
<td>6</td>
<td>5.866 ± 0.002</td>
<td>201.9 ± 0.3</td>
</tr>
<tr>
<td>39</td>
<td>5.866 ± 0.002</td>
<td>201.8 ± 0.3</td>
</tr>
<tr>
<td>103</td>
<td>5.868 ± 0.002</td>
<td>202.1 ± 0.3</td>
</tr>
<tr>
<td>145</td>
<td>5.869 ± 0.001</td>
<td>202.2 ± 0.2</td>
</tr>
<tr>
<td>153</td>
<td>5.869 ± 0.001</td>
<td>202.1 ± 0.2</td>
</tr>
<tr>
<td>230</td>
<td>5.876 ± 0.001</td>
<td>202.9 ± 0.2</td>
</tr>
<tr>
<td>263</td>
<td>5.881 ± 0.001</td>
<td>203.4 ± 0.2</td>
</tr>
<tr>
<td>296</td>
<td>5.885 ± 0.001</td>
<td>203.8 ± 0.2</td>
</tr>
</tbody>
</table>

Figure 4.15: Neutron diffraction pattern (red dots) and calculation (black line) of Mn\textsubscript{1.8}Ni\textsubscript{1.2}Ga at \( T = 296 \) K. The first two (second two) lines of green bars indicate the peak positions of the tetragonal (cubic) phase. The last line of green bars refers to the impurity phase. The blue line at the bottom marks the difference between calculation and observation.

Magnetic scattering was included in the analysis of the neutron scattering patterns. It can be confirmed that antiferromagnetic ordering between Mn atoms on different crystallographic positions is present. However, for Mn\textsubscript{1.8}Ni\textsubscript{1.2}Ga, the magnetic moments were not refined.
Figure 4.16: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.8}$Ni$_{1.2}$Ga at $T = 6$ K. The first two (second two) lines of green bars indicate the peak positions of the tetragonal (cubic) phase. The last line of green bars refers to the impurity phase. The blue line at the bottom marks the difference between calculation and observation.

4.c Mn$_{1.6}$Ni$_{1.4}$Ga

The refinement for the Mn$_{1.6}$Ni$_{1.4}$Ga (annealed at 800°C for 3 d) sample was done between 50K and room temperature in cooling mode. Due to experimental restrictions no data was collected below 50K.

The patterns comprise 3 distinct low angle Bragg reflections from the main phase. These peak intensities are determined by the nuclear structure and the ferromagnetic contribution which occurs on top of the nuclear scattering. Therefore the decrease of nuclear intensity, as determined by the isotropic, or overall, temperature factor, and magnetic scattering are able to partly compensate one another. As a result of this the refinement is rendered unstable as the programme is able to shift the scattering contribution between the thermal and the magnetic channels without significantly affecting the diffraction pattern.

In order to prevent this ambiguity the following procedure was adopted. Thermal parameters have been determined for a wide temperature range for
the compound Mn₂NiGa. These have been interpolated, as a function of temperature, and used for the Mn₁.6Ni₁.4G sample. For each pattern the temperature factor was fixed to this value. However, there is a systematic error in this approach such that it renders the absolute magnitude of the magnetic moment unreliable. Therefore the magnetic moments, as obtained in these refinements, will only be quoted using arbitrary units.

The refinement of approximately 100 diffraction patterns at various temperatures has been carried out. There was no phase transition to a low temperature phase within the temperature interval investigated in the experiment. The temperature dependence of the lattice parameter of the cubic phase and the temperature dependence of the magnetic moment on the 4a and the 8c sites are shown in figures 4.16 and 4.17.

This compound is unusual in the sense that the cubic lattice parameter remains approximately constant below a temperature of about 120 K. The temperature dependence of the magnetic moment does not follow the temperature dependence of a normal magnetic moment of a fixed moment Heisenberg model. This may be attributed to the shortcomings of the approach due to some systematic errors in the modelling procedures of the thermal parameters. Therefore the temperature dependence of the magnetic moments, as obtained by these fits, has to be interpreted with care.

For the Mn located on 8c sites a sizable magnetic moment starts to appear at the point for which the lattice parameter remains constant with decreasing temperature. While the absolute value of this magnetic moment may be uncertain, the deviation from zero is significant. This observation indicates that there may be a magnetic – lattice coupling between the magnetic system and
the lattice such that the thermal expansion is affected by the appearance of a non-zero static magnetic moment on 8c lattice sites.

A small impurity phase of the Ni$_2$Ga structure has also been included in the refinement as an additional phase. $\chi^2$ values are around 1.5 for all refinements. A diffraction pattern and superimposed model calculation of Mn$_{1.6}$Ni$_{1.4}$Ga at 228 K is shown in figure 4.19. The lattice constants and the magnetic moments are listed for a few selected temperatures in table 4.8.

![Figure 4.17: The thermal variation of the cubic lattice constant of Mn$_{1.6}$Ni$_{1.4}$Ga for temperatures above 50 K.](image)

![Figure 4.18: The thermal variation of the magnetic moments on lattice sites (4a) and (8c) for Mn$_{1.6}$Ni$_{1.4}$Ga for temperatures above 50 K.](image)
Figure 4.19: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.6}$Ni$_{1.4}$Ga at T = 228 K. The green bars indicate the peak positions of (from top to bottom) the cubic atomic, cubic magnetic and impurity phases. The blue line at the bottom marks the difference between calculation and observation.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Lattice constant a [Å]</th>
<th>Volume of the unit cell [Å$^3$]</th>
<th>m$<em>{</em>{\text{MnI}}}$ [arb. units]</th>
<th>m$<em>{</em>{\text{MnII}}}$ [arb. units]</th>
<th>m$<em>{</em>{\text{tot}}}$ [arb. units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>5.850 ± 0.002</td>
<td>200.2 ± 0.3</td>
<td>7.2 ± 0.7</td>
<td>2.6 ± 0.6</td>
<td>9.8 ± 0.8</td>
</tr>
<tr>
<td>101</td>
<td>5.848 ± 0.002</td>
<td>200.0 ± 0.3</td>
<td>5.6 ± 0.4</td>
<td>0.7 ± 0.4</td>
<td>6.3 ± 0.5</td>
</tr>
<tr>
<td>121</td>
<td>5.850 ± 0.002</td>
<td>200.2 ± 0.3</td>
<td>5.4 ± 0.4</td>
<td>0.7 ± 0.4</td>
<td>6.1 ± 0.5</td>
</tr>
<tr>
<td>181</td>
<td>5.857 ± 0.002</td>
<td>200.9 ± 0.3</td>
<td>5.2 ± 0.4</td>
<td>0.9 ± 0.4</td>
<td>6.1 ± 0.5</td>
</tr>
<tr>
<td>239</td>
<td>5.866 ± 0.002</td>
<td>201.9 ± 0.3</td>
<td>4.1 ± 0.3</td>
<td>0.0 ± 0.4</td>
<td>4.1 ± 0.5</td>
</tr>
<tr>
<td>295</td>
<td>5.866 ± 0.002</td>
<td>201.8 ± 0.3</td>
<td>4.0 ± 0.3</td>
<td>0.0 ± 0.4</td>
<td>4.0 ± 0.5</td>
</tr>
</tbody>
</table>

Table 4.8: Summary of the lattice constants of the cubic phase in Mn$_{1.6}$Ni$_{1.4}$Ga for a few selected temperatures.

4.d Mn$_{1.4}$Ni$_{1.6}$Ga

Neutron diffraction patterns were obtained for an untreated sample of Mn$_{1.4}$Ni$_{1.6}$Ga at 5 K, 30 K, 70 K, 100 K, 200 K, 300 K, 400 K and 490 K. It transforms between 30 K and 200 K from the tetragonal low temperature phase with space group $I4/mmm$ to the fcc high temperature phase with space group $Fm\bar{3}m$ in at least three steps. This is consistent with observations in chapter 3. The diffraction patterns above 200 K remain similar. There is no impurity phase. The
model calculations reach satisfactory $\chi^2$ values between 14 (for 5 K) and 7 (for 400 K).

The lattice parameter for the cubic phase between 200 K and 490 K behaves normally as shown in figure 4.20. For the tetragonal phase the a-axis expands with increasing temperature while the c-axis contracts. As a result the volume is essentially temperature independent within the accuracy as determined by the experimental error bar. Table 4.9 lists the lattice constants for Mn$_{1.4}$Ni$_{1.6}$Ga.

**Figure 4.20:** Expansion of the lattice constant a of the cubic phase above 200 K. A linear fit is indicated. The equation used in the fit is given with units a and T as printed on the axes.

<table>
<thead>
<tr>
<th>T</th>
<th>lattice constant a [Å]</th>
<th>Volume of the unit cell [Å$^3$]</th>
<th>lattice constant a [Å]</th>
<th>lattice constant c [Å]</th>
<th>Volume (x2) of the unit cell [Å$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.8452 ± 0.0009</td>
<td>199.7 ± 0.1</td>
<td>3.8904 ± 0.0003</td>
<td>6.5834 ± 0.0006</td>
<td>199.43 ± 0.04</td>
</tr>
<tr>
<td>30</td>
<td>5.8443 ± 0.0009</td>
<td>199.6 ± 0.1</td>
<td>3.8904 ± 0.0003</td>
<td>6.5875 ± 0.0006</td>
<td>199.40 ± 0.04</td>
</tr>
<tr>
<td>70</td>
<td>5.8437 ± 0.0004</td>
<td>199.6 ± 0.1</td>
<td>3.8922 ± 0.0003</td>
<td>6.5793 ± 0.0006</td>
<td>199.34 ± 0.04</td>
</tr>
<tr>
<td>100</td>
<td>5.8451 ± 0.0005</td>
<td>199.7 ± 0.1</td>
<td>3.8971 ± 0.0003</td>
<td>6.5659 ± 0.0006</td>
<td>199.44 ± 0.04</td>
</tr>
<tr>
<td>200</td>
<td>5.8508 ± 0.0002</td>
<td>200.3 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>5.8606 ± 0.0002</td>
<td>201.3 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>5.8708 ± 0.0002</td>
<td>202.3 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>490</td>
<td>5.8821 ± 0.0003</td>
<td>203.5 ± 0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.9:** Summary of the lattice constants of the cubic and tetragonal phases in Mn$_{1.4}$Ni$_{1.6}$Ga.
Figure 4.21: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.4}$Ni$_{1.6}$Ga at T = 30 K. The first two (second two) lines of green bars indicate the peak positions of the cubic (tetragonal) phase. The blue line at the bottom marks the difference between calculation and observation.

Figure 4.22: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.4}$Ni$_{1.6}$Ga at T = 70 K. The first two (second two) lines of green bars indicate the peak positions of the cubic (tetragonal) phase (atomic and magnetic contribution). The blue line at the bottom marks the difference between calculation and observation.

Figure 4.23: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.4}$Ni$_{1.6}$Ga at T = 100 K. The first two (second two) lines of green bars indicate the peak positions of the cubic (tetragonal) phase (atomic and magnetic contribution). The blue line at the bottom marks the difference between calculation and observation.
Figure 4.24: Neutron diffraction pattern (red dots) and calculation (black line) of Mn$_{1.4}$Ni$_{1.6}$Ga at T = 400 K. The green bars indicate the peak positions of the cubic phase (second line: magnetic contribution). The blue line at the bottom marks the difference between calculation and observation.

Magnetic scattering is included in the analysis of the diffraction patterns up to 400 K. The refinement results in ferrimagnetic ordering on different crystallographic positions, but not antiferromagnetic. However, large error bars on the magnetic moments as gained by the refinement restrict the possibility of any further commenting.
5  Martensitic Domains in Ni$_2$MnGa

In this chapter the physics of the martensitic phase is investigated more closely. In particular the transformation matrices from the cubic austenitic phase to the pseudo-tetragonal martensitic phase, as identified in a neutron scattering experiment by Brown et al. [Brown04] for Ni$_2$MnGa, are used as a starting point to explore the details of the crystallographic transformation. The derivation of these transformation matrices is given here again. Thereafter the properties of the transformation matrices are analysed and studied. This is followed by an exploration into the construction of martensites and the networking of martensitic domains.

There are two different kinds of domains present in the martensitic phase which is indeed surprising. It is rather to be expected that different transformation processes, as described by matrices identified as type I and type II transformations in [Brown04], would give rise to different energy values thus promoting one domain type over the other as the temperature of the system is lowered towards 0 K. Experimentally, however, this is not was is being observed. Whilst the transformation is fully accomplished within a 4 degrees interval between 200K and 196 K on cooling, there is no change in the martensitic domain distribution on further cooling. Matrices of both, type I and type II, are found in the martensite. However, they differ only by their rotational part with both types having identical distortions. Thus their free energy is the same for the bulk of each martensitic domain.

It is of interest to investigate these domains in more detail. This can be done by inspecting their transformation matrices. For a single crystal or a collection of grains in a polycrystalline material there is the need for self-accommodation.
Some aspects of the processes by which this can be achieved will also be addressed.

This chapter is organised as follows. First the derivation of the transformation matrices of type I and type II as given by Brown et al. [Brown04] is presented. Then their properties are investigated and the details of the transformation are explained. It is shown how the transformation matrices are composed of rotations and deformations. These are identified for each of the transformation matrices. The link between different domains is established. Thereafter the question of domain walls between different martensitic domains will be discussed. The interface between martensitic and austenitic phases of the crystal will also be commented on.

5.a Derivation of the Austenite-Martensite Transformation Matrices

The form of the transformation matrices, which transform the austenite crystallographic lattice from the cubic phase to the martensitic lattice in the pseudo-tetragonal phase at low temperatures, has been identified by Brown et al. [Brown04] based on experimental observations in a single crystal investigation of Ni$_2$MnGa. The derivation employed in this thesis closely adheres to the description given in [Brown04].

It is an experimental observation that the martensitic transformation in Ni$_2$MnGa is affected by shear stresses. Let a general shear be described by a vector $\vec{\tau}$. The shear acts in a plane which is characterised by a normal vector $\vec{k}$. $\vec{k}$ is oriented perpendicular to the plane and can be chosen to be a unit vector, i.e. $|\vec{k}|^2 = 1$. Obviously due to the orientation of these vectors one obtains $\vec{k} \cdot \vec{\tau} = 0$. In this
plane perpendicular to \( \vec{k} \) the displacement \( \vec{\delta} \) of an atom, which is originally located at position \( \vec{r} \), is given by \( \vec{\delta} = (\tau \otimes \vec{k}) \vec{r} \).

Here \( \tau \otimes \vec{k} \) is the tensor product which is defined as

\[
\tau \otimes \vec{k} = \begin{pmatrix} \tau_1 k_1 \\ \tau_2 k_2 \\ \tau_3 k_3 \end{pmatrix} = \begin{pmatrix} \tau_1 k_1 & \tau_1 k_2 & \tau_1 k_3 \\ \tau_2 k_2 & \tau_2 k_2 & \tau_2 k_3 \\ \tau_3 k_3 & \tau_3 k_2 & \tau_3 k_3 \end{pmatrix}
\]

Following Bhattacharya [Bhattacharya03] the expression for \( \vec{\delta} \) can be simplified according to

\[
\vec{\delta} = (\tau \otimes \vec{k}) \vec{r} = \begin{pmatrix} \tau_1 \\ \tau_2 \\ \tau_3 \end{pmatrix} \begin{pmatrix} k_1 \\ k_2 \\ k_3 \end{pmatrix}^T = (\vec{r} \cdot \vec{k}) \vec{r}
\]

Here \( \vec{r} \cdot \vec{k} \) is the scalar product of vectors \( \vec{r} \) and \( \vec{k} \). \((...)^T\) denotes the transpose of the entity in brackets.

A transformation which may be described by a matrix \( \vec{M} \) takes a point at position \( \vec{r} \) to another point with position \( \vec{r}' \)

\[
\vec{r}' = \vec{M} \vec{r}
\]

The transformation of atomic positions within the unit cell from the original position \( \vec{r} \) to a new one at \( \vec{r}' = \vec{r} + \vec{\delta} \) is obtained by the matrix \( \vec{M} \) as stated, in component form, by

\[
M_{ij} = I_{ij} + \tau_i k_j
\]

Here \( \vec{I} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \) is the unit matrix and \( I_{ij} = \delta_{ij} \) are its components. \( \delta_{ij} \) is the discrete \( \delta \)-function which is equal to 1 if \( i = j \) and zero otherwise.
For Ni$_2$MnGa the transformation to the martensitic state is affected by two successive shear displacements. Let these shear displacements be described by \( \vec{\tau} \) and \( \vec{\sigma} \) and the planes by \( \vec{k} \) and \( \vec{q} \), respectively. It is also assumed that the shear displacements are small, and that it is therefore permissible to neglect the product of the displacements. These are essentially the assumptions of a linear theory for the description of the transformation.

With these assumptions the transformation matrix \( \vec{M} \) takes the explicit form

\[
\vec{M} = \begin{pmatrix}
1 + \tau_1 k_1 + \sigma_1 q_1 & \tau_1 k_2 + \sigma_1 q_2 & \tau_1 k_3 + \sigma_1 q_3 \\
\tau_2 k_1 + \sigma_2 q_1 & 1 + \tau_2 k_2 + \sigma_2 q_2 & \tau_2 k_3 + \sigma_2 q_3 \\
\tau_3 k_1 + \sigma_3 q_1 & \tau_3 k_2 + \sigma_3 q_2 & 1 + \tau_3 k_3 + \sigma_3 q_3
\end{pmatrix}
\]

This is the most general form of the transformation matrix. In order for this matrix to actually represent an orthogonal transformation the off-diagonal parts of the matrix have to be skew-symmetric. This requires

\[
\tau_1 k_2 + \sigma_1 q_2 = -(\tau_2 k_1 + \sigma_2 q_1)
\]
\[
\tau_1 k_3 + \sigma_1 q_3 = -(\tau_3 k_1 + \sigma_3 q_1)
\]
\[
\tau_2 k_3 + \sigma_2 q_3 = -(\tau_3 k_2 + \sigma_3 q_2)
\]

The diagonal elements of \( \vec{M} \) can be related to the volume change \( \delta V \) of the unit cell due to the transformation. This is related to the trace (i.e. sum of diagonal elements) as

\[
\delta V = tr(\vec{M} - \vec{I})
\]

For the above matrix this reduces to

\[
\delta V = \tau_1 k_1 + \sigma_1 q_1 + \tau_2 k_2 + \sigma_2 q_2 + \tau_3 k_3 + \sigma_3 q_3
\]

It is obvious that
This arises due to the orthogonality of the vectors \( \vec{\tau} \) and \( \vec{k} \), as well as \( \vec{\sigma} \) and \( \vec{q} \). Thus the martensitic transformation is a volume conserving transformation.

Following Brown et al. [Brown04] shears are expected to be on \{110\} planes in \( <\bar{1}10> \) directions. Further analysis is carried out by selecting two particular shear planes and directions as follows:

Shear 1:

\[
\vec{k} = (0,1,1)
\]

\[
\vec{\tau} = [0, \bar{\tau}, \bar{\tau}]
\]

Shear 2:

\[
\vec{q} = (1,0,1)
\]

\[
\vec{\sigma} = [\sigma, 0, \bar{\sigma}]
\]

Successively inserting these values into the expression for the matrix \( \bar{M} \) yields\(^1\)

\[
\bar{M} = \begin{pmatrix}
1 + \tau_1 k_1 + \sigma_1 q_1 & \tau_1 k_2 + \sigma_1 q_2 & \tau_1 k_3 + \sigma_1 q_3 \\
\tau_2 k_1 + \sigma_2 q_1 & 1 + \tau_2 k_2 + \sigma_2 q_2 & \tau_2 k_3 + \sigma_2 q_3 \\
\tau_3 k_1 + \sigma_3 q_1 & \tau_3 k_2 + \sigma_3 q_2 & 1 + \tau_3 k_3 + \sigma_3 q_3
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 + 0 + \sigma q_1 & 0 + \sigma q_2 & 0 + \sigma q_3 \\
-\tau k_1 + 0 & 1 - \tau k_2 + 0 & -\tau k_3 + 0 \\
\tau k_1 - \sigma q_1 & \tau k_2 - \sigma q_2 & 1 + \tau k_3 - \sigma q_3
\end{pmatrix}
\]

\[
= \begin{pmatrix}
1 + \sigma & 0 & \sigma \\
0 & 1 - \tau & -\tau \\
-\sigma & \tau & 1 + \tau - \sigma
\end{pmatrix}
\]

The shears in this transformation have to give rise to a pseudo-tetragonal unit cell with a cell ratio of \( \frac{c}{a} < 1 \) for the tetragonal unit cell (this statement refers to the cubic unit cell axes and it has to be adjusted for any change of unit cell). This requires 2 of the diagonal elements to be identical. There are a total of 3 possibilities to achieve this.

\(^1\) A minor misprint has to be corrected in the matrix \( \bar{M} \) in the original publication of Brown et al. [Brown04].
**Possibility 1:** set $M_{11} = M_{22}$

This yields

$$1 + \sigma = 1 - \tau$$

or

$$\tau = -\sigma$$

Matrices obtained by setting $\tau = -\sigma$ will be referred to as describing **type I domains.** This is denoted by a subscript 1 on the matrix. These are obtained for equal magnitudes of the shear. The matrix then takes the form

$$\overline{M}_{1xy} = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}$$

**Possibility 2:** set $M_{11} = M_{33}$

This possibility yields

$$1 + \sigma = 1 + \tau - \sigma$$

or

$$\tau = 2\sigma$$

Matrices obtained by setting $\tau = 2\sigma$ will be referred to as describing **type II domains.** This is denoted by a subscript 2 on the matrix. These are obtained for shears where one shear is twice, or half, of the magnitudes of the other shear. The matrix then takes the form

$$\overline{M}_{2xy} = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 - 2\sigma & -2\sigma \\ -\sigma & 2\sigma & 1 + \sigma \end{pmatrix}$$
The indices \(x\) and \(y\) for \(\vec{M}_{2xy}\) indicate the shear and specify the positions of the zero for the first and the second shear, respectively.

**Possibility 3:** set \(M_{22} = M_{33}\)

This possibility yields

\[
1 - \tau = 1 + \tau - \sigma
\]

or

\[
\tau = \frac{1}{2} \sigma
\]

The matrix obtained by setting \(\tau = \frac{1}{2} \sigma\) takes the form

\[
\vec{M} = \begin{pmatrix}
1 + \sigma & 0 & \frac{1}{2} \sigma \\
0 & 1 - \frac{1}{2} \sigma & -\frac{1}{2} \sigma \\
-\sigma & \frac{1}{2} \sigma & 1 + \frac{1}{2} \sigma - \sigma
\end{pmatrix} = \begin{pmatrix}
1 + \sigma & 0 & \frac{1}{2} \sigma \\
0 & 1 - \frac{1}{2} \sigma & -\frac{1}{2} \sigma \\
-\sigma & \frac{1}{2} \sigma & 1 - \frac{1}{2} \sigma
\end{pmatrix}
\]

This possibility yields a matrix of type II. Setting \(\tilde{\sigma} = -\frac{\sigma}{2}\) and not writing the tilde results in

\[
\vec{M} = \begin{pmatrix}
1 - 2\sigma & 0 & -2\sigma \\
0 & 1 + \sigma & \sigma \\
2\sigma & -\sigma & 1 + \sigma
\end{pmatrix}
\]

This matrix is the same as matrix \(\vec{M}_{2xy}\) but with a different choice of axes.

This completes the derivation of the transformation matrices as carried out by Brown et al. [Brown04]. Next these matrices will be considered and their properties analysed more closely.
5.b Properties of the transformation matrix of type I

As pointed out above for a positive value of $\sigma$ the transformation of the austenitic cubic lattice to the pseudo-tetragonal martensitic lattice a matrix of type I is given as

$$\bar{M}_{1xy}(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}$$

In linear order the volume of the unit cell is constant. For the transformation 2 lattice parameters expand while the $3^{rd}$ lattice parameter shrinks. The transformation is an orthogonal transformation as the off-diagonal part of the matrix is skew-symmetric.

