Investigation of the shape-memory properties in the ferromagnetic Ni$_2$MnGa system

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Investigation of the shape-memory properties in the ferromagnetic Ni$_2$MnGa system

by

Peter Anders

A Master's Thesis
Submitted in partial fulfilment of the requirements for the award of the degree Master of Philosophy of Loughborough University United Kingdom

Supervisor: Professor Kurt R. A. Ziebeck
August 2001

© by Peter Anders (2001)
For Annika and my parents, with love.
Abstract

Transition metal compounds with compositions close to Ni$_2$MnGa are studied. The materials investigated Ni$_{2.19}$Mn$_{0.81}$Ga, Ni$_{1.9}$Co$_{0.1}$MnGa, Ni$_{1.9}$Cu$_{0.1}$MnGa, Ni$_2$MnGa$_{0.95}$In$_{0.05}$ and Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$, as well as Ni$_2$MnGa show the shape memory effect. The dependence of magnetic properties and the properties of the structural phase transition on composition is investigated. X-ray structure determination, magnetisation measurements, thermal expansion and magnetostriction measurements are performed. The specimen are prepared, and characterised at room temperature using X-ray powder diffraction. The structure of Ni$_{2.19}$Mn$_{0.81}$Ga is found to be orthorhombic, the other materials crystallise in the cubic Heusler L$_2$1 structure. Measurements of the lattice properties are important due to the intrinsic coupling of magnetic degrees of freedom with the lattice. The response of the lattice to temperature changes and applied magnetic fields have been probed by the use of the aforementioned techniques. The experimental results are presented and discussed. Various theoretical approaches are considered and compared with the obtained data. These data support the hypothesis the dominant factor influencing the martensitic transition is the conduction electron density.
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Chapter 1: Introduction

1 Introduction

The properties of metals and alloys have been under investigation since the Bronze Age, starting more than 5000 years ago. Further steps have been the production and hardening of iron and steel, and the discovery of the special properties of magnetite as the first ferromagnetic material in ancient Greece. Since these days, materials with a wide range of properties have been developed. Ferromagnetic materials have been of particular interest, due to a wide range of applications.

Until 1903, all known ferromagnetic compounds contained at least one of the ferromagnetic elements iron, cobalt or nickel. In 1903, Heusler [1] first reported ferromagnetic Mn-Cu bronze, alloyed with portions of Sn, Al, As, Sb, Bi or B, where none of the constituents was a ferromagnetic element. This discovery encouraged further investigations, resulting in the discovery of a large number of ferromagnetic alloys, which do not contain ferromagnetic elements.

The Heusler alloys form an interesting group of materials for magnetic studies, since they offer the possibility to investigate the effects of interatomic distance, atomic arrangement and atomic environment on the magnetic properties. They have a common crystal structure, the cubic $L_2\overline{1}$ Heusler structure, and a common chemical formula $X_2YZ$. $X$ is an element from the latter part of the transition metal series, $Y$ a transition metal from the earlier part of the transition metal series, and $Z$ a metal from the 3rd, 4th or 5th main group of the periodic table of elements. Of particular interest are Heusler alloys with the structure $X_2MnZ$. In these systems, the magnetic moment is localised almost totally at the Mn sites. Exceptions are alloys containing Co, where a substantial part of magnetic moment is localised at the Co sites too. Numerous $X_2MnZ$ alloys were investigated intensively by Webster [2].

Another aspect observed in some Heusler alloys is the occurrence of a structural phase transition from the high-temperature cubic $L_2\overline{1}$ structure to a low-temperature structure with lowered symmetry. This transition, known as martensitic transition, is a diffusionless, displacive first-order transformation of the crystal lattice.

This phenomenon was first observed in hardened steels (so-called martensite steels) by Dr. Martens, where the partial formation of interlocking martensites results in the observed hardening. Since the transformation involves a change of the sample shape, triggered by a
change in temperature or applied fields, there is a large number of possible applications for these materials. This number increased even further since the discovery of materials exhibiting reversible martensitic transformation. These materials are called "shape-memory alloys", since the old shape is "remembered" and restored during the reverse transformation. A detailed review of the shape-memory effect and its possible applications was given by L. McDonald Schetky [3].

Over the past 20 years, there was a huge boost in research involving Heusler alloys, triggered by the development of ferromagnetic shape-memory alloys, alloys with a martensitic transition temperature below its Curie temperature. Therefore, the martensitic transition occurs in the ferromagnetic regime and can be altered by applied magnetic fields. The most important representative of the group of ferromagnetic shape-memory alloys is Ni$_2$MnGa, with a martensitic transition temperature of $T_M=202$K and a Curie temperature of $T_C=378$K [4]. A large number of research projects were realised, both on theoretical and experimental aspects, to understand the properties of Ni$_2$MnGa and alloys with compositions close to it. A number of these projects will be mentioned later.

Theoretical research focuses on the description of the martensitic transition properties as well as on the magnetic properties of the above-mentioned alloys.

The magnetic properties are described in the framework of indirect exchange interaction, where the coupling of the localised magnetic moments is realised by the polarisation of conduction band electrons, first introduced by Ruderman & Kittel [5]. This general approach was applied to Heusler alloys by Blandin & Campbell [6], followed by further improvements by Malmstroem [7], [8], Price [9] and Kübler [10]. Detailed reviews were given by Stetsenko [11], [12]. The structural properties of the alloys under investigation, and especially the properties of the structural phase transition, are often described by a phenomenological Landau free energy description. Since the magnetisation in the ferromagnetic state contributes essentially to the free energy, the investigation of the structural properties has to consider the magnetic properties. Hence, structural and magnetic properties cannot be investigated independently. Recent research was presented e.g. by Chernenko [13] and O’Handley [14]. The crystallographic properties can be explained by the two-shear-mechanism, originally proposed for V$_3$Si by Batterman & Barrett [15]. Band structure calculations, e.g. by Fujii [16] and Ishida [17], underpin the applicability of this mechanism. In the scope of band structure calculations, the structural phase transition is explained by means of a band Jahn-
Teller distortion, where the free energy of the system is minimised by a finite deformation of the crystal lattice.

From the experimental side the magnetic and structural properties are investigated in a wide range of parameters (temperature, applied magnetic field, applied stress, composition dependencies etc., using single crystals, polycrystalline specimen and thin films). A number of recent research projects are listed below:

- The first direct observation of a band Jahn-Teller effect in the martensitic phase transition of Ni$_2$MnGa was reported by Brown et. al. [18].
- The magnetic and magnetoelastic properties of polycrystals were investigated by Albertini et. al. [19].
- The magnetic and magnetoelastic properties of single crystals under load were investigated by Tickle & James [20].
- The composition dependence of the Curie temperature ($T_C$) and the martensitic transition temperature ($T_M$), and the magnetic field dependence of $T_M$ in the system Ni$_{2+x}$Mn$_{1-x}$Ga were investigated by Vasi'Iev et. al. [21].
- A wide range of research was performed for example in the working groups of K. Inoue ([22], [23], [24], [25], with special focus on crystallographic properties), S. J. Murray and R. C. O'Handley ([26], [27], [28], with special focus on magnetic-field-induced strain) and K. Ullakko ([29], [30], with special focus on influences on the structural transition by applied magnetic fields).

The most recent publications suggest a strong dependence of the magnetic and martensitic transition properties on the electron density. However, a thorough understanding of the mechanisms leading to the observed structural phase transition is still not achieved.
Chapter 1: Introduction

1.1 References

[22] K. Inoue, K. Enami, Y. Yamaguchi, R. Note and K. Ohoyama, Shape memory effect of Heusler-type Ni2.13Mn0.87Ga (unpublished)
Chapter 1: Introduction


2 Introduction to the martensitic phase transition

The martensitic transformation is a diffusionless, displacive first-order transformation of a crystal lattice. It can be described as a displacement of a set of lattice planes. This correlated and well-defined displacement results in a change of the sample shape. There are different approaches to describe this effect. Two of them will be discussed further on: the band Jahn-Teller effect and a rather phenomenological thermodynamic approach.

In order to understand the band Jahn-Teller effect the normal Jahn-Teller effect will be described first.

2.1 Jahn-Teller Effect

This section was developed after a lecture by Prof. Takeshi Kanomata, during his time as a visiting professor in the Department of Physics at Loughborough University. He is now working at the Tohoku Gakuin University, Tagajo, Japan [1].

A quantum mechanical system is fully described by indicating its quantum numbers. For the electrons in the atomic shells proper quantum numbers are: the principal quantum number \( n \), the orbital angular momentum quantum number \( l \), the magnetic quantum number \( m \) and the spin quantum number \( s \). These quantum numbers specify the wavefunctions of the electrons, and therefore the probability density, which is the absolute square of the wavefunction. The probability density can be visualised as orbitals. The general appearance of electronic probability densities for some sets of quantum numbers is given in Figure 2.1. The general appearance does not change with the principal quantum number, but depends on \( l \) and \( m \). Simplifying it can be said, that \( l \) determines the shape of the orbitals and \( m \) governs the orientation of the orbitals in space.

![Figure 2.1: Balloon pictures of s, p and d atomic orbitals [2]](image-url)
Based on symmetry the d-orbitals can be gathered into two subsets:

\[ e_g = d_{x^2-y^2}, d_{z^2}, e_{g} \quad \text{and} \quad t_{2g} = d_{xy}, d_{xz}, d_{yz}. \]

The occurrence of a Jahn-Teller effect in a crystal depends on the symmetry properties of its crystal structure. One of the Jahn-Teller systems is the spinel type crystal structure, with the space group \( F d -3 m \) and the Strukturbericht designation \( H1_1 \).