First an illustration of the transformation is helpful. The transformation matrix is based on 2 shears with the following properties:

Shear 1: \[\vec{k} = (0,1,1)\]
\[\vec{\tau} = [0, \vec{\tau}, \vec{\tau}]\]

Shear 2: \[\vec{q} = (1,0,1)\]
\[\vec{\sigma} = [\sigma, 0, \vec{\sigma}]\]

The planes characterised by the vectors $\vec{k}$ and $\vec{q}$ are shown in figures 5.1 and 5.2, respectively. These planes are given different colours, blue and green, in order to be able to distinguish them in a combined plot.
Figure 5.1: Plot of the \( \vec{k} = (0,1,1) \) plane in real space. A suitable coordinate system within the plane is indicated. The dotted line connecting points (0,0,0) and (1,1,-1) is the line of intersection with the plane \( \vec{q} = (1,0,1) \). For details see text.

Figure 5.2: Plot of the \( \vec{q} = (1,0,1) \) plane in real space. A suitable coordinate system within the plane is indicated. The dotted line connecting points (0,0,0) and (1,1,-1) is the line of intersection with the plane \( \vec{k} = (0,1,1) \). For details see text.

Figure 5.3 (c) shows the location of the two planes within the cube \(-1 \leq x, y, z \leq 1\). The line of intersection of the two planes is a \(<111>\) direction. The shears, which for a type I matrix are restricted to \(\tau = -\sigma\), are also indicated.
Figure 5.3: Figure (a) shows the orientation of the coordinate system while in figure (b) the two shear planes for the $\vec{k} = (0,1,1)$ (blue) and $\vec{q} = (1,0,1)$ (green) are shown. The direction of the shear displacements is indicated by arrows in the respective planes. The intersection of the planes is a $<1,1,1>$ axis. The x-y-planes is shown in grey for $z = 0$. Within this plane a $<1,1,0>$ rotation axis is located. Figure (c) shows the transformation of a cube for $\sigma = 0.10$ according to the transformation shown in (b). For details see text.

The austenite-martensite transformation as described by the matrix $\overline{M}_{1xy}$ will now be considered. It is natural to ask whether or not there are any directions, or possibly planes, which are not changed by this transformation. This question can be answered by investigating the eigenvalues and the eigenvectors of the matrix. Its eigenvalues and eigenvectors have been calculated and are shown in table 5.1. It is seen from the table that indeed there is an invariant direction. An eigenvalue of 1 indicates that a vector in this direction is not altered, but remains invariant in length and direction during the transformation. Comparing the eigenvector with the plot of figure 5.3 identifies the eigenvector as being along the intersection of the two shear planes. The other eigenvectors listed in table 5.1 are lengthened or shortened by a factor of $1 + \sigma$ or $1 - \sigma$, respectively. For both eigenvectors their direction is not altered, but only their length.
Table 5.1: Determination of the eigenvalues and eigenvectors, together with their norm, for the type I transformation matrix $\tilde{M}_{1xy}(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}$.

It is pointed out that the transformation matrix $\tilde{M}_{1xy}$ represents an orthogonal transformation, but that $\tilde{M}_{1xy}$ is not hermitian. For a hermitian matrix, all eigenvalues are real, and eigenvectors to different eigenvalues are orthogonal. While for $\tilde{M}_{1xy}$ all eigenvalues are real, not all eigenvectors are orthogonal. This is seen by evaluating the scalar product of vectors 1 and 2, which yields

$$\begin{pmatrix} -1 \\ -1 \\ 1 \end{pmatrix} \cdot \begin{pmatrix} -1/2 \\ 1/2 \\ 1 \end{pmatrix} = 2 \neq 0$$

In order to extract the physics of this transformation it is useful to decompose the transformation matrix $\tilde{M}_{1xy}$ into a product of a pure rotation matrix $\tilde{Q}$ and a positive-definite symmetric matrix $\tilde{U}$ (stretch matrix) as

$$\tilde{M}_{1xy} = \tilde{Q} \cdot \tilde{U}$$

This separation is also known as the **polar decomposition** of the matrix $\tilde{M}_{1xy}$. 
Following Bhattacharya [Bhattacharya03], the decomposition is achieved with the following steps:

1. Calculate the matrix $\bar{c} = (\overline{M}_{1xy})^T \cdot \overline{M}_{1xy}$. This matrix is symmetric and positive-definite.

2. Determine the eigenvalues $\{\lambda_1, \lambda_2, \lambda_3\}$ and eigenvectors $\{\bar{c}_1, \bar{c}_2, \bar{c}_3\}$ of $\bar{c}$. As the matrix $\bar{c}$ is symmetric with real entries, it is also hermitian. Thus the eigenvectors are orthogonal and, if chosen normalised, orthonormal, i.e. $\bar{c}_i \cdot \bar{c}_j = \delta_{i,j}$. Furthermore as $\bar{c}$ is positive-definite, all eigenvalues are positive, i.e. $\lambda_i > 0$ for all $i = \{1, 2, 3\}$. It will be assumed that the eigenvectors are also normalised.

3. Calculate $\mu_i = \sqrt{\lambda_i}$. The positive root has to be chosen so that $\mu_i > 0$ for all $i = \{1, 2, 3\}$.

4. Obtain the matrix $\bar{U}$ with eigenvalues $\{\mu_1, \mu_2, \mu_3\}$ and eigenvectors $\{\bar{c}_1, \bar{c}_2, \bar{c}_3\}$. This is achieved by calculating
   \[
   \bar{U} = \mu_1 \bar{c}_1 \otimes \bar{c}_1 + \mu_2 \bar{c}_2 \otimes \bar{c}_2 + \mu_3 \bar{c}_3 \otimes \bar{c}_3
   \]

5. Obtain the rotation matrix $\bar{Q}$ by calculating
   \[
   \bar{Q} = \overline{M}_{1xy} \cdot \bar{U}^{-1}
   \]

This procedure is too complicated to carry out on the general form of the matrix $\overline{M}_{1xy}(\sigma)$ for a general value of $\sigma$. However, setting $\sigma$ to a particular numerical value will render the transformation matrix a simple matrix with numerical entries. Carrying out the calculation for such a matrix is easier.

This calculation is carried out for a value of $\sigma = 0.16$. This is an unrealistically large value. However, it will serve to bring out some of the approximations inherent in the present description. Using this value one obtains the matrix $\overline{M}_{1xy}(\sigma = 0.16)$ as
\[ \bar{M}_{1xy}(\sigma = 0.16) = \begin{pmatrix} 1.16 & 0 & 0.16 \\ 0 & 1.16 & 0.16 \\ -0.16 & -0.16 & 0.68 \end{pmatrix} \]

The matrix \( \bar{C} \) is obtained as

\[ \bar{C} = \left( \bar{M}_{1xy}(\sigma = 0.16) \right)^T \cdot \bar{M}_{1xy}(\sigma = 0.16) = \begin{pmatrix} 1.371 & 0.026 & 0.077 \\ 0.026 & 1.371 & 0.077 \\ 0.077 & 0.077 & 0.514 \end{pmatrix} \]

The eigenvalues of \( \bar{C} \) are \{0.500, 1.346, 1.410\}, and the corresponding eigenvectors are

\[ \{ \bar{c}_1, \bar{c}_2, \bar{c}_3 \} = \left\{ \begin{pmatrix} 0.085 \\ 0.085 \\ -0.993 \end{pmatrix}, \begin{pmatrix} 0.707 \\ -0.707 \\ 0.000 \end{pmatrix}, \begin{pmatrix} -0.702 \\ -0.702 \\ -0.120 \end{pmatrix} \right\} \]

The matrix \( \bar{U} \) is obtained as

\[ \bar{U} = \begin{pmatrix} 1.170 & 0.010 & 0.041 \\ 0.010 & 1.170 & 0.041 \\ 0.041 & 0.041 & 0.714 \end{pmatrix} \]

Determining \( \bar{U}^{-1} = \begin{pmatrix} 0.856 & -0.006 & -0.048 \\ -0.006 & 0.856 & -0.048 \\ -0.048 & -0.048 & 1.405 \end{pmatrix} \) and multiplying this with \( \bar{M}_{1xy}(\sigma = 0.16) \) one obtains

\[ \bar{Q} = \bar{M}_{1xy} \cdot \bar{U}^{-1} = \begin{pmatrix} 0.986 & -0.014 & 0.169 \\ -0.014 & 0.986 & 0.169 \\ -0.169 & -0.169 & 0.971 \end{pmatrix} \]

It is a straightforward matter to check the result as
This decomposition of the transformation matrix allows the presentation of the transformation to be written as a pure stretch and a rotation. The rotation part is analysed first.

Taking the rotation matrix

\[
\bar{Q} = \begin{pmatrix}
0.986 & -0.014 & 0.169 \\
-0.014 & 0.986 & 0.169 \\
-0.169 & -0.169 & 0.971 \\
\end{pmatrix}
\]

its eigenvalues and eigenvectors can be determined numerically. The eigenvalue of 1 and its associated eigenvectors are of interest, as these vectors remain invariant under the rotation. This arises because an eigenvector to the eigenvalue 1 is oriented along the axis of rotation. This axis is determined as the \( \hat{p} = \frac{1}{\sqrt{2}} (-1,1,0) \) direction. The rotation angle \( \theta \) can be obtained using the trace of \( \bar{Q} \) and the following relation with the rotation angle \( \theta \):

\[
tr(\bar{Q}) = 1 + 2\cos(\theta)
\]

Using other numeric values of \( \sigma \) reveals that the rotation axis for \( \bar{Q} \) is not changed but only the rotation angle. Thus one may obtain the rotation matrix in explicit form. The rotation axis is \( \frac{1}{\sqrt{2}} (-1,1,0) \) and its relation with respect to the planes and the direction of the shears is also shown in figure 5.3.
There exists an ambiguity with respect to the orientation of the rotation axis. As both \( \vec{p} \) as well as \(-\vec{p}\) are eigenvectors to the same eigenvalue it is prudent to choose the axis such that the rotation angle is taken as positive.

With \( \vec{p} \) denoting the rotation axis one obtains \( \bar{Q} \) as

\[
\bar{Q}(\theta) = \cos(\theta) \cdot \vec{I} + \sin(\theta) \cdot [\vec{p}]_x + (1 - \cos(\theta)) \cdot \vec{p} \otimes \vec{p}
\]

Here \( \vec{I} \) is the unit matrix, \( [\vec{p}]_x \) is the cross product matrix defined as

\[
[\vec{p}]_x = \begin{pmatrix}
0 & -p_z & p_y \\
p_z & 0 & -p_x \\
-p_y & p_x & 0
\end{pmatrix}
\]

and \( \vec{p} \otimes \vec{p} \) is the matrix of the tensor product. It has the form

\[
\vec{p} \otimes \vec{p} = \begin{pmatrix}
p_x & p_xp_x & p_xp_y & p_xp_z \\
p_y & p_xp_y & p_y & p_y \\
p_z & p_xp_z & p_y & p_z \\
p_z & p_zp_x & p_zp_y & p_zp_z
\end{pmatrix}
\]

Using the value of \( \sigma = 0.16 \) and a rotation axis with orientation \( \vec{p} = \frac{1}{\sqrt{2}}(-1,1,0) \) the angle of rotation is obtained as \( \theta = 13.818^\circ \) (measured in degrees) while the rotation matrix takes the form

\[
\tilde{Q}(\theta) = \begin{pmatrix}
\frac{1 + \cos(\theta)}{2} & \frac{1 - \cos(\theta)}{2} & \frac{\sin(\theta)}{\sqrt{2}} \\
\frac{-1 + \cos(\theta)}{2} & \frac{1 + \cos(\theta)}{2} & -\frac{\sin(\theta)}{\sqrt{2}} \\
\frac{\sin(\theta)}{\sqrt{2}} & -\frac{\sin(\theta)}{\sqrt{2}} & \frac{\cos(\theta)}{\sqrt{2}}
\end{pmatrix}
\]

Inserting the value of \( \theta = 13.818^\circ \) into this expression yields

\[
\tilde{Q}(\theta = 13.818^\circ) = \begin{pmatrix}
0.986 & -0.014 & 0.169 \\
-0.014 & 0.986 & 0.169 \\
-0.169 & -0.169 & 0.971
\end{pmatrix}
\]
This compares well with the rotation matrix \( \bar{Q} = \begin{pmatrix} 0.986 & -0.014 & 0.169 \\ -0.014 & 0.986 & 0.169 \\ -0.169 & -0.169 & 0.971 \end{pmatrix} \) which has been obtained above.

It is instructive to obtain the dependence of the rotation angle \( \theta \) on the magnitude of the strain \( \sigma \). The procedure for obtaining this dependence is to calculate \( \bar{M}_{1xy}(\sigma) \) and obtain \( \bar{Q}(\sigma) \) for each value of \( \sigma \). The rotation matrix will allow the rotation angle \( \theta(\sigma) \) to be obtained. The graph is shown in figure 5.4. A linear approximation is also included. This approximation has been obtained by using \( \theta(\sigma = 0.4) \) and dividing it by the \( \sigma \) value of 0.4. A numeric slope value of 88.161 (measured in units of degree per unit of \( \sigma \)) is obtained. The straight line, passing through the origin and having the above determined slope, is also shown in figure 5.4 as a red line.

![Figure 5.4](image)

**Figure 5.4:** Plot of the \( \theta(\sigma) \) dependence as obtained by a numerical analysis of the rotation matrix \( \bar{Q}(\sigma) \). The red line is a linear approximation which has been obtained by fixing the slope with the value of \( \theta(\sigma = 0.4) \). For details see text.

Now the matrix \( \bar{U} \) is discussed. As pointed out by Bhattacharya [Bhattacharya03] the transformation matrices for a cubic to tetragonal transformation have the generic form
Here one of the 3 possible transformation matrices has been chosen. Compared to the experimentally determined transformation matrix as identified above, which has the form

\[ \bar{U}_{exp} = \begin{pmatrix} 1.170 & 0.010 & 0.041 \\ 0.010 & 1.170 & 0.041 \\ 0.041 & 0.041 & 0.714 \end{pmatrix} \]

it is readily observed that there are some differences. The off-diagonal elements are small, but non-zero.

This essentially arises due to the approximation employed in the derivation of the transformation matrix. The derivation has been carried out under the assumption that the product of shear displacements can be neglected. This is equivalent to the approximation of the geometrically linear theory. This theory is correct up to order \( \sigma \).

Indeed the condition for the conservation of the volume of the unit cell has been derived in the form \( \delta V = \text{tr}(\bar{M} - \bar{I}) \). However, for the exact, non-linear transformation theory the condition for conservation of the unit cell volume is

\[ \text{det}(\bar{M}) = \|\bar{M}\| = 1 \]

The transformation matrices \( \bar{M} \), both type I and type II, satisfy \( \text{tr}(\bar{M} - \bar{I}) = 0 \) but one obtains

\[ \text{det}(\bar{M}_{1xy}) = \|\bar{M}_{1xy}\| = 1 - \sigma^2 \]

\[ \text{det}(\bar{M}_{2xy}) = \|\bar{M}_{2xy}\| = 1 - 2\sigma^2 \]
Thus the results are only correct to order $\sigma$. As the $\sigma$ value used for the above calculation was $\sigma = 0.16$ one obtains $\sigma^2 = 0.026$. It is readily seen that the off-diagonal values in the matrix $\bar{U}_{\text{exp}}$ are of this order of magnitude. Therefore these entries are below the accuracy of the present description, and consequently no physically relevant aspects are connected to these numbers.

It is possible to use the elements as identified by the linear description in order to set up a non-linear description. This would involve replacing $\bar{U}_{\text{exp}}$ by a matrix of the form $\bar{U}_x$ with suitable $\alpha$ and $\beta$ values. Thus one can ensure that $\|\bar{U}_x\| = 1$. Multiplying by a rotation matrix $\bar{Q}(\theta)$ such that the resulting matrix has a $(1,1,1)$ eigenvector one obtains a non-linear transformation matrix, with determinant equal to 1. The final transformation matrix has all the relevant features described above for the linear transformation, but it will be correct to higher orders in $\sigma$. However, such a discussion will be pursued only later in this chapter.

5.c Properties of the transformation matrix of type II

As pointed out for the derivation of the transformation matrices $\bar{M}$, type II transformations are obtained for the 2 strains satisfying the condition $\tau = 2\sigma$. This yields transformation matrices of the form

$$\bar{M}_{2xy}(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 - 2\sigma & -2\sigma \\ -\sigma & 2\sigma & 1 + \sigma \end{pmatrix}$$

The planes in which the shears operate are the same as those shown in figures 5.1 and 5.2. However, compared to the shear pattern in 3d, as shown for type I transformations in figure 5.3, for type II transformations the two shears have different magnitudes. The transformation is shown in figure 5.5 below. The condition $\tau = 2\sigma$ implies that one shear is twice the magnitude of the other. In
addition the direction of one of the shears in figure 5.5 is reversed compared to the direction in figure 5.3.

The analysis of the transformation matrix of type II can proceed in the same manner as the analysis for type I matrices. Determining the eigenvectors and eigenvalues of the matrix will yield information on the particular directions connected with this transformation. The list of these values is given in table 5.2. It can be seen that one eigenvalue is equal to 1 and its associated eigenvector is in the direction of the (1,1,−1) axis which constitutes the intersection of the 2 shear planes. The type II transformation has this feature in common with the
type I transformation matrix as shown in table 5.1. The remaining eigenvalues of
the matrix $\overline{M}_{2xy}$ are complex. The associated eigenvectors are also complex. It is
to be noted that the eigenvectors are also not orthogonal to one another.
Indeed if an eigenvector to eigenvalue $\lambda_i$ is denoted by $\vec{v}_i$ then one obtains
$\vec{v}_1 \cdot \vec{v}_2 = \vec{v}_1 \cdot \vec{v}_3 = \vec{v}_2 \cdot \vec{v}_3 = 2$. For this multiplication no complex conjugation
has been applied.

As discussed in connection with type I transformations the transformation
matrices are non-hermitian matrices, for which eigenvalues do not have to be
real and eigenvectors belonging to different eigenvalues are not automatically
perpendicular to one another. These features are displayed by the eigenvalues
and eigenvectors of the type II transformation matrix as shown in table 5.2.

<table>
<thead>
<tr>
<th>eigenvalue</th>
<th>eigenvector</th>
<th>norm of eigenvector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\begin{pmatrix} -1 \ -1 \ 1 \end{pmatrix}$</td>
<td>$\sqrt{3}$</td>
</tr>
<tr>
<td>2</td>
<td>$\begin{pmatrix} \frac{-1}{3} - i\frac{\sqrt{2}}{3} \ \frac{2}{3} + i\frac{\sqrt{2}}{3} \ \frac{3}{1} \end{pmatrix}$</td>
<td>$\sqrt{2}$</td>
</tr>
<tr>
<td>3</td>
<td>$\begin{pmatrix} \frac{1}{3} + i\frac{\sqrt{2}}{3} \ \frac{2}{3} - i\frac{\sqrt{2}}{3} \ \frac{3}{1} \end{pmatrix}$</td>
<td>$\sqrt{2}$</td>
</tr>
</tbody>
</table>

Table 5.2: Determination of the eigenvalues and eigenvectors, together with their norm, for the type II
transformation matrix $\overline{M}_{2xy}(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 - 2\sigma & -2\sigma \\ -\sigma & 2\sigma & 1 + \sigma \end{pmatrix}$.
Further analysis of the matrix $\overline{M}_{2xy}$ can be carried out using the same procedure as was applied for the type I transformation matrix. One seeks to write the transformation as a product of a rotation and a stretch operation as

$$\overline{M}_{2xy} = \overline{Q}^{(2)} \cdot \overline{U}^{(2)}$$

Adopting again a value of $\sigma = 0.16$ for the numerical analysis one obtains

$$\overline{M}_{2xy}(\sigma = 0.16) = \begin{pmatrix} 1.160 & 0 & 0.160 \\ 0 & 0.680 & -0.320 \\ -0.160 & 0.320 & 1.160 \end{pmatrix}$$

Following the decomposition procedure as described above one arrives at

$$\overline{Q}^{(2)} = \begin{pmatrix} 0.991 & 0.022 & 0.130 \\ 0.022 & 0.945 & -0.325 \\ -0.130 & 0.325 & 0.937 \end{pmatrix} \quad \overline{U}^{(2)} = \begin{pmatrix} 1.171 & -0.027 & 0.001 \\ -0.027 & 0.747 & 0.078 \\ 0.001 & 0.078 & 1.211 \end{pmatrix}$$

It can be readily verified that $(\overline{Q}^{(2)})^T \overline{Q}^{(2)} = I$ and that $\|\overline{Q}^{(2)}\| = 1$ as required for a rotation matrix. Investigating the eigenvalues and eigenvectors of $\overline{Q}^{(2)}$ reveals that the rotation matrix has an eigenvalue of 1 with a normalised eigenvector of $(0.929, 0.371, 0)$. This vector indicates the rotation axis. It turns out that the orientation of the rotation axis depends on the value of $\sigma$. Using a value of $\sigma = 0.016$ for $\overline{M}_{2xy}(\sigma = 0.016)$ one obtains an eigenvector, i.e. the rotation axis, at $(0.899, 0.439, 0)$. The rotation axis is close to the x-axis $(1, 0, 0)$ and located within the x-y plane. Let $\varphi$ be the angle of the rotation axis with the x-axis. This angle can be calculated as a function of $\sigma$, and it is shown in figure 5.6.
The rotation angle $\theta$ around the axis of rotation as determined by $\mathbf{Q}^{(2)}(\sigma)$ can also be calculated. The procedure is the same as for the rotation matrix of type I transformations. The result is shown in figure 5.7.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5_6.jpg}
\caption{Plot of the angle $\varphi(\sigma)$ of the rotation axis of $\mathbf{Q}^{(2)}(\sigma)$ as a function of $\sigma$. The rotation axis is located within the x-y plane. The blue circles are the numeric values, and the red line is a least squares fit to a polynomial of degree 2, namely $\varphi(\sigma) = 26.491 - 33.435 \cdot \sigma + 25.789 \cdot \sigma^2$.}
\end{figure}

Next the distortion matrix $\mathbf{U}^{(2)}$ is analysed. Consideration of the distortion matrix $\mathbf{U}^{(2)}$ reveals the same features as have been observed for matrix $\mathbf{U}^{(1)}$. The off-diagonal elements are zero to within a value of order $\sigma^2$. For the value of
99

σ used in the example above of σ = 0.16 one obtains σ² = 0.026. Thus, within this accuracy the matrix

$$
\bar{U}^{(2)} = \begin{pmatrix}
1.171 & -0.027 & 0.001 \\
-0.027 & 0.747 & 0.078 \\
0.001 & 0.078 & 1.211
\end{pmatrix}
$$

can be taken to represent

$$
\bar{U}^{(2)}_{\text{ideal}} = \begin{pmatrix}
\alpha & 0 & 0 \\
0 & \beta & 0 \\
0 & 0 & \alpha
\end{pmatrix}
$$

Within the accuracy one has \(\alpha \approx 1.171 \approx 1.211\) and \(\beta = 0.747\). As for the matrix \(\bar{U}^{(1)}\) one obtains

$$
det(\bar{U}^{(2)}) = \|\bar{U}^{(2)}\| = 1.051
$$

Given that the determinant of the transformation matrix is

$$
det(\bar{M}_{2xy}) = 1 - 2\sigma^2
$$

this is consistent with the explanations given before for the type I transformation.

The linear description as given here may be modified to obtain a more general and non-linear description by ensuring that \(det(\bar{M}_{2xy}) = 1\). This can be achieved by a modification of the distortion matrix. This approach will be discussed later in the chapter.

5.d Domain structure and transformation matrices for the martensitic phase

After having established the properties of the transformation matrices of type I and type II attention is now turned to establishing the full set of transformation matrices for the austenite-martensite transformation. Based on a geometric argument Brown et al. [Brown04] have identified that there are 12 different domains of type I and 24 different domains of type II possible for Ni₂MnGa. Here
a more formal process is used to confirm this result. Transformation matrices which transform the austenite structure to differently oriented versions of the martensite are related to one another by a symmetry transformation. The symmetry operator is a transformation which belongs to the cubic point group of the austenitic structure.

According to the *International Tables of Crystallography* [Hahn83] the point group of the Ni$_2$MnGa structure is $m\overline{3}m$. This point group has 48 elements. This group can be generated by using the following generating elements in addition to the identity element (the symmetry element number corresponds to the symmetry element as identified for space group #225 of Ni$_2$MnGa in the *International Tables of Crystallography* [Hahn83]):

<table>
<thead>
<tr>
<th>Symmetry element</th>
<th>description</th>
<th>Rotation Matrix</th>
<th>3-fold rotation around (111)-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2) (5)</td>
<td>2-fold rotation around z-axis</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; \bar{1} &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>(3) (13)</td>
<td>2-fold rotation around y-axis</td>
<td>$\begin{pmatrix} \bar{1} &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; \bar{1} \end{pmatrix}$</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; \bar{1} \end{pmatrix}$</td>
</tr>
<tr>
<td>(25)</td>
<td>Inversion operator</td>
<td>$\begin{pmatrix} \bar{1} &amp; 0 &amp; 0 \ 0 &amp; \bar{1} &amp; 0 \ 0 &amp; 0 &amp; \bar{1} \end{pmatrix}$</td>
<td></td>
</tr>
</tbody>
</table>

Note: the notation $\bar{1} = -1$ is used here.

These generating symmetry elements suffice to generate all 48 symmetry elements of the point group. Using these point group symmetry operators $R_i$ one may obtain symmetry related transformation matrices by using the similarity transformation

$$\tilde{M}_{1xy} = R_i^T \cdot M_{1xy} \cdot R_i$$
for either type I or type II transformations. Here $R_i$ is one of the rotations, or roto-inversions, or mirror operations, or inversion, which forms part of the point group. The index $i$ runs from 1 (indicating the identity element, or unit matrix) to a maximum of 48. The superscript T indicates transposition of the matrix. This is equivalent to generating the inverse as $R_i^T \cdot R_i = \bar{R} = R_1$ for all values of $i$.

5.d.i Investigation of type I Transformations

The transformation matrices for the space group are given in table 5.3. Using these tables the various transformation matrices of type I have been identified. These are given in table 5.4, together with the point group elements which transform the reference transformation matrix (which is taken to be the same as the one originally identified)

$$\tilde{M}_{1xy}(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}$$

into itself. For the symmetry related transformation matrices $\tilde{M}_1$ one transformation operator (the one with the lowest index $i$) is chosen such that $\tilde{M}_1 = R_i^T \cdot \tilde{M}_{1xy} \cdot R_i$. For convenience the invariant $(1,1,1)$-axis of the matrix $\tilde{M}_{1xy}$ as well as the rotation axis for the rotation of the matrix $Q$ in the decomposition $\tilde{M}_1 = \tilde{Q} \cdot \tilde{U}$ are also given. For later convenience and discussions the type of the U matrix is also identified by its index (using the {x, y, z} notation interchangeably with {1, 2, 3}) as shown in the last column of table 5.4.
<table>
<thead>
<tr>
<th>i</th>
<th>$R_i$</th>
<th>17</th>
<th>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 0 &amp; -1 &amp; 0 \end{pmatrix}$</th>
<th>33</th>
<th>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>18</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>34</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
</tr>
<tr>
<td>2</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>19</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>35</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>3</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>20</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>36</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>4</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>21</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; 0 &amp; 1 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>37</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>5</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>22</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>38</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>6</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>23</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>39</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
</tr>
<tr>
<td>7</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>24</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 0 &amp; 1 &amp; 0 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>40</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
</tr>
<tr>
<td>8</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>25</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>41</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>9</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>26</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>42</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>10</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>27</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>43</td>
<td>$\begin{pmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>11</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; -1 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>28</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>44</td>
<td>$\begin{pmatrix} -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \ 0 &amp; -1 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>12</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ 0 &amp; 0 &amp; -1 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
<td>29</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ -1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \end{pmatrix}$</td>
<td>45</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 0 &amp; -1 &amp; 0 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>13</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>30</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>46</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; -1 \ 0 &amp; 1 &amp; 0 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>14</td>
<td>$\begin{pmatrix} 0 &amp; -1 &amp; 0 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; -1 \end{pmatrix}$</td>
<td>31</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 1 &amp; 0 &amp; 0 \ 0 &amp; -1 &amp; 0 \end{pmatrix}$</td>
<td>47</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; -1 &amp; 0 \ -1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>15</td>
<td>$\begin{pmatrix} 0 &amp; 1 &amp; 0 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{pmatrix}$</td>
<td>32</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ -1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \end{pmatrix}$</td>
<td>48</td>
<td>$\begin{pmatrix} 0 &amp; 0 &amp; 1 \ 0 &amp; 1 &amp; 0 \ 1 &amp; 0 &amp; 0 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

Table 5.3: Rotation matrices of the point group $m\bar{3}m$. The numbering of the elements is the same as those given in the *International Tables of Crystallography* [Hahn83] for space group $Fm\bar{3}m$. 
Table 5.4: List of all domain matrices for transformations of type I. The index numbers refer to the transformation matrices of the point group as listed in table 5.3. Column 1 is a running index, column 2 states the lowest index for the matrix $R_i$ such that the reference transformation matrix is transformed to the new transformation matrix. The explicit form of the transformation matrix is given in column 3. Column 4 lists the indices of those symmetry operators $R_j$ which produce the transformation matrix recorded in the same row. Column 5 states rotation axis of the matrix which arises in the polar decomposition $\mathbf{\tilde{M}}_1 = \mathbf{\tilde{Q}} \cdot R_i$. Column 6 states the invariant axis of the matrix $\mathbf{\tilde{M}}_1$. This vector is an eigenvector of $\mathbf{\tilde{M}}_1$ with an eigenvalue of 1. The last column lists the index for the positive-definite displacement matrix $U_i$ with $U_x = \begin{pmatrix} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{pmatrix}$, $U_y = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{pmatrix}$, and $U_z = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{pmatrix}$.

<table>
<thead>
<tr>
<th>index</th>
<th>Index i for $R_i$</th>
<th>$\mathbf{\tilde{M}}_1$</th>
<th>Invariance index $\mathbf{\tilde{M}}<em>1 = R_i^T \cdot \mathbf{\tilde{Q}}</em>{12} \cdot R_i$</th>
<th>Invariant $\varphi$ axis of $\mathbf{\tilde{M}}_1$</th>
<th>Invariant $\mathbf{\tilde{Q}}$ axis of $\mathbf{\tilde{M}}_1$</th>
<th>Index of $U_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; \sigma \ 0 &amp; 1 + \sigma &amp; \sigma \ -\sigma &amp; -\sigma &amp; 1 - 2\sigma \end{pmatrix}$</td>
<td>1,14, 25,38</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$z$</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; -\sigma \ 0 &amp; 1 + \sigma &amp; -\sigma \ \sigma &amp; \sigma &amp; 1 - 2\sigma \end{pmatrix}$</td>
<td>2,13, 26,37</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td>$y$</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; -\sigma \ 0 &amp; 1 + \sigma &amp; -\sigma \ -\sigma &amp; -\sigma &amp; 1 - 2\sigma \end{pmatrix}$</td>
<td>3,16, 27,40</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$x$</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; -\sigma \ 0 &amp; 1 + \sigma &amp; \sigma \ -\sigma &amp; -\sigma &amp; 1 - 2\sigma \end{pmatrix}$</td>
<td>4,15, 28,39</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; \sigma \ -\sigma &amp; 1 - 2\sigma &amp; -\sigma \ 0 &amp; \sigma &amp; 1 + \sigma \end{pmatrix}$</td>
<td>5,19, 29,43</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; 0 &amp; -\sigma \ -\sigma &amp; 1 - 2\sigma &amp; -\sigma \ 0 &amp; -\sigma &amp; 1 + \sigma \end{pmatrix}$</td>
<td>6,20, 30,44</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; -\sigma &amp; 0 \ 0 &amp; 1 - 2\sigma &amp; \sigma \ 0 &amp; \sigma &amp; 1 + \sigma \end{pmatrix}$</td>
<td>7,17, 31,41</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>$\begin{pmatrix} 1 + \sigma &amp; -\sigma &amp; 0 \ -\sigma &amp; 1 - 2\sigma &amp; \sigma \ 0 &amp; -\sigma &amp; 1 + \sigma \end{pmatrix}$</td>
<td>8,18, 32,42</td>
<td>$\begin{pmatrix} -1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>$\begin{pmatrix} 1 - 2\sigma &amp; -\sigma &amp; \sigma \ \sigma &amp; 1 + \sigma &amp; 0 \ 0 &amp; \sigma &amp; 1 + \sigma \end{pmatrix}$</td>
<td>9,24, 33,48</td>
<td>$\begin{pmatrix} 0 \ -1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 1 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>$\begin{pmatrix} 1 - 2\sigma &amp; -\sigma &amp; \sigma \ \sigma &amp; 1 + \sigma &amp; 0 \ -\sigma &amp; 0 &amp; 1 + \sigma \end{pmatrix}$</td>
<td>10,23, 34,47</td>
<td>$\begin{pmatrix} 0 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 1 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>$\begin{pmatrix} 1 - 2\sigma &amp; \sigma &amp; -\sigma \ -\sigma &amp; 1 + \sigma &amp; 0 \ \sigma &amp; 0 &amp; 1 + \sigma \end{pmatrix}$</td>
<td>11,22, 35,46</td>
<td>$\begin{pmatrix} 0 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 1 \end{pmatrix}$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>$\begin{pmatrix} 1 - 2\sigma &amp; \sigma &amp; -\sigma \ -\sigma &amp; 1 + \sigma &amp; 0 \ -\sigma &amp; 0 &amp; 1 + \sigma \end{pmatrix}$</td>
<td>12,21, 36,45</td>
<td>$\begin{pmatrix} 0 \ -1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 1 \end{pmatrix}$</td>
<td></td>
</tr>
</tbody>
</table>
Some observations can be made from table 5.4. The invariant axis of the matrix \( \vec{M}_{1xy} \), as represented by the vector \( \vec{m} \), has an ambiguity with respect to its orientation. As both \( \vec{m} \) as well as \( -\vec{m} \) represent this axis one is free to choose one of them. Here the choice has been made such that the component corresponding to the last column, which indicates the index of the matrix \( U_i \), is taken to be positive. The same argument applies to the vector \( \vec{q} \) which signifies the axis of rotation of the matrix \( \vec{Q}_{1xy} \). In principle this ambiguity can be eliminated by demanding that the angle of rotation is positive. This selects one of the two orientations. This numerical procedure, however, has not been carried out here as an argument will be presented below which will resolve the issue on physical grounds. The vector \( \vec{q} \) has a zero for the index characterising the matrix \( U_i \). Thus \( \vec{q} \) is perpendicular to both \( \vec{m} \) as well as \( \vec{e}_i \). Here \( \vec{e}_i \) represents the unit vector along the axis with index \( i \).

The transformation matrices in column 3 of table 5.4 have the same sequence of diagonal elements for each type of \( U_i \) matrix. Also the position of the off-diagonal zero is the same for each group of transformation matrices with the same \( U_i \) matrix. Within one group which is related to a particular \( U_i \) matrix the various transformation matrices differ by the distribution of minus signs in the non-zero off-diagonal positions. The distribution always ensures that the transformation is an orthogonal transformation.

From a notational point of view it is observed that the notation used here for the transformation matrix \( \vec{M}_{1xy} \) is insufficient to uniquely denote all variants. The index \( xy \) gives an indication of the position of the zero in the matrix, and the missing index identifies the index of the \( U_i \) matrix. However, this notation is insufficient to distinguish between the various variants within one \( U_i \) group of transformations. It is therefore suggested that the index of the transforming
symmetry element be used to indicate the variant. This index corresponds to the number in the 1st or 2nd column of table 5.4. A variant is then conveniently indicated by using the symbol

\[ \bar{M}_1^{(i)} = \bar{R}_i^T \cdot \bar{M}_1^{(ref)} \cdot \bar{R}_i \]

to represent the \( i \)th variant of the transformation.

The above description and the information in table 5.4 also suggest a simple physical explanation and a straightforward visualisation of the transformation process. This will be discussed here in order to enable the transformation to be illustrated. The discussion will also enable a unique procedure to be identified for scaling the transformation matrices of the linear theory to the correct ones for the non-linear description.

5.d i.a Visualisation of Transformation Process

Consider a test transformation matrix without any rotation. Within the linear theory of Brown et al. [Brown04] this will have the form

\[ \bar{U}_{test} = \begin{pmatrix} 1 + \sigma & 0 & 0 \\ 0 & 1 + \sigma & 0 \\ 0 & 0 & 1 - 2\sigma \end{pmatrix} \]

This indicates that the distances in the x-y plane are increased by a factor of \( 1 + \sigma \) (for \( \sigma \) positive) and decreased by a factor of \( 1 - 2\sigma \) along the z-axis. Consider now a vector \( \vec{b} \) on the unit sphere. As the description is invariant with respect to a rotation around the z-axis it suffices to consider the x-z plane. Within this plane let the vectors \( \vec{b} \) take the form
The angle $\alpha$ is the angle the vector makes with respect to the z-axis. If the vector is subject to the transformation $\mathbf{U}_{test}$ one obtains the transformed vector $\mathbf{\tilde{b}}$ as

\[
\mathbf{\tilde{b}} = \mathbf{U}_{test} \mathbf{\hat{b}} = \begin{pmatrix}
1 + \sigma & 0 & 0 \\
0 & 1 + \sigma & 0 \\
0 & 0 & 1 - 2\sigma
\end{pmatrix} \begin{pmatrix}
\sin(\alpha) \\
0 \\
\cos(\alpha)
\end{pmatrix} = \begin{pmatrix}
(1 + \sigma)\sin(\alpha) \\
0 \\
(1 - 2\sigma)\cos(\alpha)
\end{pmatrix}
\]

The length of the unit vector has changed. One obtains

\[
\|\mathbf{\tilde{b}}\| = \sqrt{(1 + \sigma)^2 \sin^2(\alpha) + (1 - 2\sigma)^2 \cos^2(\alpha)}
\]

The length change of the vector depends on the inclination of the vector with respect to the z-axis as given by the angle $\alpha$. The length of the transformed unit vector decreases for $\alpha = 0$, while for $\alpha = \frac{\pi}{2}$ its length increases. For some angle $\alpha$ with $0 \leq \alpha \leq \frac{\pi}{2}$ the length of the vector remains unchanged in this transformation. This angle can be obtained by solving the equation

\[
\|\mathbf{\tilde{b}}\|^2 = (1 + \sigma)^2 \sin^2(\alpha) + (1 - 2\sigma)^2 \cos^2(\alpha) = \|\mathbf{\hat{b}}\|^2 = \sin^2(\alpha) + \cos^2(\alpha) = 1
\]

This equation can be solved for $\cos^2(\alpha)$ as a function of $\sigma$. The numeric dependence of $\cos^2(\alpha)$ as a function of $\sigma$ is shown in figure 5.8 by the blue line.

All vectors for which the length is not changed by this transformation lie on a cone centred around the z-axis with an opening angle of $\alpha$ as determined above. The cone represents the invariant surface. Any vector on this surface remains on this surface in the transformation with its length and orientation unchanged. The opening of the invariant cone is a function of $\sigma$. 

\[
\mathbf{\hat{b}} = \begin{pmatrix}
\sin(\alpha) \\
0 \\
\cos(\alpha)
\end{pmatrix}
\]
The limit of \( \sigma \) tending to zero yields the angle for the invariant cone for small shears. It is necessary for this cone to include the (111) symmetry axis of the transformation in this limit, as otherwise this symmetry is not respected for the transformations with \( \sigma \) tending to zero. The angle between the (1,1,1) axis and the z-axis gives rise to a \( \cos^2(\alpha_{(111)}) \) value of \( \frac{1}{3} \). For larger values of \( \sigma \) the opening of the cone for which the lengths of vectors remain unchanged in the transformation becomes wider resulting in the (1,1,1) axis to be outside the cone for values of \( \sigma \) larger than zero. For the resulting transformation matrix \( \bar{M}_{\text{test}} \) to have the (1,1,1) axis as an invariant axis the cone needs rotating. The rotational part can be presented by a \( \bar{Q}_{\text{test}} \) matrix such that \( \bar{M}_{\text{test}} = \bar{Q}_{\text{test}} \cdot \bar{U}_{\text{test}} \).

**Figure 5.8:** Plot of the \( \cos^2(\alpha) \) dependence as a function of \( \sigma \) for the invariant cone. This cone is made up of all vectors which do not change their length under the stretch transformation. A rotation around a (1,1,0) axis is required to make the (111) axis coincide with the invariant cone. The blue line represents the calculation for the linear theory using the stretch matrix \( \bar{U}_{\text{test}} \). The red line is obtained using the non-linear description with the stretch matrix \( \bar{U}_{\text{non-linear}} \) (uniform scaling by factor \( ((1 + \sigma)^2 \cdot (1 - 2\sigma))^{\frac{1}{3}} \)). For details see text.
5.d.i.β  Extension of description to Non-Linear Order

This process also allows the extension of the description from a linear theory of the transformation to the full non-linear one. To achieve this extension note that the transformation matrix $\hat{U}_{test}$ is only volume conserving in linear order as $\text{tr}(\hat{U}_{test} - I) = 0$ but $\|\hat{U}_{test}\| = (1 + \sigma)^2 \cdot (1 - 2\sigma) \neq 1$ for non-zero values of $\sigma$. The value of $\|\hat{U}_{test}\| = 1$ is required for the volume conserving transformation in the non-linear description. Given the general stretch matrix 
\[
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix}
\]
it is possible to either scale the values of $\alpha$, or of $\beta$, or a weighted combination of the two such that the determinant of this matrix is equal to 1. Here 3 different scaling procedures are considered.

**Case 1: scaling of the parameter $\alpha$**

This scaling results in a stretch matrix

\[
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = \begin{pmatrix}
\frac{1 + \sigma}{\sqrt{(1 + \sigma)^2(1 - 2\sigma)}} & 0 & 0 \\
0 & \frac{1 + \sigma}{\sqrt{(1 + \sigma)^2(1 - 2\sigma)}} & 0 \\
0 & 0 & 1 - 2\sigma
\end{pmatrix} = \begin{pmatrix}
\frac{1}{\sqrt{(1 - 2\sigma)}} & 0 & 0 \\
0 & \frac{1}{\sqrt{(1 - 2\sigma)}} & 0 \\
0 & 0 & 1 - 2\sigma
\end{pmatrix}
\]

Expanding the above expression as a function in powers of $\sigma$ yields

\[
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = I + \sigma \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{pmatrix} + \frac{\sigma^2}{2} \cdot \begin{pmatrix}
3 & 0 & 0 \\
0 & 3 & 0 \\
0 & 0 & 0
\end{pmatrix} + O(\sigma^3)
\]
Case 2: scaling of the parameter $\beta$

This scaling results in a stretch matrix

$$
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = \begin{pmatrix}
1 + \sigma & 0 & 0 \\
0 & 1 + \sigma & 0 \\
0 & 0 & 1 - 2\sigma
\end{pmatrix}_{(1 + \sigma)^2(1 - 2\sigma)} = \begin{pmatrix}
1 + \sigma & 0 & 0 \\
0 & 1 + \sigma & 0 \\
0 & 0 & 1
\end{pmatrix}_{(1 + \sigma)^2}
$$

Expanding this expression in powers of $\sigma$ yields

$$
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = \bar{I} + \sigma \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{pmatrix} + \frac{\sigma^2}{2} \cdot \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 6
\end{pmatrix} + O(\sigma^3)
$$

Case 3: uniform scaling of the parameters $\alpha$ and $\beta$

This scaling results in a stretch matrix

$$
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = \begin{pmatrix}
\frac{1 + \sigma}{\sqrt{(1 + \sigma)^2(1 - 2\sigma)}} & 0 & 0 \\
0 & \frac{1 + \sigma}{\sqrt{(1 + \sigma)^2(1 - 2\sigma)}} & 0 \\
0 & 0 & \frac{1 - 2\sigma}{\sqrt{(1 + \sigma)^2(1 - 2\sigma)}}
\end{pmatrix}
$$

Expanding each element of the diagonal as a powers series in $\sigma$ yields

$$
\begin{pmatrix}
\alpha & 0 & 0 \\
0 & \alpha & 0 \\
0 & 0 & \beta
\end{pmatrix} = (1 + \sigma^2) \cdot \bar{I} + \sigma \cdot \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & -2
\end{pmatrix} + O(\sigma^3)
$$

Out of these examples it is seen that uniform scaling results in a stretch matrix which, if expanded in a power series in the shear parameter $\sigma$, has a contribution in 2nd order in $\sigma$ which is proportional to the unit matrix $\bar{I}$.

Indeed if one seeks solutions to the scaling problem in the form
with $\sigma$ dependent scaling functions $a(\sigma)$ and $b(\sigma)$ under the condition that the determinant of this matrix is equal to 1 and that the trace of this matrix minus the identity matrix is equal to 0 then the only solutions will be of the form that

$$\frac{a}{a(\sigma)} = const \text{ and } \frac{\beta}{b(\sigma)} = const$$

where both constants are different.

It is already evident from the examples discussed above that the requirement of the trace of the matrix being equal to 3 and its determinant being equal to 1 are not compatible. All traces of the matrices for all 3 cases are equal to 3 for all cases up to linear order in $\sigma$, but the trace is different from 3 to second order in $\sigma$ for all cases discussed above.

Thus it seems reasonable to seek an extension to non-linear order in such a manner that the next order in $\sigma$ takes a form which is most convenient for calculations. A particular convenient contribution of the $\sigma^2$ contribution is provided for case number 3, for which $\sigma^2$ gives rise to a contribution which is proportional to the unit matrix.

Thus the extension of the description to non-linear order should use a stretch matrix of the form

$$\bar{U}_{\text{non-linear}} = \frac{1}{\sqrt{(1 + \sigma)^2 \cdot (1 - 2\sigma)}} \begin{pmatrix}
0 & \frac{1}{1 + \sigma} & 0 \\
\frac{1 + \sigma}{(1 + \sigma)^2} & 0 & \frac{1}{1 - 2\sigma} \\
0 & \frac{1 - \sigma}{(1 - 2\sigma)} & \frac{1}{1 - 2\sigma}
\end{pmatrix}$$

for which

$$tr(\bar{U}_{\text{non-linear}} - I) = 0$$
to linear order in $\sigma$ and

$$\| \bar{U}_{\text{non-linear}} \| = 1$$

to all orders of $\sigma$.

Using the non-linear stretch matrix the dependence of $\cos^2(\alpha)$ as a function of $\sigma$ has been obtained numerically and it is shown in figure 5.8 as the red line. Both lines intersect the y-axis at the same value of $\frac{1}{3}$.

The analysis as given here has confirmed the existence of 12 different domains of type I. This is in agreement with the results of Brown et al. [Brown04] which have determined the number of different domains based on geometric arguments. Here the explicit form of the transformation matrices has been derived using symmetry operators of the cubic point group. The symmetry elements have been identified, which leave the transformation matrices unaltered as well as those which are needed to transform the reference matrix $\bar{M}_{1xy}$ to its symmetry related forms. In addition the characteristic entities, such as the axis of rotation involved in the transformation, the invariant (111) axis and the $\bar{U}_i$ matrix have been identified for each transformation matrix. The physics of the transformation process has been elucidated with a simple model which allows identifying the geometric features of the transformation process from the austenitic phase. A unique extension has been given which will allow the description of the transformation to be extended from a linear theory to a non-linear description.

This completes the derivation and the analysis of the transformation matrices of type I. Next the transformation matrices of type II are considered.
5.d.ii  Investigation of type II transformations

The investigation of the transformation matrices of type II can be conducted in the same manner as for type I transformations. The results are shown in table 5.5. As transformation matrices of type II also have a (1,1,1) symmetry axis this is identified in the table. Similarly to the case of type I domains the component of \( \bar{m} \) which corresponds to the index \( i \) of the \( U_i \) matrix is taken to be positive. Due to the shift, as a function of \( \sigma \), of the rotation axis of \( \bar{Q}_2 \), the axis is indicated by using a capital letter for the larger entry and a small letter for the numerically smaller value. Details of this rotation axis have been discussed in the section on the basic properties of a type II transformation matrix.

The form of transformation matrices of type II is similar to the form of type I matrices. The sequence of diagonal elements depends on the index of the matrix \( U_i \), and it is not varied within the same group of \( i \) values. The off-diagonal elements above the diagonal are all different for non-zero values of \( \sigma \). The elements below the diagonal are fixed to the negative value by the requirement that the transformation matrix is an orthogonal transformation.

Compared to type I matrices, for which two of the off diagonal elements above the diagonal have the same absolute value, the ability to distinguish entries of \( \sigma \) and \( 2\sigma \) gives rise to twice the number of transformation matrices and domains.

All 24 different transformation matrices of type II have been identified in table 5.5, with their characteristics listed as for type I matrices. It is also helpful to represent the various domain matrices by using the index \( i \) of the group element which generates the particular transformation matrix from the one used as a reference. Thus the following notation will be used:

\[
\bar{M}_2^{(i)} = \bar{R}_i^T \cdot \bar{M}_2^{(ref)} \cdot \bar{R}_i
\]
Here the index $i$ runs, in principle, over all 48 symmetry elements of the austenitic point group. However, for generating the particular transformation matrix it suffices to use the index $i$ in column 1 or 2 of table 5.5 and the transformation operator $i$ as identified in table 5.3. The reference transformation matrix $\hat{M}_{2xy}$ is the matrix as identified by Brown et al. [Brown04].
<table>
<thead>
<tr>
<th>index</th>
<th>Index i for $R_i$</th>
<th>$\bar{M}_2$</th>
<th>Invariance index $\bar{Q}<em>2 = R_i^T \bar{M}</em>{2xy} R_i$</th>
<th>Invariant $\bar{q}$ axis of $\bar{Q}_2$</th>
<th>Invariant $\bar{m}$ axis of $\bar{M}_1$</th>
<th>Index of $U_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$(1 + \sigma\ 0\ \sigma\ 0)\ 0\ 1 - 2\sigma\ -2\sigma\ 2\sigma\ 1 + \sigma)$</td>
<td>1, 25</td>
<td>$(X\ y\ 0)$</td>
<td>$(1\ 1\ -1)$</td>
<td>y</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$(1 + \sigma\ 0\ -\sigma\ 0)\ 0\ 1 - 2\sigma\ 2\sigma\ -2\sigma\ 1 + \sigma)$</td>
<td>2, 26</td>
<td>$(X\ y\ 0)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>$(1 + \sigma\ 0\ \sigma\ 0)\ 0\ 1 - 2\sigma\ 2\sigma\ -2\sigma\ 1 + \sigma)$</td>
<td>3, 27</td>
<td>$(X\ -y\ 0)$</td>
<td>$(-1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>$(1 + \sigma\ 0\ -\sigma\ 0)\ 0\ 1 - 2\sigma\ 2\sigma\ -2\sigma\ 1 + \sigma)$</td>
<td>4, 28</td>
<td>$(X\ -y\ 0)$</td>
<td>$(-1\ 1\ -1)$</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>$(1 - 2\sigma\ -2\sigma\ 0\ 0)\ 2\sigma\ -1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>5, 29</td>
<td>$(X\ 0\ Z)$</td>
<td>$(1\ -1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>$(1 - 2\sigma\ -2\sigma\ 0\ 0)\ 2\sigma\ -1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>6, 30</td>
<td>$(-X\ 0\ Z)$</td>
<td>$(1\ 1\ 1)$</td>
<td>x</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>$(1 - 2\sigma\ 2\sigma\ 0\ 0)\ -2\sigma\ -1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>7, 31</td>
<td>$(X\ 0\ Z)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>$(1 - 2\sigma\ 2\sigma\ 0\ 0)\ -2\sigma\ -1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>8, 32</td>
<td>$(-X\ 0\ Z)$</td>
<td>$(1\ 1\ -1)$</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>$(1 + \sigma\ -\sigma\ 2\sigma\ 0)\ \sigma\ 1 + \sigma\ 0\ -2\sigma\ 1 - 2\sigma)$</td>
<td>9, 33</td>
<td>$(0\ Y\ z)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>$(1 + \sigma\ -\sigma\ -2\sigma\ 0)\ \sigma\ 1 + \sigma\ 0\ -2\sigma\ 1 - 2\sigma)$</td>
<td>10, 34</td>
<td>$(0\ -Y\ z)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>$(1 + \sigma\ -\sigma\ 2\sigma\ 0)\ -\sigma\ 1 + \sigma\ 0\ -2\sigma\ 1 - 2\sigma)$</td>
<td>11, 35</td>
<td>$(0\ -Y\ z)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>$(1 + \sigma\ -\sigma\ -2\sigma\ 0)\ -\sigma\ 1 + \sigma\ 0\ -2\sigma\ 1 - 2\sigma)$</td>
<td>12, 36</td>
<td>$(0\ Y\ z)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>13</td>
<td>$(1 - 2\sigma\ 0\ 2\sigma\ 0)\ 0\ 1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>13, 37</td>
<td>$(X\ Y\ 0)$</td>
<td>$(1\ 1\ 1)$</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>14</td>
<td>$(1 - 2\sigma\ 0\ -2\sigma\ 0)\ 0\ 1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>14, 38</td>
<td>$(X\ Y\ 0)$</td>
<td>$(1\ 1\ -1)$</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>$(1 - 2\sigma\ 0\ 2\sigma\ 0)\ 0\ 1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>15, 39</td>
<td>$(X\ -Y\ 0)$</td>
<td>$(1\ 1\ -1)$</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>$(1 - 2\sigma\ 0\ -2\sigma\ 0)\ 0\ 1 + \sigma\ -\sigma\ 1 + \sigma)$</td>
<td>16, 40</td>
<td>$(X\ -Y\ 0)$</td>
<td>$(1\ 1\ -1)$</td>
<td></td>
</tr>
</tbody>
</table>

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Table 5.5: List of all domain matrices for transformations of type II. The index numbers refer to the transformation matrices of the point group as listed in table 5.3. Column 1 is a running index, column 2 states the lowest index for the matrix \( R_i \) such that the reference transformation matrix is transformed to the new transformation matrix. The explicit form of the transformation matrix is given in column 3. Column 4 lists the indices of those symmetry operators \( R_i \) which leave the transformation matrix unchanged. Column 5 states rotation axis of the matrix which arises in the decomposition. Column 6 states the invariant axis of the matrix. This vector is an eigenvector of \( M \) with an eigenvalue of 1. The last column lists the index for the positive-definite displacement matrix \( U \), with \( U_x = \left( \begin{array}{ccc} \beta & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \alpha \end{array} \right) \), \( U_y = \left( \begin{array}{ccc} \alpha & 0 & 0 \\ 0 & \beta & 0 \\ 0 & 0 & \alpha \end{array} \right) \), and \( U_z = \left( \begin{array}{ccc} \alpha & 0 & 0 \\ 0 & \alpha & 0 \\ 0 & 0 & \beta \end{array} \right) \).

This completes the analysis of the transformation matrices of type II. A total of 24 different type II domains have been identified. This number is identical to the one derived by Brown et al. [Brown04] using geometric arguments. Next the question is considered of matching the various domains to one another. This requires an interface linking two different domains.
5.e Martensite-Martensite Interfaces

After having obtained all transformation matrices, and after having identified all martensitic domains, it is possible to address the question of the pairwise fitting together of the various domains within the martensitic state. It is observed experimentally that the domain boundary between martensitic variants is atomically sharp [Bhattacharya03]. Furthermore, repeated heating and cooling through the transition is observed not to affect the quality of a single crystal in experiments [Brown04]. This resilience of the crystal to repeated strong deformations is surprising. A major contributing factor to these properties must arise from the domain interfaces in the martensitic phase. Experimentally these interfaces have a high mobility, enabling different domains to be converted from one type to another in order to accommodate external or internal forces or constraints in shape. While the dynamics of the interface poses very interesting physical questions which, however, will not be investigated in this thesis, it is the static arrangement which will be considered here. For the following discussion the linear form of the transformation matrices will be used for the analysis.

5.e.i Conditions for the existence of a martensite-martensite interface

Consider a single crystal of Ni$_2$MnGa. The whole crystal is taken to be atomically ordered in the perfect structure. As the crystal is cooled below the martensitic transition temperature the various parts of the crystal may transform according to different transformation matrices. Consider the interface between two such variants of the martensitic phase. To be specific let these be domains of type I according to transformation matrices $\bar{M}_1^{(1)}$ and $\bar{M}_1^{(2)}$. Let $\vec{b}$ be a vector located
within the boundary between the two domains. The interface vector $\vec{b}$ has to transform such that

$$\vec{M}^{(1)} \vec{b} = \vec{M}^{(2)} \vec{b}$$

This must be correct for any value of $\sigma$. In order to identify the interface one has to find two different and non-zero vectors $\vec{b}$ which span the interface. It is instructive to carry on the analysis using the above example.

Any vector $\vec{b}$ which fulfils $\vec{M}^{(1)} \vec{b} = \vec{M}^{(2)} \vec{b}$ must also fulfil the equation $(\vec{M}^{(1)} - \vec{M}^{(2)}) \vec{b} = 0$. From this equation it follows that $\vec{b}$ is an eigenvector of the matrix $\vec{M}^{(1)} - \vec{M}^{(2)}$ with the eigenvalue of 0. For an interface to exist one has to find two such vectors. These vectors have to be non-zero and must not be multiples of one another. Thus the eigenvalue 0 has to be two-fold degenerate.

This condition puts severe restrictions on the matrix $\vec{M}^{(1)} - \vec{M}^{(2)}$ which, for most cases, will not be fulfilled.

Considering the example used here and inserting the form for the matrices as listed in table 5.4 one obtains

$$\left(\vec{M}^{(1)} - \vec{M}^{(2)}\right) \vec{b} = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix} - \begin{pmatrix} 1 + \sigma & 0 & -\sigma \\ 0 & 1 + \sigma & -\sigma \\ \sigma & \sigma & 1 - 2\sigma \end{pmatrix} \vec{b}$$

$$= \sigma \begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 2 \\ -2 & -2 & 0 \end{pmatrix} \vec{b} = 0$$

The first observation which can be made is that the difference matrix is linear in $\sigma$. As a result each eigenvector $\vec{b}$ for the eigenvalue 0, if there exists one, is independent of $\sigma$. Determining the eigenvalues and eigenvectors of

$$\begin{pmatrix} 0 & 0 & 2 \\ 0 & 0 & 2 \\ -2 & -2 & 0 \end{pmatrix}$$

yields, in addition to two complex eigenvalues, one eigenvalue of 0 with associated eigenvector

$$\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}. $$
This result is not surprising. As can be verified from table 5.4 both transformations share the same rotation axis of the rotation matrix $\bar{Q}$. Thus they have this eigenvector in common. For any common eigenvectors, by construction, one obtains that this eigenvector is also an eigenvector of the difference of these matrices, $\bar{M}^{(1)}_1 - \bar{M}^{(2)}_1$. The eigenvalue of $\begin{pmatrix} 1 & -1 \\ 0 & 0 \end{pmatrix}$ is 1 for both $\bar{M}^{(1)}_1$ as well as for $\bar{M}^{(2)}_1$; thus the eigenvalue of the difference of these matrices is 0.

In order to be able to describe an interface one requires a second vector for the interface. This second vector, however, cannot be obtained for the above case as the remaining eigenvectors have non-zero eigenvalues. Thus under the conditions specified above there is no interface possible between domains of transformation matrices $\bar{M}^{(1)}_1$ and $\bar{M}^{(2)}_1$.

Before the argument is developed further it is instructive to discuss and clarify some basic concepts which will aid these discussions. For any difference of transformation matrices, including type I and type II matrices, a matrix is obtained which is linear in $\sigma$. This arises as the form for the transformation matrix is $\bar{M} = \bar{I} + \sigma \cdot \bar{X}$, where $\bar{X}$ is a matrix containing only numeric entries. In particular, $\bar{X}$ is independent of $\sigma$. In taking the difference of two transformation matrices, the unit matrices $\bar{I}$ cancels in the difference and one obtains a matrix proportional to $\sigma$. The determination of the interface vectors thus reduces to the analysis of a matrix with only numeric entries. This matrix is determined as

$$\frac{1}{\sigma} \left( \bar{M}^{(i)}_{1,2} - \bar{M}^{(j)}_{1,2} \right)$$

for suitable indices $i$ and $j$ and for either type I (subscript 1) or type II (subscript 2) matrices.
For an interface it suffices to identify two non-collinear vectors $\vec{b}_1$ and $\vec{b}_2$. As both vectors are situated within the interface they fulfil the conditions

$$\frac{1}{\sigma} \cdot \left( \vec{M}_{1,2}^{(i)} - \vec{M}_{1,2}^{(j)} \right) \cdot \vec{b}_1 = 0$$

and

$$\frac{1}{\sigma} \cdot \left( \vec{M}_{1,2}^{(i)} - \vec{M}_{1,2}^{(j)} \right) \cdot \vec{b}_2 = 0.$$ 

Adding of these two equations with weights $\alpha$ and $\beta$ yields

$$\frac{1}{\sigma} \cdot \left( \vec{M}_{1,2}^{(i)} - \vec{M}_{1,2}^{(j)} \right) \cdot (\alpha \vec{b}_1 + \beta \vec{b}_2) = 0$$

for any real numeric values of $\alpha$ and $\beta$. If two non-collinear vectors $\vec{b}_1$ and $\vec{b}_2$ can be found which fulfil above conditions then one has obtained a plane of invariant vectors, i.e. the interface between two domains $\vec{M}_{1,2}^{(i)}$ and $\vec{M}_{1,2}^{(j)}$.

Returning to the analysis of the possible domains one has 12 domains of type I and 24 domains of type II. In total there are $\frac{(12+24) \cdot (12+24-1)}{2} = 630$ different interfaces between different domains. This number comprises 66 possible combinations of type I domains, 276 interface possibilities involving only type II domains and $12 \cdot 24 = 288$ interfaces involving one type I and one type II domain.

All interface possibilities have been studied numerically identifying eigenvectors $\vec{b}$ of the matrix $\frac{1}{\sigma} \left( \vec{M}_{1,2}^{(i)} - \vec{M}_{1,2}^{(j)} \right)$ such that $\frac{1}{\sigma} \left( \vec{M}_{1,2}^{(i)} - \vec{M}_{1,2}^{(j)} \right) \cdot \vec{b} = 0$. The results of this calculation are shown in tables 5.6 to 5.8 for type I – type I, type II – type II and for the mixed type domain interfaces, respectively.
Table 5.6: List of the invariant vectors for type I – type I domains. These vectors are eigenvectors to the numeric matrix $\mathbf{M}_{ij} - \mathbf{M}_{ij}$ for $i, j = \{1, 2, ..., 12 \mid i < j\}$. 

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Table 5.6: List of the invariant vectors for type I – type I domains. These vectors are eigenvectors to the numeric matrix $\mathbf{M}_{ij} - \mathbf{M}_{ij}$ for $i, j = \{1, 2, ..., 12 \mid i < j\}$. 

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Table 5.7a: List of the invariant vectors for type II – type II domains. These vectors are eigenvectors to the numeric matrix $\frac{1}{\sigma} \cdot (\overline{M}_2^{(i)} - \overline{M}_2^{(j)})$ for $i,j = \{1,2,..,12 \mid i < j \}$. If positions above the diagonal are void, then there is no invariant vector.
Table 5.7b: List of the invariant vectors for type II – type II domains. These vectors are eigenvectors to the numeric matrix $\frac{1}{\sigma} \left( \mathcal{M}^{(i)}_2 - \mathcal{M}^{(j)}_2 \right)$ for $i, j = 1, 2, \ldots, 12 \mid i < j$. If positions are void, then there is no invariant vector.
Table 5.7c: List of the invariant vectors for type II – type II domains. These vectors are eigenvectors to the numeric matrix \( \frac{1}{\sigma} \cdot (\overline{M}_2^{(i)} - \overline{M}_2^{(j)}) \) for \( i, j = \{1,2,\ldots,12 \mid i < j \} \). If positions above the diagonal are void, then there is no invariant vector.

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</table>
Table 5.8a: List of the invariant vectors for type I \( \rightarrow \) type II domains. These vectors are eigenvectors to the numeric matrix \( \sigma^{-1} (\overline{M}_1^{(i)} - \overline{M}_2^{(j)}) \) for \( i = \{1,2,\ldots,12\} \) and \( j = \{1,2,\ldots,12\} \). If positions are void, then there is no invariant vector.
Table 5.8.b: List of the invariant vectors for type I – type II domains. These vectors are eigenvectors to the numeric matrix $\frac{1}{\sigma} \cdot (\overline{M}_1^{(i)} - \overline{M}_2^{(j)})$ for $i = \{1,2,\ldots,12\}$ and $j = \{13,14,\ldots,24\}$. If positions are void, then there is no invariant vector.
It transpires that for most combinations no coherent interface is possible, at least with the conditions mentioned above. In this case and if it exists, the tables state the invariant vector, which is the eigenvector of the matrix \( \frac{1}{\sigma} (\overline{M}_{1,2}^{(i)} - \overline{M}_{1,2}^{(j)}) \) with the eigenvalue 0. For only a few combinations an interface is possible with the above conditions. Among those are, e.g. interfaces between domains \( \overline{M}_1^{(i)} \) and \( \overline{M}_2^{(i)} \) for equal indices \( i \).

An interface arises, as an example, between domains \( \overline{M}_1^{(1)} \) and \( \overline{M}_2^{(1)}, \overline{M}_2^{(14)} \). The matrices for the first combination give rise to the following equation:

\[
\frac{1}{\sigma} \cdot (\overline{M}_1^{(1)} - \overline{M}_2^{(1)}) \cdot \vec{b} = \frac{1}{\sigma} \cdot \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix} \cdot \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 - 2\sigma & -2\sigma \\ -\sigma & 2\sigma & 1 + \sigma \end{pmatrix} \cdot \vec{b} = 0
\]

This equation is fulfilled for the following two orthogonal \( \vec{b} \)-vectors:

\[
\vec{b}_1 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \text{ and } \vec{b}_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}.
\]

For the interface between matrices \( \overline{M}_1^{(1)} \) and \( \overline{M}_2^{(14)} \) a similar calculation yields

\[
\frac{1}{\sigma} \cdot (\overline{M}_1^{(1)} - \overline{M}_2^{(14)}) \cdot \vec{b} = \frac{1}{\sigma} \cdot \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix} \cdot \begin{pmatrix} 1 - 2\sigma & 0 & -2\sigma \\ 0 & 1 + \sigma & \sigma \\ 2\sigma & -\sigma & 1 + \sigma \end{pmatrix} \cdot \vec{b} = 0
\]

\[
= \begin{pmatrix} 3 & 0 & 3 \\ 0 & 0 & 0 \\ -3 & 0 & -3 \end{pmatrix} \cdot \vec{b} = 0
\]
with \( \vec{b} \)-vectors \( \vec{b}_1 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \) and \( \vec{b}_2 = \begin{pmatrix} 1 \\ 0 \\ -1 \end{pmatrix} \).

These vectors and modulations of the 1 in vector \( \vec{b}_1 \) and of the 0 in vector \( \vec{b}_2 \), such that there is exactly one \( \pm 1 \) in each line, are highlighted in yellow in tables 5.8a and 5.8b. Only these combinations, a total of 24 out of 630 will be able to form a coherent interface under the conditions stipulated above. The type of interface described by these solutions is an interface which is independent of the strain value \( \sigma \). This interface is only possible between a type I domain and two different type II domains, one of them being the domain with the same \( i \)-index. As the different sets of solutions do not have any domain in common, it is not possible to build up a network or an arrangement of domains as required for the description of a shape memory crystal in the martensitic phase.

For the other combinations of domains, most have one non-zero eigenvector of the difference matrix. These are listed in the various tables 5.6, 5.7, and 5.8. The indices of these vectors are low. In addition to the cubic axis vectors, such as \( \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} \), linear combinations of those are also found. These include \( \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \) and \( \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \) type of vectors. Also \( \begin{pmatrix} 2 \\ 1 \\ 0 \end{pmatrix} \) eigenvectors are found for a few combinations. In addition there are vectors of the form \( \begin{pmatrix} 2n + 1 \\ 1 \\ 1 \end{pmatrix} \) with \( n = 0, 1, 2, 3 \) resulting in vectors of the form \( \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \), \( \begin{pmatrix} 3 \\ 1 \\ 1 \end{pmatrix} \), \( \begin{pmatrix} 5 \\ 1 \\ 1 \end{pmatrix} \) and \( \begin{pmatrix} 7 \\ 1 \\ 1 \end{pmatrix} \).

For other combinations of domains there are no entries in the tables. One such case is the combination of the transformation matrices \( \bar{M}_1^{(1)} \) and \( \bar{M}_2^{(6)} \). Evaluating the eigenvalues of this combination of matrices one obtains
eigenvalues of 2.315 and two complex ones, $-1.158 \pm i \cdot 3.004$. It is clear that the condition of a zero eigenvalue is not fulfilled, not even approximately, for this combination of matrices.

While the present approach has identified some possibilities for a coherent interface between martensitic domains, the question of the formation of such interfaces remains generally open. Therefore in the next section this question is addressed again using a different approach. A procedure is derived for constructing a suitable interface between some other combinations of domains.

5.f Construction of martensite – martensite interfaces in linear approximation

Following Bhattacharya [Bhattacharya03] the condition for an interface as given above can be cast into the form

$$\bar{F} - \bar{G} = f(\sigma) \bar{a} \otimes \bar{n}$$

where $\bar{F}$ and $\bar{G}$ are transformation matrices of different domains (including both type I and type II domains), $\bar{a}$ is a vector of the interface and $\bar{n}$ is the normal vector to the interface. The vectors can be chosen to be unit vectors. Here $f(\sigma)$ is a scalar function of the shear parameter $\sigma$. Bhattacharya [Bhattacharya03] uses $f(\sigma) = 1$. However, it will be shown below that the above definition is more useful and appropriate.

The condition for an interface can be generalised to include the mutual rotation of the domains with respect to one another. Considering a rotation matrix $\bar{R}$ the twinning equation is generalised to

$$\bar{R} \cdot \bar{F} - \bar{G} = f(\sigma) \bar{a} \otimes \bar{n}$$
Solving this equation necessitates the identification of the vectors \( \vec{a} \) and \( \vec{n} \) as well as the rotation matrix \( \tilde{R} \). The latter involves the specification of the rotation axis and the angle of rotation.

For the transformations of interest here within the \( \text{Ni}_2\text{MnGa} \) crystal one can take the point of view that the values of the shear displacement, as specified by \( \sigma \), are small. It thus suffices to consider the transformations to linear order in \( \sigma \). This considerably simplifies the analysis.

Consider the matrix \( \tilde{M}_1^{(1)} \)

\[
\tilde{M}_1^{(1)} = \begin{pmatrix}
1 + \sigma & 0 & \sigma \\
0 & 1 + \sigma & \sigma \\
-\sigma & -\sigma & 1 - 2\sigma
\end{pmatrix}
\]

Within a linear description this matrix is the product of a rotation matrix \( \tilde{Q}_1^{(1)} \), defined as

\[
\tilde{Q}_1^{(1)} = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix} + \sigma \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 1 \\
-1 & -1 & 0
\end{pmatrix} = \tilde{I} + \sigma \begin{pmatrix}
0 & 0 & 1 \\
0 & 0 & 1 \\
-1 & -1 & 0
\end{pmatrix}
\]

and a diagonal matrix

\[
\tilde{U}_z = \begin{pmatrix}
1 + \sigma & 0 & 0 \\
0 & 1 + \sigma & 0 \\
0 & 0 & 1 - 2\sigma
\end{pmatrix}
\]

Indeed evaluating \( \tilde{Q}_1^{(1)}(\sigma) \cdot \tilde{U}_z(\sigma) \) one obtains
\[ \bar{Q}^{(1)}_1(\sigma) \cdot \bar{U}_z(\sigma) \]
\[ = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \]
\[ \cdot \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \]
\[ = \bar{I} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} + \left( \text{contributions } \sim \sigma^2 \text{ and higher} \right) \]

Up to linear order in \( \sigma \) one obtains

\[ \bar{Q}^{(1)}_1(\sigma) \cdot \bar{U}_z(\sigma) \approx \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix} \]

Here the \( \bar{U}_i \) matrices are defined as

\[ \bar{U}_x(\sigma) = \begin{pmatrix} 1 - 2\sigma & 0 & 0 \\ 0 & 1 + \sigma & 0 \\ 0 & 0 & 1 + \sigma \end{pmatrix} \]
\[ \bar{U}_y(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & 0 \\ 0 & 1 - 2\sigma & 0 \\ 0 & 0 & 1 + \sigma \end{pmatrix} \]
\[ \bar{U}_z(\sigma) = \begin{pmatrix} 1 + \sigma & 0 & 0 \\ 0 & 1 + \sigma & 0 \\ 0 & 0 & 1 - 2\sigma \end{pmatrix} \]

Restricting the description to linear order in \( \sigma \) allows the rotation axis to be identified with ease. Comparing the form of the rotation matrix

\[ \bar{Q}^{(1)}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \]

with the general form of the rotation matrix (up to linear order in the rotation angle)
where \( \vec{p} = \begin{pmatrix} p_x \\ p_y \\ p_z \end{pmatrix} \) is the rotation axis, one identifies the rotation axis in \( \vec{Q}_i^{(1)} \) as \( \vec{p}_{rot} = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \). In general \( \vec{p}_{rot} \) should be a unit vector. However, keeping the vector un-normalised simplifies the formulæ; but it has to be kept in mind that in order to obtain the physical rotation angle the value of \( \sigma \) in the rotation matrix has to be multiplied with the norm of the vector \( \vec{p}_{rot} \).

The linear approximation and the fact that rotations commute with one another in this limit allows some interfaces to be constructed. However, before this process is attempted it is worthwhile to point out those circumstances under which the process does not work. One such case is the following:

**An interface cannot be constructed for domains which share a common form of the diagonal matrix \( \vec{U}_i(\sigma) \).**

**Prove:** Let \( \vec{F} \) and \( \vec{G} \) be of the form \( \vec{F} = \bar{Q}_F \cdot \vec{U}_i(\sigma) \) and \( \vec{G} = \bar{Q}_G \cdot \vec{U}_i(\sigma) \) with each \( \vec{U} \) having the same index \( i \). Choose the matrix \( \bar{R} \) to be of the form \( \bar{R} = \bar{Q}_G \cdot \bar{Q}_F^{-1} \), then one obtains

\[
\bar{R} \cdot \bar{F} - \bar{G} = \bar{Q}_G \cdot \bar{Q}_F^{-1} \cdot \bar{Q}_F \cdot \vec{U}_i(\sigma) - \bar{Q}_G \cdot \vec{U}_i(\sigma) = \\
= \bar{Q}_G \cdot \vec{U}_i(\sigma) - \bar{Q}_G \cdot \vec{U}_i(\sigma) = \\
= 0 = f(\sigma) \, \vec{a} \otimes \vec{n}
\]

Therefore, there are no non-zero vectors \( \vec{a} \) and \( \vec{n} \) such that the twinning equation is fulfilled.
Essentially, the rotation of two domains with the same index in the $\overline{U}_i$-matrix transforms one domain $\overline{F}$ into the other domain $\overline{G}$. The rotated domain $\overline{F}$ is then identical to $\overline{G}$, and no interface arises in this situation.

The above argument applies both to type I and type II domains. It therefore suffices to only consider the pairing of domains with different $\overline{U}_i$ matrices.

The working of the procedure is best illustrated with an example. Let the $\overline{F}$ domain be of type I and $i = 1$ with

$$\overline{F} = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}$$

Let the $\overline{G}$ domain also be of type I and $i = 5$ with

$$\overline{G} = \begin{pmatrix} 1 + \sigma & \sigma & 0 \\ -\sigma & 1 - 2\sigma & -\sigma \\ 0 & \sigma & 1 + \sigma \end{pmatrix}$$

Thus one obtains $\overline{R} \cdot \overline{F} - \overline{G}$ as

$$\overline{R} \cdot \overline{F} - \overline{G} =$$

$$= \left( \overline{R} + \sigma \begin{pmatrix} 0 & -p_x & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} \right) \cdot \left( \overline{G} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \right) \cdot \left( \overline{G} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \right)$$

$$- \left( \overline{G} + \sigma \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \right) \cdot \left( \overline{G} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right)$$

$$= \overline{R} - \overline{G} + \sigma \cdot \left( \begin{pmatrix} 0 & -p_x & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} - \begin{pmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} + \begin{pmatrix} 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right) =$$
The choice which is still available is the selection of the axis of rotation. The rotation axis is chosen such that the difference matrix $\tilde{R} \cdot \tilde{F} - \tilde{G}$ has two linear independent eigenvectors for the eigenvalue 0. If one picks

$$\vec{p} = \begin{pmatrix} -1 \\ -1 \\ -1 \end{pmatrix}$$

this results in

$$\tilde{R} \cdot \tilde{F} - \tilde{G} = \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 3 & 3 \\ 0 & -3 & -3 \end{pmatrix}$$

This matrix is degenerate. It is readily shown that the vectors $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ and $\begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}$ are eigenvectors with eigenvalue of 0. Using the non-normalised vectors

$$\vec{a}_1 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix} \quad \quad \text{and} \quad \quad \vec{n}_1 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$$

one obtains

$$\vec{a}_1 \otimes \vec{n}_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & -1 & -1 \end{pmatrix}$$

This matrix is, up to a scaling factor $f(\sigma) = 3\sigma$, the same as the matrix

$$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 3 & 3 \\ 0 & -3 & -3 \end{pmatrix}.$$
\[
\vec{p} = \begin{pmatrix} 5 \\ -1 \\ -1 \end{pmatrix}
\]

This results in

\[
\vec{R} \cdot \vec{F} - \vec{a} = \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 3 & -3 \\ 0 & 3 & -3 \end{pmatrix}
\]

This matrix is also degenerate and the vectors \(\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}\) and \(\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}\) are eigenvectors with eigenvalue of 0. Using the non-normalised vectors

\[
\vec{a}_2 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}
\]

and

\[
\vec{n}_2 = \begin{pmatrix} 0 \\ 1 \\ -1 \end{pmatrix}
\]

one obtains

\[
\vec{a}_2 \otimes \vec{n}_2 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 1 & -1 \end{pmatrix}
\]

Again, up to a scaling factor, this matrix is the same as the matrix \(\begin{pmatrix} 0 & 0 & 0 \\ 0 & 3 & -3 \\ 0 & 3 & -3 \end{pmatrix}\) if one chooses the scaling factor as \(f(\sigma) = 3\sigma\).

This calculation has identified two possible interfaces between domains \(\overline{M}_{1}^{(1)}\) and \(\overline{M}_{1}^{(5)}\). Their characteristics are shown in table 5.9.
Table 5.9: Characteristic entities for the two possible interfaces between domains $\tilde{M}_1^{(1)}$ and $\tilde{M}_1^{(5)}$.

<table>
<thead>
<tr>
<th></th>
<th>Interface type 1</th>
<th>Interface type 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotation vector $\tilde{p}$</td>
<td>$\begin{pmatrix} -1 \ -1 \ -1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 5 \ -1 \ -1 \end{pmatrix}$</td>
</tr>
<tr>
<td>Rotation angle</td>
<td>$\sigma \sqrt{3}$</td>
<td>$\sigma \sqrt{27}$</td>
</tr>
<tr>
<td>2 vectors in interface</td>
<td>$\begin{pmatrix} 1 \ 0 \ 0 \ 0 \ 1 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \ 0 \ 1 \ 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>Normal vector $\tilde{n}$</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \ 1 \end{pmatrix}$</td>
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</table>

It is pointed out that the interface equation as given by Bhattacharya [Bhattacharya03] or the generalised form $\tilde{R} \cdot \tilde{F} - \tilde{G} = f(\sigma) \tilde{a} \otimes \tilde{n}$ with $f(\sigma) \neq 1$ captures the description of the transformation matrices for a given solution. Including the scalar function $f(\sigma)$ in the formula allows freedom for the choice of vectors $\tilde{a}$ and $\tilde{n}$. It also takes into account the parameter $\sigma$ such that the matrix $\tilde{a} \otimes \tilde{n}$ is a purely numeric matrix. This process is fully illustrated by the examples discussed above.

Indeed the requirement that the interface vectors are eigenvectors of the matrix $\tilde{R} \cdot \tilde{F} - \tilde{G}$ with an eigenvalue of 0 is entirely sufficient for the characterisation of the interface.

The rotation angles associated with the rotation matrices are proportional to $\sigma$. Therefore for small values of $\sigma$ the rotation angle is also small. This is a requirement for the consistency of the description and has to be checked at the end of the calculation as only a linear approximation is considered. Here the proportionality of the rotation angle to $\sigma$ suffices to ensure this characteristic.
The rotation vector fully specifies the rotation. Its direction defines the positive axis of rotation according to the right hand rule. The rotation angle $\varphi$ is determined by $\varphi = \sigma \cdot |\vec{p}|$. Knowledge of vector $\vec{p}$ is sufficient to determine the sense of the rotation, the rotation axis and the angle of the rotation as measured in units of $\sigma$. While the rotation angle $\varphi$ is a linear function of $\sigma$, with $\varphi = \text{const} \cdot \sigma$, the constant $\text{const}$ is determined by the magnitude of the vector $\vec{p}$, i.e. $\text{const} = |\vec{p}|$. The direction of rotation is the same as specified by the right hand rule. This is readily verified by explicit calculation for an infinitesimal rotation around the z-axis.

It is of interest to look at all possible interfaces between the various domains. The specification of results will have to include the axis of rotation for the rotation $\vec{R}$ in the term $\vec{R} \cdot \vec{F} - \vec{G}$, two interface vectors and the normal vector $\vec{n}$, which is normal to the interface. However, all calculations will produce an interface normal vector of type $\langle 1,1,0 \rangle$ and interface vectors of the form $\langle 1,0,0 \rangle$ and $\langle 1,1,0 \rangle$. The exact nature of the vectors can be inferred from the index of the $\vec{U}_i$ matrices for the two domains for which the interface is sought. Let the $\vec{U}_i$ matrix index of the first domain be $i$ and of the second domain $j$. By necessity these indices must be different. Then the index $k$ which is not equal to either $i$ or $j$, is the index for the value 1 of the interface vector $\langle 1,0,0 \rangle$. The entries of 1 in $\langle 1,1,0 \rangle$ appear at positions of the indices of $i$ and $j$ for both the other interface vector and the normal vector $\vec{n}$. The distribution of plus and minus signs is readily established for any particular domain combination.

This only leaves the rotation vectors to be listed. The calculations have been done for all of 630 combinations of domains. Only those combinations yield a non-zero result for which the $\vec{U}_i$ matrix indices are different. These results are listed in tables 5.10 to 5.12.
Table 5.10: List of the rotation vectors for combinations of type I – type I domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the second solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their $\mathcal{D}_l$ matrices.
Table 5.11a: List of the rotation vectors for combinations of type II – type II domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the 2nd solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their $\bar{\Omega}_I$ matrices.
Table 5.11b: List of the rotation vectors for combinations of type II – type II domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the 2\textsuperscript{nd} solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their \( \overline{U}_i \) matrices.
Table 5.11c: List of the rotation vectors for combinations of type II – type II domains. The entries above the diagonal are associated with normal vector of type \((1,1,0)\) with the same sign for the non-zero entries, while the 2\textsuperscript{nd} solution below the diagonal is associated with normal interface vectors of \((1,1,0)\) and unequal signs. Empty patches indicate domain combinations with the same index for their \(\vec{U}_I\) matrices.

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Table 5.11d: List of the rotation vectors for combinations of type II – type II domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the 2nd solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their matrices.
Table 5.12a: List of the rotation vectors for combinations of type I – type II domains. The entries above the diagonal are associated with normal vector of type \( (1,1,0) \) with the same sign for the non-zero entries, while the 2\(^{nd} \) solution below the diagonal is associated with normal interface vectors of \( (1,1,0) \) and unequal signs. Empty patches indicate domain combinations with the same index for their \( \hat{\Omega}_t \) matrices.
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Table 5.12b: List of the rotation vectors for combinations of type I – type II domains. The entries above the diagonal are associated with normal vector of type $(1,1,0)$ with the same sign for the non-zero entries, while the 2nd solution below the diagonal is associated with normal interface vectors of $(1,1,0)$ and unequal signs. Empty patches indicate domain combinations with the same index for their $\bar{U}_1$ matrices.
Table 5.12c: List of the rotation vectors for combinations of type I – type II domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the 2nd solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their $\vec{U}_i$ matrices.
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Table 5.12d: List of the rotation vectors for combinations of type I – type II domains. The entries above the diagonal are associated with normal vector of type (1,1,0) with the same sign for the non-zero entries, while the 2nd solution below the diagonal is associated with normal interface vectors of (1,1,0) and unequal signs. Empty patches indicate domain combinations with the same index for their \( \mathbf{U}_f \) matrices.
The above consideration has identified possible interfaces between martensitic domains. The possibility of having two different domain walls between two domains is restricted to domains with different $i$ index for their stretch matrix $\tilde{U}_i$. In particular the solutions include the ones identified before. An inspection reveals that these solutions are those for which the rotation is zero and the rotation matrix is equal to the unit matrix.

An attempt to use the same procedure for constructing an interface between the martensitic and the austenitic phases is not successful. As the austenitic phase is represented by a unit matrix the matrix equation $\mathbf{R} \cdot \bar{\mathbf{F}} - \bar{\mathbf{I}} = f(\sigma) \bar{\mathbf{a}} \otimes \bar{n}$ does not have any solutions.

This result is not unexpected. As discussed in Bhattacharya [Bhattacharya03] an interface between the austenitic and the martensitic phases requires a process of fine twins, with a construction involving twins in twins. As this process has already been described extensively in the literature it is not repeated here. For a more extensive discussion see Bhattacharya [Bhattacharia03].

However, it is not only the interface between austenite and martensite which creates a challenge for the description of the material. If one considers creating a network of domains for a single crystal one encounters some issues of compatibility as it is not yet possible to construct such a network. It turns out that despite the large number of solutions already obtained there is not enough flexibility available within this set of solutions for constructing a network.

The ease with which networks are actually obtained experimentally in a crystal suggests that there must be other solutions. The construction and discussion of these solutions will be the topic of the next section.
5.g Generalised Interface Equation and its Solution in Linear Approximation

The derivation of martensitic interfaces as accomplished above has resulted in a huge number of domain interfaces being identified. Despite this it is still a challenge to construct a network of domains and interfaces within a single crystal. This problem arises as the interface conditions are rather restrictive. There are no further degrees of freedom to allow an easy fitting of interfaces at a junction such as a line where two, or more, interfaces meet.

It is therefore appropriate to search for further interface solutions by enlarging the parameter space available for obtaining martensitic interfaces. The additional degree of freedom is offered by the possibility of having a displacement of one part of the crystal at the interface with respect to the other part on the other side of the interface. The need to remain consistent with previous derivations requires the consideration to be restricted to linear order in $\sigma$.

A translation of a vector $\vec{b}$ can be affected by a translation matrix $\vec{T}$ with

$$\vec{T} \cdot \vec{b} = \begin{pmatrix} 1 + \sigma \delta_1 & 0 & 0 \\ 0 & 1 + \sigma \delta_2 & 0 \\ 0 & 0 & 1 + \sigma \delta_3 \end{pmatrix} \cdot \begin{pmatrix} b_1 \\ b_2 \\ b_3 \end{pmatrix} = \begin{pmatrix} b_1 + \sigma \delta_1 b_1 \\ b_2 + \sigma \delta_2 b_2 \\ b_3 + \sigma \delta_3 b_3 \end{pmatrix}$$

The displacement in direction $\vec{\delta} = \begin{pmatrix} \delta_1 \\ \delta_2 \\ \delta_3 \end{pmatrix}$ is measured in units of the shear parameter $\sigma$ for later convenience.

The interface equation $\vec{R} \cdot \vec{F} - \vec{G} = f(\sigma) \vec{a} \otimes \vec{n}$ can be generalised to include uniform translations of one part of the crystal on one side of the interface by looking for vectors $\vec{b}$ such that

$$\left( \vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G} \right) \cdot \vec{b} = 0$$
This is equivalent to having the interface equation in the form

\[ \vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G} = f(\sigma) \vec{a} \otimes \vec{n} \]

It is instructive again to first consider an example. Here the same domains are considered as for the original derivation. The domain \( \vec{F} \) is taken to be of type I and \( i=1 \) with

\[
\vec{F} = \begin{pmatrix} 1 + \sigma & 0 & \sigma \\ 0 & 1 + \sigma & \sigma \\ -\sigma & -\sigma & 1 - 2\sigma \end{pmatrix}
\]

and the domain \( \vec{G} \) is chosen as type I and \( i=5 \) with

\[
\vec{G} = \begin{pmatrix} 1 + \sigma & \sigma & 0 \\ -\sigma & 1 - 2\sigma & -\sigma \\ 0 & \sigma & 1 + \sigma \end{pmatrix}
\]

Up to linear order, i.e. by neglecting contributions of order \( \sigma^2 \) and higher, the above interface equation takes the form

\[
\vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G} \approx \left( \vec{I} + \sigma \begin{pmatrix} 0 & -p_z & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} \right) \cdot \left( \vec{I} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \right)
\]

\[
= \vec{R} \vec{F} - \vec{U}_z \vec{F} \quad = \vec{U}_z 
\]

\[
\cdot \left( \vec{I} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \right) - \left( \vec{I} + \sigma \begin{pmatrix} \delta_1 & 0 & 0 \\ 0 & \delta_2 & 0 \\ 0 & 0 & \delta_3 \end{pmatrix} \right)
\]

\[
= \vec{R} \vec{G} - \vec{U}_G \vec{G} \quad = \vec{U}_G 
\]

\[
\cdot \left( \vec{I} + \sigma \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix} \right) \cdot \left( \vec{I} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \right) = \vec{U}_y 
\]
\[
\vec{l} - \vec{l} + \sigma \cdot \left\{ \begin{pmatrix} 0 & -p_z & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} + \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} + \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \right\} \\
= \sigma \cdot \left( \begin{pmatrix} -\delta_1 & -1 - p_z & 1 + p_y \\ p_z + 1 & 3 - \delta_2 & 2 - p_x \\ -1 - p_y & p_x - 2 & -3 - \delta_3 \end{pmatrix} \right)
\]

By choosing \( \delta_1 = 0, p_z = -1 \) and \( p_y = -1 \) one obtains the matrix

\[
\vec{R} \cdot \vec{F} - \vec{l} \cdot \vec{G} \approx \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 3 - \delta_2 & 2 - p_x \\ 0 & p_x - 2 & -3 - \delta_3 \end{pmatrix}
\]

For \( \delta_2 = \delta_3 = 0 \) the 2 known interface solutions can be obtained as listed in table 5.10.

However, choosing \( \delta_2 = 1 \) and \( \delta_3 = -1 \) one arrives at

\[
\vec{R} \cdot \vec{F} - \vec{l} \cdot \vec{G} \approx \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 2 - p_x \\ 0 & p_x - 2 & -2 \end{pmatrix}
\]

Here the choices of \( p_x = 0 \) and \( p_x = 4 \) yield \( \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & 2 \\ 0 & -2 & -2 \end{pmatrix} \) and \( \begin{pmatrix} 0 & 0 & 0 \\ 0 & 2 & -2 \\ 0 & -2 & -2 \end{pmatrix} \), respectively. These are the same generic matrices as have been obtained before in the discussion of the domain wall equation without translation. In particular the domain wall properties are the same for these solutions as for the previous ones. The interface normal is again a \( \langle 1,1,0 \rangle \) direction with a \( \langle 1,0,0 \rangle \) and another \( \langle 1,1,0 \rangle \) vector being among the interface vectors.

Yet more solutions may be obtained by, for example, choosing \( \delta_2 = 2 \) and \( \delta_3 = -2 \). This results in
\[ \bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 2-p_x \\ p_x - 2 & -1 \end{pmatrix} \]

For this matrix two solutions are obtained with \( p_x = 1 \) and \( p_x = 3 \) with, again, the same interface.

By contrast, choosing a value of \( \delta_2 = 3 \) and \( \delta_3 = -3 \) yields the matrix

\[ \bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 2-p_x \\ p_x - 2 & 0 \end{pmatrix} \]

This matrix has only one solution of \( p_x = 2 \). As the resulting matrix is the zero matrix this necessitates that

\[ \bar{R} \cdot \bar{F} = \bar{T} \cdot \bar{G} \]

Therefore this particular solution has to be excluded from the selection of solutions as no interface is possible.

All these solutions of the generalised interface equation \( (\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}) \cdot \vec{b} = 0 \) have the same interface vectors and the same interface normal vector (up to sign reversal). The various solutions differ by the rotation axis and the rotation angle as well as the size of the translation at the interface. Note that for all solutions the direction of the translations always remains the same with

\[ \vec{\delta} = \text{integer} \cdot \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \]

Here \text{integer} is a positive or negative integer with the exclusion of \text{integer} = 3.

It is pointed out that the translations of the interface have resulted in a pair of 2 solutions for each of the allowed translations. These solutions correspond to new solutions at type 1 and type 2 interfaces.
However, only one of these solutions is a physically acceptable one. It is instructive to illustrate the difficulties which arise with the non-physical solution.

The translation direction $\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$ lies within the interface for interfaces of type 1 and it is oriented perpendicular to the interface for interfaces of type 2. However, the latter translations have to be considered unphysical as a uniform translation perpendicular to an interface would result in a change of the density of the material at the interface. This is not an energetically favourable process. Indeed a translation perpendicular to the interface would result in a separation of the two halves of the crystal and yield a disjoint sample. Thus the translation solutions should only be applied to type 1 interfaces for which the translation is within, i.e. parallel to, the interface.

The distinction between the two possible interfaces needs some further investigation. Crystallographically the interfaces with either normal vector $\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$ for a type 1 interface or with a normal vector of the form $\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$ for a type 2 interface are identical in a cubic lattice. However, the required rotation directions and rotation angles for the interface solution without translation need to be considered in more detail and in conjunction with the translations in order to address this question.

The rotations for the example interfaces discussed above are represented by the vectors $\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} 5 \\ 1 \\ 1 \end{pmatrix}$, respectively. The translations are such that the translation vector and the rotation axis are perpendicular to one another. If the rotation axis is within the interface, as for type 2 interfaces, then a homogeneous translation...
would not be confined to the interface region. However, for a type 1 interface
the translation is strictly within the interface plane, with the rotation axis being
oriented perpendicular to the translation vector \( \mathbf{\delta} \). For solutions with translations
within the interface a rotation axes is not altered in its relationship to the
interface plane. Therefore the analysis as given here for the solutions without
translations applies equally well to the solutions which involve translations.

The example given above can be generalised. This generalisation results in the
description of some solutions. The description is stated as follows:

**Given two domain transformation matrices** \( \overline{F} \) and \( \overline{G} \). Let their \( \overline{U} \) matrices be \( \overline{U}_F \) and \( \overline{U}_G \) with \( \overline{U}_F \neq \overline{U}_G \). Then there exists an interface solution of a type 1
interface for these domains with a translation vector \( i \cdot \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix} \), \( i \neq 3 \), with the
entry of 1 at the position of the index of \( \overline{U}_F \) and a value of -1 at the position of
the index of \( \overline{U}_G \) and a rotational part as listed in tables 5.10 to 5.12. The
rotational parts of the solution have to be modified by \( \pm i \) at the index \( k \) which
is not the index of either \( \overline{U}_F \) or \( \overline{U}_G \). The difference of the rotation vectors for
the \( k \) index must be \( \pm (6 - 2i) \).

For the above example one obtains the \( \overline{U}_F \) index as \( z \) and the \( \overline{U}_G \) index as \( y \).
Then for \( i = 0 \) the \( k \)-index is \( x \) and the rotational part of the solution is obtained
as \( \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \) and \( \begin{pmatrix} 5 \\ 1 \\ 1 \end{pmatrix} \).
For $i = 1$ the translation vector is $\vec{\delta} = \begin{pmatrix} 0 \\ i \\ -i \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$ and the rotation part of the solution is obtained as $\begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} 4 \\ 1 \\ 1 \end{pmatrix}$. The difference of these vectors in the $x$-component is $6 - 2 \cdot 1 = 4$.

For $i = 2$ the translation vector is $\vec{\delta} = \begin{pmatrix} 0 \\ 2i \\ -2i \end{pmatrix} = \begin{pmatrix} 0 \\ 2 \\ 2 \end{pmatrix}$. The rotation part of the solution has the form $\begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$ and $\begin{pmatrix} 3 \\ 1 \\ 1 \end{pmatrix}$ with a difference of these vectors in the $x$-component of $6 - 2 \cdot 2 = 2$.

The description works in a similar manner for other positive or negative integer values of $i$ with the exception of $i = 3$.

It is appropriate to seek a physical interpretation of these solutions. For this consider the equation $(\vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G}) \cdot \vec{b} = 0$ and investigate the effect of the translation. The translation part of the equation is given as

$$\vec{T} \cdot \vec{G} \cdot \vec{b}$$

The calculation can be done in two different ways as signified by using brackets. The first method of calculation yields

$$\vec{T} \cdot (\vec{G} \cdot \vec{b})$$

Here the interface vector $\vec{b}$ is first transformed according to the martensitic transformation matrix $\vec{G}$, then the interface is translated according to the translation matrix $\vec{T}$.

The second manner of doing the calculation is represented by
Here the whole domain $\vec{G}$ is translated first and then the interface vector is transformed according to the transformation matrix $\vec{T} \cdot \vec{G}$.

The first interpretation only involves the interface, while the second requires the transformation of the whole domain $\vec{G}$; and both ways of interpreting the equation are consistent with the form $\vec{T} \cdot \vec{G} \cdot \vec{b}$.

In order to resolve the apparent contradiction one has to note that the description given by the equation $(\vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G}) \cdot \vec{b} = 0$ is for an interface. A simple consideration will reveal that the description is the same for the interface whether the whole of the domain $\vec{G}$ is translated or alternatively one considers the interface of the domain $\vec{T} \cdot \vec{G}$. As far as the interface is concerned both descriptions are identical.

This interpretation suggests the possibility of transforming one domain into another one by the propagation of translations from the interface through the whole martensitic domain. These may be created at the interface between domains and then allowed to travel through the whole of one domain.

Indeed if the above example is considered for a translation of the form $\vec{\delta} = \begin{pmatrix} 0 \\ 3 \\ -3 \end{pmatrix}$ then the matrix $\vec{G}$ is transformed as

\[
\vec{T} \cdot \vec{G} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 + 3\sigma & 0 \\ 0 & 0 & 1 - 3\sigma \end{pmatrix} \cdot \begin{pmatrix} 1 + \sigma & \sigma & 0 \\ -\sigma & 1 - 2\sigma & -\sigma \\ 0 & \sigma & 1 + \sigma \end{pmatrix} = \begin{pmatrix} 1 + \sigma & \sigma & 0 \\ -\sigma & 1 + \sigma & -\sigma \\ 0 & \sigma & 1 - 2\sigma \end{pmatrix} + \text{higher orders in } \sigma
\]
This translation has transformed the $\mathcal{G} = \mathcal{M}_1^{(5)}$ domain with a $\mathcal{U}$ matrix of type $\mathcal{U}_y$ into a rotated transformation matrix with a $\mathcal{U}$ matrix of type $\mathcal{U}_z$.

Compared to the rotated matrix $\mathcal{F} = \mathcal{M}_1^{(1)}$ with a rotation vector of $\begin{pmatrix} 2 \\ 1 \\ 1 \end{pmatrix}$, one obtains $\bar{\mathcal{R}} \cdot \mathcal{F} \approx \left( \bar{\mathcal{I}} + \sigma \begin{pmatrix} 0 & -p_z & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} \right) \cdot \left( \bar{\mathcal{I}} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \right) = \bar{\mathcal{Q}}_F$.

Thus it can be concluded that for $\bar{\delta} = \begin{pmatrix} 0 \\ 3 \\ -3 \end{pmatrix}$ the domain $\mathcal{M}_1^{(5)}$ is transformed, by translation and rotation, to domain $\mathcal{M}_1^{(1)}$.

It is also readily seen that a translation of the form $\bar{\delta} = \begin{pmatrix} 3 \\ 3 \\ 0 \end{pmatrix}$ transforms the domain $\mathcal{M}_1^{(5)}$ with a $\mathcal{U}_y$ matrix into a rotated domain characterised by a $\mathcal{U}_z$ matrix. Indeed transforming any domain matrix into any other domain matrix by a combined rotation and translation transformation is possible, at least to linear order in $\sigma$. The transformation can be obtained and written down by a simple inspection of the pair of domain matrices.

If it is possible to transform any domain into any other, is it then also possible to obtain interfaces between any pair of different domains? This question can be given an affirmative answer. In order to demonstrate this process, interfaces will be constructed between domains with the same $\mathcal{U}_i$ matrix. In the absence of a translation at the interface it has not been possible to construct such interfaces,
and no solutions have been identified in tables 10.10 to table 10.12. Finally the question of a coherent interface between martensite and austenite will be addressed.

Consider, by way of an example, the domains $\tilde{F} = \tilde{M}_1^{(1)}$ and $\tilde{G} = \tilde{M}_1^{(2)}$. Both domains are characterised by a $\tilde{U}_z$ matrix. For these domains the interface equation takes the form

$$
\tilde{R} \cdot \tilde{F} - \tilde{R} \cdot \tilde{G} \equiv \left( \tilde{I} + \sigma \begin{pmatrix} 0 & -p_z & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} \right) \cdot \left( \tilde{I} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \right) - \left( \tilde{I} + \sigma \begin{pmatrix} \delta_1 & 0 & 0 \\ 0 & \delta_2 & 0 \\ 0 & 0 & \delta_3 \end{pmatrix} \right)
$$

Various solutions are possible. The different cases will be discussed in turn.
Case 1: Choose $\delta_1 = 0$ and $p_y = p_z = 0$. For this choice the matrix is obtained as

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & -\delta_2 & -p_x \\ 0 & p_x & -\delta_3 \end{pmatrix}$$

Solutions are obtained for $\delta_2 = -\delta_3 = \pm p_x$ with the same interfaces as obtained for other solutions.

Case 2: Choose $\delta_2 = 0$ and $p_x = p_z = 0$. For this choice the matrix is obtained as

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix} -\delta_1 & 0 & p_y \\ 0 & 0 & 0 \\ -p_y & 0 & -\delta_3 \end{pmatrix}$$

Solutions are obtained for $\delta_1 = -\delta_3 = \pm p_y$.

Case 3: Choose $\delta_3 = 0$ and $p_x = p_y = 0$. For this choice the matrix is obtained as

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix} -\delta_1 & -p_z & 0 \\ p_z & -\delta_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Solutions are obtained for $\delta_1 = -\delta_2 = \pm p_z$.

The physics of these solutions is no different from that already discussed. Therefore it suffices to state the solutions. For other combinations of domain transformation matrices very similar results will be obtained. Indeed as the $\bar{U}_i$ cancel on taking the difference the solutions are of identical form for all combinations of domain matrices with the same $\bar{U}_i$ part.
Finally the interface between a martensitic domain and the austenitic phase is considered. The austenitic phase is presented by the unit matrix with $\bar{G} = \bar{I}$. Within a linear approximation and taking $\bar{F} = M_1^{(1)}$, the domain wall equation reads

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}_{aust} \approx \left( \bar{I} + \sigma \begin{pmatrix} 0 & -p_z & p_y \\ p_z & 0 & -p_x \\ -p_y & p_x & 0 \end{pmatrix} \right) \cdot \left( \bar{I} + \sigma \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 1 \\ -1 & -1 & 0 \end{pmatrix} \right)$$

$$\cdot \left( \bar{I} + \sigma \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix} \right) \cdot \left( \bar{I} + \sigma \begin{pmatrix} \delta_1 & 0 & 0 \\ 0 & \delta_2 & 0 \\ 0 & 0 & \delta_3 \end{pmatrix} \right) \cdot \bar{I} =$$

$$= \sigma \cdot \begin{pmatrix} 1 - \delta_1 & -p_z & 1 + p_y \\ p_z & 1 - \delta_2 & 1 - p_x \\ -1 - p_y & p_x - 1 & -2 - \delta_3 \end{pmatrix}$$

Again various solutions can be identified. These are considered in turn.

**Case 1:** Choose $\delta_1 = 1$ and $p_y = -1$, $p_z = 0$. For this choice the matrix takes the form

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}_{aust} \approx \sigma \cdot \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 - \delta_2 & 1 - p_x \\ 0 & p_x - 1 & -2 - \delta_3 \end{pmatrix}$$

Solutions are obtained for $\delta_2 = -p_x = -\delta_3 - 1$ and for $\delta_2 = 2 - p_x = -\delta_3 - 1$. Inserting these solutions into the above matrices yields
Apart from the value of $\delta_2 = 1$, which yields a zero matrix, there are 2 different solutions possible. The interface is again of $\begin{pmatrix} 1 \\ 1 \end{pmatrix}$ type.

<table>
<thead>
<tr>
<th></th>
<th>Solution 1</th>
<th>Solution 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation $\vec{\hat{d}}[\sigma]$</td>
<td>$\begin{pmatrix} 1 \ \delta_2 \ -1 - \delta_2 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ \delta_2 \ -1 - \delta_2 \end{pmatrix}$</td>
</tr>
<tr>
<td>Rotation $\vec{\hat{p}}[\sigma]$</td>
<td>$\begin{pmatrix} \delta_2 \ 1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 2 - \delta_2 \ 1 \ 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>Interface vectors</td>
<td>$\begin{pmatrix} 1 \ 0 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \ 1 \end{pmatrix}$</td>
</tr>
<tr>
<td>Normal vector $\vec{n}$</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

**Case 2:** Choose $\delta_2 = 1$ and $p_x = 1, p_z = 0$. For this choice the matrix takes the form

$$\vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G}_{\text{aust}} \approx \sigma \cdot \begin{pmatrix} 1 - \delta_1 & 0 & 1 + p_y \\ 0 & 0 & 0 \\ -1 - p_y & 0 & -2 - \delta_3 \end{pmatrix}$$

Solutions are obtained for $\delta_1 = -p_y = -\delta_3 - 1$ and for $\delta_1 = 2 + p_x = -1 - \delta_3$. Inserting these solutions into the above matrices yields

$$\vec{R} \cdot \vec{F} - \vec{T} \cdot \vec{G}_{\text{aust}}|_{\text{solution 1}} \approx \sigma \cdot \begin{pmatrix} 1 - \delta_1 & 0 & 1 - \delta_1 \\ 0 & 0 & 0 \\ -1 + \delta_1 & 0 & -1 + \delta_1 \end{pmatrix}$$
The value of $\delta_1 = 1$ has to be excluded as a possible solution. For any other value of $\delta_1$ one obtains 2 solutions as listed below.

<table>
<thead>
<tr>
<th></th>
<th>Solution 1</th>
<th>Solution 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Translation $\tilde{\delta} [\sigma]$</td>
<td>$\begin{pmatrix} \delta_1 \ 1 \ -1 - \delta_1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} \delta_1 \ 1 \ -1 - \delta_1 \end{pmatrix}$</td>
</tr>
<tr>
<td>Rotation $\tilde{p} [\sigma]$</td>
<td>$\begin{pmatrix} 1 \ -\delta_1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ \delta_1 - 2 \ 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>Interface vectors</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \ 0 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 0 \ 1 \ 1 \ 0 \end{pmatrix}$</td>
</tr>
<tr>
<td>Normal vector $\vec{n}$</td>
<td>$\begin{pmatrix} 1 \ 0 \ 0 \ 1 \end{pmatrix}$</td>
<td>$\begin{pmatrix} 1 \ 0 \ 0 \ 1 \end{pmatrix}$</td>
</tr>
</tbody>
</table>

**Case 3:** Choose $\delta_3 = -2$ and $p_x = 1, p_y = -1$. Now the matrix becomes

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}_{aust} \approx \sigma \cdot \begin{pmatrix} 1 - \delta_1 & -p_z & 0 \\ p_z & 1 - \delta_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Solutions are obtained for $\delta_1 = 1 - p_z = 2 - \delta_2$ and for $\delta_1 = 1 + p_z = 2 - \delta_2$. Inserting these solutions into the above matrices yields

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}_{aust} \bigg|_{solution_1} \approx \sigma \cdot \begin{pmatrix} 1 - \delta_1 & 1 - \delta_1 & 0 \\ -1 + \delta_1 & -1 + \delta_1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G}_{aust} \bigg|_{solution_2} \approx \sigma \cdot \begin{pmatrix} 1 - \delta_1 & -1 + \delta_1 & 0 \\ 1 - \delta_1 & -1 + \delta_1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Excluding the value of $\delta_1 = 1$ as a possible solution for all other values of $\delta_1$ the following solutions are obtained:
The interface equations for an interface between the austenitic and one martensitic domain $M^{(1)}_1$ have a total of 6 different solutions, with each solution again being parameterised by a parameter which can, in principle, take on an infinite number of different integers. Each solution is characterised by a combination of a translation and a rotation contribution.

The solutions are grouped into 3 cases, with each case having 2 types of solution. For each case the translational part of the solution is identical for each of the two solutions. The rotational parts of the solution differ in the component for which the interface vectors have a zero entry.

For an interface to exist it is advantageous to have the translation within the plane of the interface. However, for all solutions the one value of the component of the translation which can be varied, for which the translation would within the interface between domains, had to be excluded from the set of possible solutions.

An analysis of the excluded solutions reveals that these correspond to a transformation which, if applied to the whole of the martensitic domain $M^{(1)}_1$,
effectively transforms this domain into the austenitic structure. Under such conditions no interface exists.

This completes the analysis of the domain walls. Given the equation which has to be solved for obtaining domain walls, namely \( \bar{R} \cdot \bar{F} - \bar{G} = f(\sigma) \bar{a} \otimes \bar{n} \) and its generalisation involving translations at the interface, \( \bar{R} \cdot \bar{F} - \bar{T} \cdot \bar{G} = f(\sigma) \bar{a} \otimes \bar{n} \), an infinite number of possible interfaces has been identified. Not all of these possible solutions of the interface equations are physically acceptable solutions. In addition the details of the interface, with respect to energetic considerations, will also be of importance for selecting those interface configurations which are physically acceptable.

Despite these constraints the chance of using so many different interfaces provides the necessary flexibility to construct a domain network. This question will be explored more fully in the next section. Conditions will be derived for the intersection of domain walls and the geometry of this network.

5.h Domain Wall Networks

Once the interface between 2 different domains has been established it is appropriate to ask how it is possible for many domains to arrange themselves within a single crystal. This arrangement requires more than 2 domains to be matched into a fitting pattern such that interfaces do not give rise to crystallographic defects. This criterion is necessary as a macroscopic single crystal can undergo repeated cycles of heating and cooling between the martensitic and the austenitic phases without a degradation of the crystal quality within the cubic, austenitic phase.
The first possibility to be investigated is the arrangement of 2 different domain walls between two domains. Such a possibility exists as there are 2 different solutions to the domain wall problem between two domains. Either no solution exists, or alternatively two different solutions exist. Such a case is illustrated in figure 5.9.

![Figure 5.9](image)

*Figure 5.9:* A domain wall between two different martensitic domains M1 and M2. Without an interface translation there are two possible solutions for these domains, with the green and blue representing these solutions. Thus this domain wall is envisaged to consist of both solutions in different parts.

Here the green and the blue parts of the picture represent the two different solutions for the domain wall between uniform martensitic domains M1 and M2. However, from the physics related to the formation of such a domain wall arrangement this is not possible. In order to appreciate the difficulties of constructing such an interface, note that the solutions require the two homogeneous domains to be rotated around different axes and different angles for each interface. Therefore fixing one domain and rotating the other cannot produce one part of the interface with one type of interface and another part with another type. This would require a splitting of the domain into different parts, which thereby would create another interface within such a domain. This is contrary to the original assumption of a uniform domain before and after the matching process. Therefore such an interface does not exist.
Now consider the same configuration but allowing an interface translation to occur for one of these interfaces. The condition that one interface must be of type 1 and the other of type 2, and taking into account the remarks made above with respect to translations let the translational part be associated with the interface of type 1 (see table 5.9). Then the rotational part of the solution is determined by the interface of type 2.

Considering again an example for which the matrix $\bar{F}$ is given by $M_1^{(1)}$ and the matrix $\bar{G}$ is given by $M_1^{(5)}$. Then a type 2 interface requires the rotation to be 
\[
\begin{pmatrix}
5 \\
1 \\
1
\end{pmatrix}
\] according to table 5.9. Having the rotational part of the solution to the interface of type 1 fixed to 
\[
\begin{pmatrix}
5 \\
1 \\
1
\end{pmatrix}
\] one may proceed to determine the translational part of the solution. A simple calculation confirms the translation to be of the form 
\[
\vec{\delta} = \begin{pmatrix}
0 \\
6 \\
6
\end{pmatrix}
\] as measured in units of $\sigma$.

Indeed fixing the value of $p_x$ to $p_x = 5$ one obtains the equation
\[
\bar{R} \cdot \bar{F} - \bar{F} \cdot \bar{G} \cong \sigma \cdot \begin{pmatrix}
0 & 0 & 0 \\
0 & 3 - \delta_3 & 2 - p_x \\
0 & p_x - 3 & 3 - \delta_3
\end{pmatrix} = \sigma \cdot \begin{pmatrix}
0 & 0 & 0 \\
0 & 3 - \delta_2 & -3 \\
0 & 3 & -3 + \delta_2
\end{pmatrix}
\]

For an interface of type 1 one needs to have lines with the same non-zero numerical entries. This requires
\[
3 - \delta_2 = -3 \\
3 - \delta_3 = 3
\]
Combined with the requirement that $\delta_1 = 0$ one obtains an interface for a translation of the form $\vec{\delta} = \begin{pmatrix} 0 \\ 6 \\ \frac{1}{6} \end{pmatrix}$ and multiplied by the value of $\sigma$. This translation is consistent with the conditions derived and described before.

It is, however, not sufficient for a solution to exist to fulfil the above interface conditions. This condition is only a necessary, but not a sufficient, condition. In addition one has to require that the line, along which both interfaces meet, transforms in the same manner if transformed according to $\vec{F}$ or $\vec{G}$. That is the following line has to be true:

$$(\vec{R}_1 \vec{F}_1)\vec{b}_{int} = (\vec{T}_1 \vec{n}_1)\vec{b}_{int} = (\vec{R}_2 \vec{F}_2)\vec{b}_{int} = (\vec{T}_2 \vec{n}_1)\vec{b}_{int}$$

Here the intersection line is represented by a vector $\vec{b}_{int}$, the indices 1 and 2 correspond to the interfaces $I_1$ and $I_2$. As $\vec{b}_{int}$ has to be an interface vector of both interfaces, it has to be perpendicular to the normal vectors of these interfaces. Let the normal vectors of interfaces 1 and 2 be denoted by $\vec{n}_1$ and $\vec{n}_2$.

Then $\vec{b}_{int}$ can be obtained as the vector product of $\vec{n}_1$ and $\vec{n}_2$, namely

$$\vec{b}_{int} = \vec{n}_1 \times \vec{n}_2$$

This defines, up to inversion, the direction of the intersection of domain walls. For brevity this intersection of domain interfaces or domain walls will be referred to as a domain line.

For the above example one obtains

$$\vec{b}_{int} = \vec{n}_1 \times \vec{n}_2 = \vec{b}_{int} = \frac{1}{\sqrt{2}} \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \times \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$$

For the interface line one requires that

$$(\vec{R} \cdot \vec{F}) \cdot \vec{b}_{int} = (\vec{T} \cdot \vec{G}) \cdot \vec{b}_{int}$$
for both interfaces. This, however, is guaranteed by the very process by which the interface vector has been constructed.

The fact that the interface involves a translation gives rise to a distortion field. Thus as the translation comes to an end at the domain line some elastic deformation is involved in the formation of such a domain line. Given that the translations are measured in multiples of $\sigma$, and given the underlying assumption of $\sigma$ being small the elastic energy can also be taken to be small. However, for a discussion of the energetics of domain walls and domain lines within a domain network this contribution has to be taken into account.

Next one may consider the case of three domains meeting at a domain line. This configuration is depicted schematically in figure 5.10. However, it is more appropriate to immediately generalise the description.

![Figure 5.10](image)

**Figure 5.10:** Three different domain walls between uniform martensitic domains M1, M2 and M3 are joined with a common line of contact. It is oriented perpendicular to the line of intersection of the three domain walls. The two-dimensional section is shown on the left. The 3-dimensional picture is shown on the right.

In order to obtain all possible domain lines one has to investigate the vector product of all combinations of normal vectors of various interfaces. For martensitic domains these normal vectors are of type $(1,1,0)$. There are 6 unique
(1,1,0) vectors, increasing to 12 if vectors related by inversion are being taken as distinct. All these vectors are shown below in figure 5.11.

The possible vectors $\vec{b}_{\text{int}}$ are readily identified by evaluating all vector products between the various $\langle 110 \rangle$ directions in figure 5.11. It turns out that there are 2 different possibilities for the planes in which normal vectors can lie. The first possibility is a $\langle 100 \rangle$ plane, as already obtained above for the example of a domain line with 2 domain walls and as shown in figure 5.12, and the second possibility is a $\langle 111 \rangle$ plane as shown in 5.13. This is readily verified by evaluating all vector products between any combinations of $\langle 110 \rangle$ vectors.

![Diagram](image1)

**Figure 5.11:** The above plot shows the directions of all different $\langle 110 \rangle$ directions within the cube.

![Diagram](image2)

**Figure 5.12:** Location of 3 possible $\langle 100 \rangle$ planes in which the normal vectors of 3 or 4 interfaces may lie.
The different planes also determine the angles at which the various domain walls join in the projection onto the plane spanned by the normal vectors. This is evident as the normal vectors have to be perpendicular to the interfaces. Thus for the projections onto a (100) plane there is only one possibility. The plane has two [1,1,0] vectors at 90° to one another. A third domain wall must be one for which the normal domain wall vector is equal, up to a sign change, to one of these vectors. Therefore one domain wall must have 180° and the other 90°. This configuration is shown in figure 5.14 on the left. Another possibility is the meeting of 4 domains at the domain line. This configuration is shown in figure 5.14 on the right hand side. Domain lines for either 3 domains or 4 domains are
the only possibilities for \(\langle 100 \rangle\) planes. The angles between domain walls must be a multiple of \(90^\circ\). For domain lines on \(\langle 111 \rangle\) planes there must be a distribution of up to six domains as indicated in the bottom part of figure 5.14. Directions of domain lines are also given. Neighbouring sections may not necessarily be different domains. Thus the angles between domain lines in \(\langle 111 \rangle\) planes are multiples of \(60^\circ\).

![Diagram showing domain lines and angles](image)

**Figure 5.14:** Distribution of 3 or 4 domain lines on \(\langle 100 \rangle\) planes and up to 6 domain lines on \(\langle 111 \rangle\) planes. The distribution on domains on \(\langle 111 \rangle\) planes yields angles of multiples of \(60^\circ\) for the domain lines.

The above discussion has enabled some characteristics of the domain network to be determined. Interface lines have been identified as line either along \(\langle 1,0,0 \rangle\) or along \(\langle 1,1,1 \rangle\) directions. There is the possibility of between 2 and 6 domains meeting at one domain line. An explicit example has been given for a domain line between 2 different domains.

A similar discussion of domain lines can also be carried out for interfaces between martensitic and austenitic phases. This, however, will not be done here. It is conjectured that given the large number of possible interfaces between
domains and also the austenitic phase that a solution may be found for any combination of domains. The proof of such a statement, however, would involve the checking of a very large number of combinations. This work will not be attempted here.

5.1 Discussion

The investigation of the transformation matrices as obtained by Brown et al. [Brown04] has enabled some microscopic features of the transformation process to be addressed. In particular the properties of the transformation matrices have been investigated. All matrices have been characterised as to their invariant vector of type (1,1,1) and their rotation axis of the rotational part of the transformation. A list of the explicit form of all different transformation matrices has been obtained and their relationship to the symmetry elements of the crystallographic point group has been given.

The question of the formation of interfaces between martensitic domains has been addressed. Interfaces have been identified between different domains without the need of invoking rotations. This restriction has resulted in some interfaces being identified between one type I domain and two other type II domains. The individual groups of domains being connected to one another are distinct and any two groups of connected domains do not contain a common element. The number of domain interfaces identified by such a process is too limited. Further possibilities for interfaces are obtained if one of the domains is allowed to rotate. The possible rotations have been determined and all possible interfaces have been listed in appropriate tables.
It is observed that the rotation axes as identified by solving \( \vec{R} \cdot \vec{F} - \vec{G} = f(\sigma) \vec{a} \otimes \vec{n} \) bear a resemblance to the invariant vectors identified for the non-rotated matrix combinations. For example in table 5.6 the invariant vector between the transformation matrices \( \overline{M}_1^{(1)} \) and \( \overline{M}_1^{(5)} \) is obtained as \( \left( \begin{array}{c} 5 \\ 1 \\ 1 \end{array} \right) \). The same vector appears in table 5.10 as one of the rotation axes.

This is not a surprise. Physically a rotation around an invariant vector will preserve the invariance of the rotation axis, and thereby the invariance of the original vector. Thus the rotation serves to bring into line and to optimize one other vector in order to form an interface. Similar relationships can be observed for other combinations of transformation matrices in the various tables.

The interface equation has been generalised further to include translations at the interface. This generalisation has resulted in an essentially infinite number of solutions to be obtained for possible interfaces. While it is satisfying to have available sufficient flexibility in constructing domain configurations within a crystal it is necessary to consider the physics, and in particular the energetics, of such interfaces. Translations will involve distortions, at least at the interface line, and thereby create an elastic energy contribution to the domain line energy. However, energetic considerations are beyond the discussion as given here as these will require a more detailed modelling of the interface.

All martensitic interfaces have been identified as \( \langle 1,1,0 \rangle \) planes. For \( \text{Ni}_2\text{MnGa} \) there are 2 different \( \langle 1,1,0 \rangle \) planes as shown in figure 5.15. The composition of each plane is the same, and it corresponds to the chemical formula \( \text{Ni}_2\text{MnGa} \). Also the arrangement of atoms is the same in both planes. They differ by a translation with respect to one another. For any actual interface such interface details have to be taken into account. Indeed as the two planes alternate in
(1,1,0) direction an interface has to involve one plane on one side and the other plane on the other side. Therefore there is one unique interface. In addition the translations which form part of the interface solution must take into account that the interfaces are not flat on an atomic level, but rather are modulated as determined by the sizes of the various atoms. Thus translations with out of plane components may be energetically advantageous.

![Diagram](image)

**Figure 5.15**: Plot of the two possible (1,1,0) planes. For the plot at the top the origin of the coordinate axes is at (0,0,0) while for the bottom plot the origin of the coordinate system in the figure is located at \(\left(\frac{1}{4}, \frac{1}{4}, 0\right)\). Ni atoms are indicated in green, Mn atoms in red and Ga atoms by a blue colour.

While the identification of possible domain interfaces is an important contribution to the understanding of the low temperature phase of Ni\(_2\)MnGa it is worth pointing out which questions have not been addressed here.
The discussion of the possible interfaces within the pseudo-tetragonal phase of Ni$_2$MnGa does not address the question of the lattice modulation. Indeed the main focus of the investigation has been the matching of parts of the crystal with larger differences of the lattice parameter as induced by the martensitic phase transformation. The much smaller effect of an orthorhombic distortion and a lattice modulation along a cubic (110) direction are much smaller effects which have been entirely neglected in the discussion focussed on domain walls. Therefore the description of domain interfaces can only be a first approximation to a full description which, of course, has to include these effects.

In summary the analysis of the transformation matrices has resulted in the identification of domain interfaces within the martensitic phase. The linear approximation, which has been used for this analysis, is appropriate for this purpose. A possible path for extending the description to non-linear order, and including terms up to order $\sigma^2$, has been identified. Explicit and extensive information has been listed for possible interfaces and the transformations required for achieving these on a microscopic level.

This proves that it is possible to have atomically sharp and plane interfaces between martensitic domains. This is one requirement for enabling crystallographic transformations to occur without a degradation of a single crystal. It is also of practical importance to find out how the various domains link up within a crystal in a three dimensional domain network. Some steps in this direction have been described above.

The process of starting from the transformation matrices is complementary to the macroscopic approach as described in the literature [Bhattacharya03]. On a macroscopic level it is observed that domains occur within domains within domains... The macroscopic description therefore seeks to establish a
hierarchical description of domains. Within the approach described here this process is attempted from the other extreme, namely starting from an atomic point of view and going towards the macroscopic level. By starting from the atomic description and the transformation matrices, which describe the rearrangement and changes on the atomic scale, the lowest level of the domain hierarchy is addressed. It must be possible to progress from such a model towards a more macroscopic description. The present analysis is a first step in this direction.

It is now instructive to return to the question which has been posed at the beginning of this chapter, namely the question of the existence of two different martensitic domains of type I and type II. It is to be anticipated that if type I and type II domains were to form independently of one another, and at approximately the same rate in the austenite–martensite transition, that due to the larger numbers of type II domain the ratio of type I to type II domains should be 1:2. If, however, only type I domains are formed and type II domains only arise as a 2nd choice solution (for example when domain walls cannot form involving only rotations such as in 1/3 of all cases in tables 5.10 to 5.12 and with all interface translations propagating through one domain) then one would expect their abundance to be close to 2/3:1/3. An experimentally observed ratio of type I to type II domains is such that type I domains are found more than twice as frequent compared to type II domains. If the above argument is accepted then it can be argued that type I domains are the fundamental domains which are created in the phase transition. Type II domains can then be viewed as derived from type I domains due to the need of translations at the interface with some of these translations propagating through one domain and changing a type I domain to a type II domain. Evidently the argument as presented here will need
refining but it is helpful in demonstrating that a more detailed knowledge of the interfaces allows more general questions to be addressed relating to the domain network, domain generation and domain transformation.
6 Discussion

For an alloy for which the structure is stable there is a relationship between the slope of the spontaneous magnetization at low temperatures and the value of \( T_c \). However, for the Ni\(_{2-x}\)Mn\(_{1+x}\)Ga samples there is a martensitic phase transition within the ferromagnetically ordered state. This phase transition changes the distances between nearest neighbours and thereby the strength of the magnetic interaction. It is therefore not, a priory, clear whether or not this relationship still holds for this alloy series.

**Figure 6.1:** \( T_c \) as a function of the slope of the spontaneous magnetization at low temperatures (top left) and the spin wave stiffness constant (top right) as well as \( T_c \) versus \( M_0^2 \) (bottom left) and D versus Mn content (bottom right) for Mn\(_{1+x}\)Ni\(_{2-x}\)Ga and \( 0 < x \leq 1 \). A guide to the eye is given by the black line.
In order to test this correlation the slope of the magnetization at low temperatures is plotted against the $T_c$ value for $\text{Mn}_{1+x}\text{Ni}_{2-x}\text{Ga}$ and $0 < x \leq 1$ as may be seen in figure 6.1 (top left). A correlation between $T_c$ and the slope of the spontaneous magnetization or rather the spin wave stiffness constant is not visible within the graphs of figure 6.1, neither is there a relationship between $T_c$ and $M_0^2$ nor between the spin stiffness constant and Mn content. Such a correlation would be expected on the basis of energy arguments and based on a fixed moment system with a constant value of the exchange constant.

Thus a correlation between the slope of the spontaneous magnetization at low temperatures and the Curie temperature is not present in the compounds of the series investigated here. The spin wave stiffness constant $D$ was calculated using the values $M_0$ and $\text{slope}$ as obtained in chapter 3 and the lattice constant $a$ of the cubic phase at 300 K as obtained in chapter 4. A list of the $D$ values is given in appendix B.

The variation of the spontaneous magnetization, the ground state magnetization, the Curie temperatures and the martensitic transition temperatures as a function of Mn content were already discussed at the end of chapter 3. The spontaneous magnetization is strongly dependent on whether or not a sample is annealed, but not on the temperature of annealing. The Curie temperature is linearly dependent on the Mn content. It shows a slightly larger scattering for untreated samples, but overall it is not dependent on the annealing of a sample nor on the temperature of the annealing process.

The martensitic transformation temperatures depend strongly on the temperature of annealing. A shift of about 100 K towards higher temperatures is observed for compounds annealed at 900°C with respect to those annealed at 800°C. This is confirmed by measurements of the magnetization, the electric
resistivity and neutron diffraction on Mn$_{1.15}$Ni$_{1.85}$Ga and Mn$_{1.8}$Ni$_{1.2}$Ga. However, if present in the untreated sample, there is no shift in the temperature of the martensitic transition regarding whether or not the sample was annealed. The variation of the martensitic transition temperatures as a function of the Mn content shows a parabola like behaviour with its minimum for compounds of equal Mn and Ni content.

A martensitic transition is not observed in the untreated sample of Mn$_{1.15}$Ni$_{1.85}$Ga, although a structural transition is present in the annealed samples of the same composition. However, for Mn$_{1.8}$Ni$_{1.2}$Ga a martensitic transition was detected at the same temperatures in an untreated sample and in a sample annealed at 800°C.

Measurements on untreated samples are generally more varied, and thus it is better to anneal samples. However, the annealing temperature is strongly correlated to the temperatures of the martensitic transition. In contrast the ground state magnetization and the magnetic transition temperature $T_c$ are hardly affected by the annealing temperature. These results are in agreement with Soltys et al. who showed that the degree of order in a Heusler alloy is highest after an anneal at 800°C and with Kreissl et al. who showed that the martensitic transition temperature is lowered by $\sim$100 K for Ni$_2$MnGa following an anneal at 1000°C [Soltys74], [Soltys75], [Kreissl03].

The magnetization, as described in chapter 3, diminishes as the Mn content is raised. It is generally understood that the magnetic moments are located on the Mn atoms in Ni$_2$MnGa related Heusler alloys. Thus, the diminishing is consistent with a ferrimagnetic ordering of magnetic moments on different Mn positions.
The atomic structure of the Mn rich alloys investigated in this series is related to the L2₁ Heusler structure as found in Ni₂MnGa. However, the surplus Mn atoms occupy depleted Ni position (position 8c (4d) in the cubic (tetragonal) structure). Therefore the distance between Mn atoms is reduced with respect to Ni₂MnGa and the ordering between Mn atoms on different positions is ferrimagnetic. Neutron scattering has confirmed the ferrimagnetic ordering for Mn₂NiGa and Mn₁₈Ni₁₂Ga at both, low and high temperatures. However, in the case of Mn₁₄Ni₁₆Ga antiparallel ordering of magnetic moments could not be confirmed using the tool of neutron scattering.

The symmetry of the low temperature structure of the off-stoichiometric and Mn rich alloys investigated here is related to the high temperature L2₁ Heusler structure by a group - sub group relationship. The symmetry of the high temperature cubic phase is described by space group Fm̅3m. The sub group of the symmetry at low temperatures is I4/mmm. However, whilst for Ni₂MnGa the low temperature structure is marked by a seven-fold superstructure, and thus the symmetry is further reduced, here there is no modulation present at low temperatures. This was also observed for the Ni –rich compound Ni₂.1₇Mn₀.₈₃Ga [Fröhlich04].

A complete transition between the cubic high temperature and the tetragonal low temperature phase takes place in Mn₂NiGa around 300 K. In the neutron diffraction pattern at this temperature both, the cubic and the tetragonal phase are present. The transition is not complete in Mn₁₈Ni₁₂Ga as there are remnants of the tetragonal (cubic) phase even at 296 K (6 K). The temperature interval (between 100 K and 150 K whilst heating) in which the structural transition in Mn₁₈Ni₁₂Ga takes place is large.
It is also the case for Mn$_{1.4}$Ni$_{1.6}$Ga that the cubic phase is still present at low temperatures. Furthermore, the evolvement of the lattice parameters in this compound is not strictly linear, especially for the tetragonal phase.

A list of the change of the lattice parameters as the Mn content is changed is given in table 6.1. A plot is given figure 6.2 for the cubic phase at 300 K.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Composition</th>
<th>Lattice constant a [Å]</th>
<th>Lattice constant c [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>~5</td>
<td>MnNi$_2$Ga</td>
<td>4.2152 (Pnnm)</td>
<td>5.5570 (Pnnm)</td>
</tr>
<tr>
<td></td>
<td>Mn$<em>{1.4}$Ni$</em>{1.6}$Ga</td>
<td>3.8904 ± 0.0003</td>
<td>6.5883 ± 0.0006</td>
</tr>
<tr>
<td></td>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>3.897 ± 0.002</td>
<td>6.650 ± 0.004</td>
</tr>
<tr>
<td></td>
<td>Mn$_2$NiGa</td>
<td>3.8874 ± 0.0003</td>
<td>6.7643 ± 0.0008</td>
</tr>
<tr>
<td>~300</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MnNi$_2$Ga</td>
<td></td>
<td>5.8229 ± 0.0002</td>
</tr>
<tr>
<td></td>
<td>Mn$<em>{1.4}$Ni$</em>{1.6}$Ga</td>
<td>5.8606 ± 0.0002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn$<em>{1.6}$Ni$</em>{1.4}$Ga</td>
<td>5.866 ± 0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>5.885 ± 0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn$_2$NiGa</td>
<td>5.9102 ± 0.0003</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1: Lattice parameters as a function of Mn content for the tetragonal phase at 5 K and the cubic phase at 300 K. As a reference the lattice parameters for Ni$_2$MnGa are also given [Brown02]. It may be noticed that the low temperature phase of Ni$_2$MnGa has a seven fold modulation along the b-axis.

Figure 6.2: Evolvement of the lattice parameter a of the cubic high temperature phase of Mn$_{1+x}$Ni$_{2-x}$Ga as a function of the Mn content at 300 K.
Figure 6.2 shows a kink in the evolvement of the cubic lattice parameter around $x = 0.5$. In addition, the size of the tetragonal lattice parameters is hugely different from the low temperature lattice parameters in Ni$_2$MnGa. This seems to suggest that the additional Mn atoms hugely affect the atomic and magnetic structure of the alloys.

Lattice parameters and in particular the change of the lattice parameter in the transition to the martensitic phase is also of importance for the alloy series. While for Ni$_2$MnGa, and alloys close to this composition, the c/a ratio is smaller than 1 it is observed to increase to a value larger than 1 with increasing Mn content. This has an effect on the formation of martensitic domains. Therefore the analysis of the transformation mechanism, and consequently also the formation and orientation of domain walls, is affected by this change. It is to be expected that the analysis of domain walls and domain wall networks, as presented in chapter 5, will only be applicable to alloys in the vicinity of Ni$_2$MnGa. However, the methods and descriptions developed for Ni$_2$MnGa are of general applicability. Thus once the transformation matrices are known, e.g. from separate experimental observations on suitable single crystals, the method is expected to be applicable to other alloys within the series. However, without the detailed knowledge of the transformation matrices any further modelling has to draw on additional assumptions. Here such an approach will not be pursued further, but rather advances and further developments will have to be left for future investigations.
7 Conclusions

The atomic and magnetic structures of Mn rich Ni$_2$MnGa compounds, Mn$_{1+x}$Ni$_2$-xGa, have been investigated. At T = 0 K the magnetization diminishes as the Mn content is increased. Structural transition temperatures depend strongly on the annealing temperature. The Curie temperatures and the ground state magnetization are not significantly affected by the annealing temperature. However, it is important to anneal the compounds due to a more pronounced variation of experimental results in untreated samples.

Mn$_2$NiGa was found to exhibit the same atomic structure as Ni$_2$MnGa; however, surplus Mn atoms occupy depleted Ni positions. Ni$_2$MnGa transforms from the cubic Heusler structure with space group Fm$ar{3}$m to a related orthorhombic superstructure with space group Pnnm. The c/a ratio is 0.95 for Ni$_2$MnGa. In contrast, Mn$_2$NiGa transforms from the Heusler structure to a related tetragonal structure with space group I4/mmm and a c/a ratio of 1.14. This suggests a different transformation mechanism. Also, the variation of lattice constants as a function of Mn content as given in figure 6.2 suggests that there is a different transformation process at work for Mn$_2$NiGa compared to Ni$_2$MnGa.

The transformation process for Ni$_2$MnGa and the domain building in the martensite has been theoretically investigated in detail. Further work needs to concentrate on the transformation process and martensite building in Mn$_2$NiGa.

The structures for alloys in between Ni$_2$MnGa and Mn$_2$NiGa are all related to the Heusler structure with surplus Mn atoms on depleted Ni positions. There is complete disorder on the ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) site between Ni and Mn atoms. However, not all compounds exhibit a structural transition as is evident in the graphs of the magnetization. Also, the analysis of the temperature dependence of the atomic
structures shows that different principles apply for samples with different Mn content. Whilst Mn$_2$NiGa and Mn$_{1.8}$Ni$_{1.2}$Ga exhibit antiparallel alignment of magnetic moments on different crystallographic sites, for the other structures experimental data are consistent with a parallel alignment of magnetic moments. Also, whilst in Mn$_2$NiGa and Ni$_2$MnGa the low and high temperature phases completely transform into one another, this is not the case for the compounds with $x = 0.4$ and $x = 0.8$. In addition, the temperature variation of the cubic lattice parameter in Mn$_{1.6}$Ni$_{1.4}$Ga displays unconventional characteristics as there are extended regions at low and high temperatures where it stays almost constant.

Where a structural transition was identified in Mn$_{1+x}$Ni$_{2-x}$Ga it is extended over a substantially larger temperature interval with a larger hysteresis compared to Ni$_2$MnGa. It is open to debate whether or not the Mn rich compounds can be classified as shape memory alloys due to the many anomalies within this series. A contributing factor for this non-conformity with respect to structural properties of the alloys may be the totally random occupation of Mn atoms on (8c) sites. More research is necessary in order to investigate the effect of annealing and ordering on the structural transitions in these alloys. However, as the hysteresis and the transition interval were observed to be large for all values of $x$, and consistent with other investigations reported in the literature for Mn$_2$NiGa, it may just be that the Mn rich compounds are not very useful shape memory alloys.

The attempt of addressing the martensitic transformation on an atomic level has led to the investigation of domain walls. Based on the experimental observation of transformation matrices it has been possible to characterise and classify domain walls in terms of their crystallographic orientation. This analysis has
resulted in novel descriptions to be proposed for the transformation process and the matching of domains. While the details of this description, and also its extension to the question of domain networks, have been worked out explicitly for Ni$_2$MnGa it is of interest to await its experimental testing and its extensions to other compounds and alloys.

The alloy series spanning the range between Ni$_2$MnGa and Mn$_2$NiGa has been characterised experimentally in terms of structural and magnetic properties using a range of techniques. The experimental investigations were accompanied by modelling of domains and domain walls on an atomic level. Both approaches have enabled some insight to be gained, but the work has also identified a series of additional questions and experimental challenges, which will have to be addressed in further experimental and theoretical investigations.
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<tr>
<th>Reference</th>
<th>Authors/Details</th>
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<tbody>
<tr>
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<td>P.J. Webster, K.R.A. Ziebeck, S.L. Town, M.S. Peak: Magnetic Order and Phase Transformation in Ni$_2$MnGa, Phil. Mag. 49, (1984), 295</td>
</tr>
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Appendix A

Coefficients of equations used in linear fits

Coefficients *slope* and *intersect.* of linear equations $M^2 (B/M) = slope \cdot B/M + intersect.$ used in linear fits of the high field sections of Arrott plots in chapter 3 are listed. The intersections *intersect.* with the $M^2$ axis correspond to the square of the spontaneous magnetization at the respective temperature.

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$M^2 (B/M) = slope \cdot B/M + intersect.$</th>
<th>$R^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$slope$ [J$^2$/kg$^3$/T$^4$]</td>
<td>$intersect.$ [J$^2$/kg$^2$/T$^2$]</td>
</tr>
<tr>
<td>5</td>
<td>2838 ± 164</td>
<td>5005 ± 13</td>
</tr>
<tr>
<td>20</td>
<td>3144 ± 137</td>
<td>4981 ± 10</td>
</tr>
<tr>
<td>50</td>
<td>3167 ± 135</td>
<td>4886 ± 10</td>
</tr>
<tr>
<td>100</td>
<td>3748 ± 129</td>
<td>4571 ± 10</td>
</tr>
<tr>
<td>150</td>
<td>3681 ± 117</td>
<td>4102 ± 10</td>
</tr>
<tr>
<td>200</td>
<td>3311 ± 100</td>
<td>3472 ± 9</td>
</tr>
<tr>
<td>250</td>
<td>2824 ± 79</td>
<td>2640 ± 8</td>
</tr>
<tr>
<td>300</td>
<td>3071 ± 53</td>
<td>1504 ± 7</td>
</tr>
<tr>
<td>350</td>
<td>3493 ± 27</td>
<td>111 ± 5</td>
</tr>
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</table>

*Table A.1:* Coefficients of the linear fit equations to the Arrott plots of Mn$_{1.05}$Ni$_{1.95}$Ga, sample (A), as displayed in figure 3.2. B/M is measured in units of T$^3$kg/J.
Table A.2: Coefficients of the linear fit equations to the Arrott plots of Mn$_{1.05}$Ni$_{1.95}$Ga, sample (B), as displayed in figure 3.4. B/M is measured in units of T$^2$kg/J.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.}$</th>
<th>( R^2 )-value</th>
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<tr>
<td>250</td>
<td>$3610 \pm 184$</td>
<td>1.00</td>
</tr>
<tr>
<td>275</td>
<td>$3133 \pm 152$</td>
<td>0.99</td>
</tr>
<tr>
<td>300</td>
<td>$2725 \pm 91$</td>
<td>0.99</td>
</tr>
<tr>
<td>325</td>
<td>$3071 \pm 70$</td>
<td>1.00</td>
</tr>
<tr>
<td>350</td>
<td>$2815 \pm 46$</td>
<td>0.99</td>
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Table A.3: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.1}$Ni$_{1.9}$Ga as displayed in figures 3.10 and 3.11. B/M is measured in units of T$^2$kg/J.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>$M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.}$</th>
<th>( R^2 )-value</th>
</tr>
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<tbody>
<tr>
<td>5</td>
<td>$-40 \pm 166$</td>
<td>0.99</td>
</tr>
<tr>
<td>25</td>
<td>$-42 \pm 166$</td>
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<tr>
<td>50</td>
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<td>90</td>
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</tr>
<tr>
<td>110</td>
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<td>130</td>
<td>$-94 \pm 101$</td>
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<tr>
<td>140</td>
<td>$-64 \pm 150$</td>
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</tr>
<tr>
<td>150</td>
<td>$-131 \pm 61$</td>
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<tr>
<td>175</td>
<td>$-106 \pm 61$</td>
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</tr>
<tr>
<td>200</td>
<td>$-60 \pm 58$</td>
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<tr>
<td>250</td>
<td>$-11 \pm 71$</td>
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</tr>
<tr>
<td>300</td>
<td>$92 \pm 23$</td>
<td>0.99</td>
</tr>
<tr>
<td>350</td>
<td>$222 \pm 13$</td>
<td>0.99</td>
</tr>
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</table>
\[ M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect}. \]

<table>
<thead>
<tr>
<th>T [K]</th>
<th>slope [J^2/kg^3/T^4]</th>
<th>intersect [J^2/kg^2/T^2]</th>
<th>R(^2)-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3535 ± 596</td>
<td>8550 ± 30</td>
<td>0.99</td>
</tr>
<tr>
<td>25</td>
<td>4449 ± 424</td>
<td>8473 ± 20</td>
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<td>50</td>
<td>3072 ± 552</td>
<td>8503 ± 28</td>
<td>0.99</td>
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<td>100</td>
<td>510 ± 515</td>
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<tr>
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<td>2225 ± 273</td>
<td>7435 ± 12</td>
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<td>200</td>
<td>2875 ± 208</td>
<td>6527 ± 10</td>
<td>0.89</td>
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<tr>
<td>250</td>
<td>3519 ± 215</td>
<td>5407 ± 12</td>
<td>0.96</td>
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<tr>
<td>300</td>
<td>4581 ± 133</td>
<td>3903 ± 8</td>
<td>0.91</td>
</tr>
<tr>
<td>350</td>
<td>5560 ± 70</td>
<td>2118 ± 5</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table A.4: Coefficients of the linear equations used in the Arrott plot fits of Mn\(_{1.15}\)Ni\(_{1.85}\)Ga, sample (B), as displayed in figure 3.14. B/M is measured in units of T\(^2\)kg/J.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>slope [J^2/kg^3/T^4]</th>
<th>intersect [J^2/kg^2/T^2]</th>
<th>R(^2)-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>6641 ± 215</td>
<td>3863 ± 15</td>
<td>0.98</td>
</tr>
<tr>
<td>25</td>
<td>7182 ± 218</td>
<td>3813 ± 15</td>
<td>0.98</td>
</tr>
<tr>
<td>50</td>
<td>6731 ± 212</td>
<td>3787 ± 15</td>
<td>0.97</td>
</tr>
<tr>
<td>100</td>
<td>6508 ± 204</td>
<td>3607 ± 14</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>6825 ± 148</td>
<td>3228 ± 10</td>
<td>0.97</td>
</tr>
<tr>
<td>200</td>
<td>6062 ± 131</td>
<td>2831 ± 10</td>
<td>0.98</td>
</tr>
<tr>
<td>250</td>
<td>4757 ± 108</td>
<td>2318 ± 9</td>
<td>0.92</td>
</tr>
<tr>
<td>300</td>
<td>3570 ± 80</td>
<td>1618 ± 8</td>
<td>0.99</td>
</tr>
<tr>
<td>350</td>
<td>2534 ± 38</td>
<td>782 ± 5</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Table A.5: Coefficients of the linear equations used in the Arrott plot fits of Mn\(_{1.15}\)Ni\(_{1.85}\)Ga, sample (A). B/M is measured in units of T\(^2\)kg/J.
\[ M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.} \]

<table>
<thead>
<tr>
<th>T [K]</th>
<th>slope [ J^2/kg^2/T^4 ]</th>
<th>intersect. [ J^2/kg^2/T^2 ]</th>
<th>( R^2 )-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>3225 ± 518</td>
<td>7437 ± 25</td>
<td>0.74</td>
</tr>
<tr>
<td>25</td>
<td>805 ± 702</td>
<td>7516 ± 36</td>
<td>0.71</td>
</tr>
<tr>
<td>50</td>
<td>2197 ± 420</td>
<td>7398 ± 21</td>
<td>0.92</td>
</tr>
<tr>
<td>75</td>
<td>1047 ± 471</td>
<td>7359 ± 25</td>
<td>0.92</td>
</tr>
<tr>
<td>100</td>
<td>1290 ± 1018</td>
<td>7119 ± 43</td>
<td>0.91</td>
</tr>
<tr>
<td>150</td>
<td>-502 ± 582</td>
<td>6538 ± 31</td>
<td>0.80</td>
</tr>
<tr>
<td>200</td>
<td>742 ± 180</td>
<td>5756 ± 10</td>
<td>0.73</td>
</tr>
<tr>
<td>250</td>
<td>1177 ± 151</td>
<td>4800 ± 9</td>
<td>0.99</td>
</tr>
<tr>
<td>300</td>
<td>619 ± 167</td>
<td>3655 ± 12</td>
<td>0.99</td>
</tr>
<tr>
<td>350</td>
<td>-4769 ± 93</td>
<td>2427 ± 8</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table A.6: Coefficients of the linear equations used in the Arrott plot fits of Mn\(_{1.2}\)Ni\(_{1.8}\)Ga, sample (A), as displayed in figure 3.21. B/M is measured in units of T\(^2\)kg/J.
\[ \text{M}^2 (\text{B/M}) = \text{slope} \cdot \text{B/M} + \text{intersect.} \]

$\text{slope}$: [J$^2$/kg$^2$/T$^4$]

$\text{intersect.}$: [J$^2$/kg$^2$/T$^2$]

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$\text{slope}$</th>
<th>$\text{intersect.}$</th>
<th>$R^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1725 ± 281</td>
<td>5727 ± 13</td>
<td>0.96</td>
</tr>
<tr>
<td>40</td>
<td>1245 ± 224</td>
<td>5675 ± 13</td>
<td>0.95</td>
</tr>
<tr>
<td>60</td>
<td>857 ± 275</td>
<td>5633 ± 15</td>
<td>0.91</td>
</tr>
<tr>
<td>70</td>
<td>829 ± 513</td>
<td>5604 ± 26</td>
<td>0.84</td>
</tr>
<tr>
<td>80</td>
<td>918 ± 505</td>
<td>5545 ± 33</td>
<td>0.94</td>
</tr>
<tr>
<td>90</td>
<td>301 ± 379</td>
<td>5535 ± 24</td>
<td>0.90</td>
</tr>
<tr>
<td>100</td>
<td>417 ± 269</td>
<td>5473 ± 16</td>
<td>1.00</td>
</tr>
<tr>
<td>110</td>
<td>693 ± 262</td>
<td>5385 ± 14</td>
<td>0.93</td>
</tr>
<tr>
<td>125</td>
<td>187 ± 360</td>
<td>5292 ± 21</td>
<td>0.90</td>
</tr>
<tr>
<td>150</td>
<td>963 ± 158</td>
<td>5000 ± 9</td>
<td>0.96</td>
</tr>
<tr>
<td>200</td>
<td>1313 ± 141</td>
<td>4412 ± 9</td>
<td>0.93</td>
</tr>
<tr>
<td>250</td>
<td>1426 ± 112</td>
<td>3666 ± 7</td>
<td>0.98</td>
</tr>
<tr>
<td>300</td>
<td>1466 ± 94</td>
<td>2758 ± 7</td>
<td>1.00</td>
</tr>
<tr>
<td>350</td>
<td>2392 ± 62</td>
<td>1723 ± 5</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table A.7: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.4}$Ni$_{1.6}$Ga, sample (B), as displayed in figure 3.25. B/M is measured in units of T$^2$kg/J.
Table A.8: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.5}$Ni$_{1.5}$Ga, sample (B), as displayed in figure 3.29. B/M is measured in units of T$^2$kg/J.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.} )</th>
<th>R$^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>( 1862 \pm 62 ) ( 1367 \pm 6 )</td>
<td>0.98</td>
</tr>
<tr>
<td>300</td>
<td>( 1921 \pm 72 ) ( 2060 \pm 6 )</td>
<td>0.99</td>
</tr>
<tr>
<td>250</td>
<td>( 1892 \pm 93 ) ( 2788 \pm 7 )</td>
<td>1.00</td>
</tr>
<tr>
<td>200</td>
<td>( 1690 \pm 245 ) ( 3450 \pm 16 )</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>( 1371 \pm 129 ) ( 3993 \pm 8 )</td>
<td>0.92</td>
</tr>
<tr>
<td>100</td>
<td>( 992 \pm 139 ) ( 4403 \pm 9 )</td>
<td>0.94</td>
</tr>
<tr>
<td>50</td>
<td>( 660 \pm 147 ) ( 4652 \pm 9 )</td>
<td>0.92</td>
</tr>
<tr>
<td>25</td>
<td>( 532 \pm 255 ) ( 4715 \pm 14 )</td>
<td>0.97</td>
</tr>
<tr>
<td>5</td>
<td>( 557 \pm 154 ) ( 4731 \pm 9 )</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Table A.9: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.6}$Ni$_{1.4}$Ga, sample (A), as displayed in figure 3.33. B/M is measured in units of T$^2$kg/J.

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.} )</th>
<th>R$^2$-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( 2005 \pm 62 ) ( 916 \pm 8 )</td>
<td>0.99</td>
</tr>
<tr>
<td>25</td>
<td>( 1745 \pm 63 ) ( 983 \pm 8 )</td>
<td>1.00</td>
</tr>
<tr>
<td>50</td>
<td>( 1618 \pm 63 ) ( 990 \pm 8 )</td>
<td>0.99</td>
</tr>
<tr>
<td>75</td>
<td>( 1592 \pm 61 ) ( 970 \pm 8 )</td>
<td>1.00</td>
</tr>
<tr>
<td>100</td>
<td>( 1510 \pm 59 ) ( 944 \pm 8 )</td>
<td>1.00</td>
</tr>
<tr>
<td>150</td>
<td>( 1488 \pm 43 ) ( 842 \pm 6 )</td>
<td>0.84</td>
</tr>
<tr>
<td>200</td>
<td>( 1148 \pm 47 ) ( 734 \pm 7 )</td>
<td>1.00</td>
</tr>
<tr>
<td>250</td>
<td>( 975 \pm 38 ) ( 563 \pm 7 )</td>
<td>1.00</td>
</tr>
<tr>
<td>300</td>
<td>( 754 \pm 27 ) ( 351 \pm 6 )</td>
<td>1.00</td>
</tr>
<tr>
<td>350</td>
<td>( 626 \pm 17 ) ( 100 \pm 5 )</td>
<td>1.00</td>
</tr>
</tbody>
</table>
\[ M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect}. \]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>309 ± 85</td>
<td>2186 ± 11</td>
<td>0.97</td>
</tr>
<tr>
<td>25</td>
<td>352 ± 84</td>
<td>2152 ± 10</td>
<td>0.95</td>
</tr>
<tr>
<td>50</td>
<td>448 ± 84</td>
<td>2125 ± 10</td>
<td>0.99</td>
</tr>
<tr>
<td>75</td>
<td>387 ± 80</td>
<td>2037 ± 10</td>
<td>0.99</td>
</tr>
<tr>
<td>100</td>
<td>459 ± 80</td>
<td>2010 ± 10</td>
<td>0.99</td>
</tr>
<tr>
<td>150</td>
<td>483 ± 78</td>
<td>1927 ± 10</td>
<td>1.00</td>
</tr>
<tr>
<td>200</td>
<td>482 ± 70</td>
<td>1748 ± 10</td>
<td>0.99</td>
</tr>
<tr>
<td>250</td>
<td>563 ± 60</td>
<td>1458 ± 9</td>
<td>0.99</td>
</tr>
<tr>
<td>300</td>
<td>576 ± 49</td>
<td>1139 ± 8</td>
<td>1.00</td>
</tr>
<tr>
<td>350</td>
<td>676 ± 37</td>
<td>792 ± 7</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table A.10: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.8}$Ni$_{1.2}$Ga, sample (A), as displayed in figure 3.33. B/M is measured in units of T$^2$kg/J.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>605 ± 66</td>
<td>962 ± 8</td>
<td>0.97</td>
</tr>
<tr>
<td>300</td>
<td>647 ± 90</td>
<td>1355 ± 10</td>
<td>0.99</td>
</tr>
<tr>
<td>250</td>
<td>400 ± 126</td>
<td>1800 ± 11</td>
<td>0.82</td>
</tr>
<tr>
<td>200</td>
<td>431 ± 130</td>
<td>2054 ± 12</td>
<td>0.89</td>
</tr>
<tr>
<td>150</td>
<td>426 ± 106</td>
<td>2314 ± 8</td>
<td>0.67</td>
</tr>
<tr>
<td>100</td>
<td>238 ± 268</td>
<td>2548 ± 17</td>
<td>0.74</td>
</tr>
<tr>
<td>50</td>
<td>-252 ± 338</td>
<td>2701 ± 27</td>
<td>0.82</td>
</tr>
<tr>
<td>25</td>
<td>274 ± 343</td>
<td>2694 ± 21</td>
<td>0.78</td>
</tr>
<tr>
<td>5</td>
<td>-156 ± 260</td>
<td>2736 ± 22</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table A.11: Coefficients of the linear equations used in the Arrott plot fits of Mn$_{1.8}$Ni$_{1.2}$Ga, sample (B), as displayed in figure 3.33. B/M is measured in units of T$^2$kg/J.
<table>
<thead>
<tr>
<th>T [K]</th>
<th>( M^2 (B/M) = \text{slope} \cdot B/M + \text{intersect.} )</th>
<th>( \text{slope} ) [J/(kg^3/T^4)]</th>
<th>( \text{intersect.} ) [J/(kg^2/T^2)]</th>
<th>( R^2 )-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>( 810 \pm 118 )</td>
<td>( 979 \pm 15 )</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>( 931 \pm 155 )</td>
<td>( 951 \pm 21 )</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>( 1113 \pm 109 )</td>
<td>( 928 \pm 15 )</td>
<td>0.94</td>
<td></td>
</tr>
<tr>
<td>75</td>
<td>( 970 \pm 105 )</td>
<td>( 906 \pm 15 )</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>( 975 \pm 81 )</td>
<td>( 888 \pm 11 )</td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>( 921 \pm 97 )</td>
<td>( 821 \pm 14 )</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>( 790 \pm 87 )</td>
<td>( 733 \pm 13 )</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>( 574 \pm 77 )</td>
<td>( 677 \pm 12 )</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>( 401 \pm 57 )</td>
<td>( 664 \pm 9 )</td>
<td>0.99</td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>( 313 \pm 52 )</td>
<td>( 551 \pm 9 )</td>
<td>0.98</td>
<td></td>
</tr>
</tbody>
</table>

Table A.12: Coefficients of the linear equations used in the Arrott plot fits of Mn2NiGa as displayed in figure 3.33. B/M is measured in units of \( T^2 kg/J \).
Appendix B

Results in tables of study into magnetic and structural properties

In the following the ground state magnetization, the ground state magnetic moment and the martensitic and magnetic transition temperatures are summarized. Further, the atomic symmetry and lattice parameters are summarized as well as the spin wave stiffness constants.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar weight [g/mol]</th>
<th>$M_0$ [J/kg/T]</th>
<th>m per Mn atom [$\mu_B$]</th>
<th>m per f.u. [$\mu_B$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.15}$Ni$</em>{1.85}$Ga</td>
<td>241.484</td>
<td>92.53 ± 0.20</td>
<td>3.48 ± 0.01</td>
<td>4.00 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.2}$Ni$</em>{1.8}$Ga</td>
<td>241.296</td>
<td>86.53 ± 0.12</td>
<td>3.12 ± 0.01</td>
<td>3.74 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.4}$Ni$</em>{1.6}$Ga</td>
<td>240.545</td>
<td>75.75 ± 0.07</td>
<td>2.33 ± 0.01</td>
<td>3.26 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.5}$Ni$</em>{1.5}$Ga</td>
<td>240.170</td>
<td>68.96 ± 0.07</td>
<td>1.98 ± 0.01</td>
<td>2.97 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>239.043</td>
<td>52.48 ± 0.07</td>
<td>1.25 ± 0.01</td>
<td>2.25 ± 0.01</td>
</tr>
<tr>
<td>Mn$_2$NiGa</td>
<td>238.292</td>
<td>30.9 ± 0.2</td>
<td>0.66 ± 0.01</td>
<td>1.32 ± 0.01</td>
</tr>
</tbody>
</table>

Table B.1: Spontaneous magnetization and magnetic moment at $T = 0$ K for annealed samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar weight [g/mol]</th>
<th>$M_0$ [J/kg/T]</th>
<th>m per Mn atom [$\mu_B$]</th>
<th>m per f.u. [$\mu_B$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.05}$Ni$</em>{1.95}$Ga</td>
<td>241.859</td>
<td>70.90 ± 0.06</td>
<td>2.92 ± 0.01</td>
<td>3.07 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.1}$Ni$</em>{1.9}$Ga</td>
<td>241.672</td>
<td>34.41 ± 0.26</td>
<td>1.35 ± 0.01</td>
<td>1.49 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.15}$Ni$</em>{1.85}$Ga</td>
<td>241.484</td>
<td>62.38 ± 0.08</td>
<td>2.35 ± 0.01</td>
<td>2.70 ± 0.01</td>
</tr>
<tr>
<td>Mn$<em>{1.6}$Ni$</em>{1.4}$Ga</td>
<td>239.794</td>
<td>30.27 ± 0.13 (5 K)</td>
<td>0.81 ± 0.01 (5 K)</td>
<td>1.30 ± 0.01 (5 K)</td>
</tr>
<tr>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>239.043</td>
<td>46.60 ± 0.12</td>
<td>1.11 ± 0.01</td>
<td>1.99 ± 0.01</td>
</tr>
</tbody>
</table>

Table B.2: Spontaneous magnetization and magnetic moment at $T = 0$ K for untreated samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar weight [g/mol]</th>
<th>$S_z$ per Mn atom</th>
<th>$p_{eff}$ per Mn atom [$\mu_B$]</th>
<th>D [meV Å$^2$]</th>
</tr>
</thead>
</table>

B-1
Table B.3: Spin $S_z$, effective moment $p_{\text{eff}}$, and spin wave stiffness constant $D$ for annealed samples.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molar weight [g/mol]</th>
<th>$S_z$ per Mn atom</th>
<th>$p_{\text{eff}}$ per Mn atom [$\mu_B$]</th>
<th>$D$ [meV $\text{Å}^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.15}$Ni$</em>{1.85}$Ga</td>
<td>241.484</td>
<td>1.74</td>
<td>4.37</td>
<td>62 ± 4</td>
</tr>
<tr>
<td>Mn$<em>{1.2}$Ni$</em>{1.8}$Ga</td>
<td>241.296</td>
<td>1.56</td>
<td>3.99</td>
<td>79 ± 4</td>
</tr>
<tr>
<td>Mn$<em>{1.4}$Ni$</em>{1.6}$Ga</td>
<td>240.545</td>
<td>1.17</td>
<td>3.18</td>
<td>69 ± 4</td>
</tr>
<tr>
<td>Mn$<em>{1.5}$Ni$</em>{1.5}$Ga</td>
<td>240.170</td>
<td>0.99</td>
<td>2.80</td>
<td>50 ± 4</td>
</tr>
<tr>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>239.043</td>
<td>0.62</td>
<td>2.01</td>
<td>57 ± 4</td>
</tr>
<tr>
<td>Mn$_2$NiGa</td>
<td>238.292</td>
<td>0.33</td>
<td>1.32</td>
<td>43 ± 5</td>
</tr>
</tbody>
</table>

Table B.4: Spin $S_z$, effective moment $p_{\text{eff}}$, and spin wave stiffness constant $D$ for untreated samples.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Mn$<em>{1.15}$Ni$</em>{1.85}$Ga</td>
<td>800°C 900°C</td>
<td>241.484</td>
<td>413 ± 5</td>
<td>75 ± 25</td>
<td>150 ± 50</td>
</tr>
<tr>
<td>Mn$<em>{1.2}$Ni$</em>{1.8}$Ga†</td>
<td>800°C</td>
<td>241.296</td>
<td>453 ± 3</td>
<td>77.7 ± 0.4</td>
<td>(76 ± 2 in 1 T)</td>
</tr>
<tr>
<td>Mn$<em>{1.4}$Ni$</em>{1.6}$Ga</td>
<td>800°C</td>
<td>240.545</td>
<td>439 ± 3</td>
<td>76.6 ± 0.3</td>
<td>-</td>
</tr>
<tr>
<td>Mn$<em>{1.5}$Ni$</em>{1.5}$Ga</td>
<td>900°C</td>
<td>240.170</td>
<td>447 ± 4</td>
<td>no 1$^{\text{st}}$ order transition</td>
<td>-</td>
</tr>
<tr>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>900°C</td>
<td>239.043</td>
<td>465 ± 10</td>
<td>216.7 ± 2.9</td>
<td>-</td>
</tr>
<tr>
<td>Mn$_2$NiGa</td>
<td>800°C</td>
<td>238.292</td>
<td>&gt; 500</td>
<td>-</td>
<td>275 ± 25</td>
</tr>
</tbody>
</table>

Table B.5: Curie temperatures $T_C$ and martensitic transformation temperatures $M = \frac{M_S + M_F}{2}$ and $A = \frac{A_S + A_F}{2}$ for annealed samples. M and A are given as obtained from the thermal variation of the magnetization in a field of 0.1 T. (†) The thermal variation of the magnetization was also measured in a field of 1 T. (Δ) Stairs like variation of magnetization continues after $A'$, see text for details.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_C$</th>
<th>$T_T$</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$<em>{1.1}$Ni$</em>{1.9}$Ga$^+$</td>
<td>241.672</td>
<td>407 ± 9</td>
<td>122 ± 2 (126 ± 8 in 1 T)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>142 ± 4 (138 ± 7 in 1 T)</td>
</tr>
<tr>
<td>Mn$<em>{1.15}$Ni$</em>{1.85}$Ga</td>
<td>241.484</td>
<td>401 ± 4</td>
<td>no 1st order transition</td>
</tr>
<tr>
<td>Mn$<em>{1.5}$Ni$</em>{1.5}$Ga</td>
<td>240.170</td>
<td>-</td>
<td>no 1st order transition</td>
</tr>
<tr>
<td>Mn$<em>{1.6}$Ni$</em>{1.4}$Ga</td>
<td>239.794</td>
<td>372 ± 9</td>
<td>phase transition below 50 K</td>
</tr>
<tr>
<td>Mn$<em>{1.8}$Ni$</em>{1.2}$Ga</td>
<td>239.043</td>
<td>475 ± 13</td>
<td>96.9 ± 3.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>150.8 ± 5.0</td>
</tr>
</tbody>
</table>

Table B.6: Curie temperatures $T_C$ and martensitic transformation temperatures $T_T$ for untreated samples. $M = \frac{M_S + M_P}{2}$ and $A = \frac{A_S + A_P}{2}$ for untreated samples. $M$ and $A$ are given as obtained from the thermal variation of the magnetization in a field of 0.1 T. ($^+$) The thermal variation of the magnetization was also measured in a field of 1 T.
Appendix C

Overview over crystallographic symbols and terms

Crystallographic symbols and terms have been used in conjunction with the *International Tables for Crystallography* (Hahn83). Square or arrow shaped brackets are used for directions within the crystallographic lattice, whilst a crystal face or net plane is described by round or curly brackets. It is differentiated between a single direction (or single net plane) and a set of symmetry equivalent lattice directions (or net planes). The table below gives a more detailed overview over these terms.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[uvw]</td>
<td>Indices of a lattice direction</td>
</tr>
<tr>
<td>&lt;uvw&gt;</td>
<td>Indices of a set of all symmetrically equivalent lattice directions</td>
</tr>
<tr>
<td>(hkl)</td>
<td>Indices of a crystal face or a single net plane</td>
</tr>
<tr>
<td>{hkl}</td>
<td>Indices of a set of all symmetrically equivalent crystal faces or net planes</td>
</tr>
</tbody>
</table>
Acknowledgements

I wish to thank my husband Klaus who has always encouraged me to strive for the best. I am grateful for his support, and also criticism, and for our discussions, which have been both a source of frustration as well as inspiration.

I have been encouraged by my children Anne and Rebecca, now 5 and 4 years old. For a long period of time they have repeatedly asked me: Mummy, when will your PhD be finished? Finally I am able to assure them that it is written.

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