Assume this spinel-type crystal structure, e.g. \( \text{Cu}^{2+}\text{Cr}^{3+}\text{O}_4^2^- \). In this lattice, the \( \text{Cu}^{2+} \) is in the centre of a tetrahedron of \( \text{O}^{2-} \) ions. This configuration is responsible for the Jahn-Teller effect, as will be described in this section. Each \( \text{Cr}^{3+} \) ion is in the centre of an \( \text{O}^{2-} \) octahedron. The electron configurations are: \([\text{Ar}]\ 3d^3\) for \( \text{Cr}^{3+}\), \([\text{Ar}]\ 3d^9\) for \( \text{Cu}^{2+}\) and \([\text{Ne}]\) for \( \text{O}^{2-}\). All d-orbitals are degenerated in the free state.

In the crystal field of the surrounding \( \text{O}^{2-} \) ions the different d-orbitals of the \( \text{Cr}^{3+}\) and the \( \text{Cu}^{2+}\) are overlapping to different amounts with the oxygen orbitals. The overlap refers to the exchange integral, describing the exchange energy contribution to the total energy of the crystal. Therefore, the degeneracy is partly removed. The subsets are still degenerated, but now separated by an energy gap. For the \( \text{Cr}^{3+}\) ion the energy of \( e_g \) is raised and the energy of \( t_{2g} \) is lowered. For the \( \text{Cu}^{2+}\) ion the energy of \( e_g \) is lowered and the energy of \( t_{2g} \) is raised. The electrons are distributed following Hund’s rules. The theory describing this phenomenon is the crystal field theory (CFT). The mean energy of all orbitals remains unchanged for every splitting.
As the crystal undergoes a cubic-to-tetragonal transformation (like the martensitic transformation in \( \text{Ni}_2\text{MnGa} \)), the energy levels in the \( e_g \) and \( t_{2g} \) subsets split again, due to the lowered symmetry of the system. Nevertheless, two \( t_{2g} \) levels are still degenerated, because two out of three lattice parameters are still the same. The electrons are redistributed, following Hund’s rules.

Since the mean energy value in every branch stays constant, the splitting of the \( e_g \) orbitals, caused by the structural transition, does not change the total energy. All orbitals are occupied with two electrons, two with raised energy and two with lowered energy. However, in the \( t_{2g} \) branch the total energy is lowered, because the energetically highest orbital is occupied by one electron only. Hence, the total energy of the \( \text{Cu}^{2+} \) system is lowered by the energy gained by the splitting of the \( t_{2g} \) subset.
For the Cr\(^{3+}\) ion, the total energy remains unchanged, because the electrons are distributed in such a way, that every orbital is equally occupied by one electron.

Summarising, the energy gain due to redistribution of the electrons in the t\(_{2g}\) orbitals of Cu\(^{2+}\) results in an overall energy gain for the whole crystal.
It can be shown, that the energy gained by the electronic redistribution increases linearly, and the energy required for deforming the crystal increases quadratic [1].

As illustrated in Figure 2.4, the resulting total energy reaches a minimum for a non-zero value of the deformation, the Jahn-Teller distortion.

2.2 Band Jahn-Teller Effect

In general, the band Jahn-Teller effect is similar to the normal Jahn-Teller effect, as described in Section 2.1. The only difference is the electrons not being redistributed into orbitals with different symmetries, but into sub-bands with different symmetries. The experimental prove of a band Jahn-Teller effect driving the martensitic phase transformation in Ni$_2$MnGa was given by [3]. The authors observed a redistribution of the electrons into bands with symmetry along the c-axis of the tetragonal phase.

The band Jahn-Teller effect is most effective with a peak in the density of states near the Fermi energy. Due to the cubic-to-tetragonal transformation, this peak splits, and the total energy of the system is reduced. The existence of this peak near the Fermi energy for Ni$_2$MnGa is expected following the band calculations by [4].
Chapter 2: Introduction to the martensitic phase transition

2.3 Thermodynamic approach

As schematically shown in Figure 2.5, the martensitic transformation can be described from the thermodynamic point of view. In the austenitic region, the austenitic free energy $F_a$ is lower than the martensitic free energy $F_m$. With decreasing temperature, the system passes the (theoretical) transition temperature $T_h$ while still being in the austenitic state. Only when the free energies difference $\Delta F$ exceeds a certain activation energy $\Delta F^{a \rightarrow m}$ the system transforms spontaneously into the martensitic state. This transformation occurs at the temperature $T_m$. While heating through $T_h$ the system stays in the martensitic state, up to the temperature $T_a$. At this temperature the difference between the free energies exceeds the activation energy $\Delta F^{m \rightarrow a}$ and the system goes back to the austenitic phase. This model explains very easily the observed hysteresis ($\Delta T_H = T_a - T_m$). The occurrence of an activation energy and hysteresis is a common sign for a first-order transition.
2.4 Application to Ni$_2$MnGa derivatives

Crystal structure of Ni$_2$MnGa derivatives
As shown by [5] the intermetallic compound Ni$_2$MnGa crystallises in the cubic L2$_1$ Heusler structure, given in Figure 2.6. By cooling below $T_M = 202K$ the structure changes to a tetragonal structure, given in Figure 2.7.

![Cubic L2$_1$ Heusler structure](image)

Figure 2.6: Cubic L2$_1$ Heusler structure [5]

![Tetragonal structure](image)

Figure 2.7: Tetragonal structure of Ni$_2$MnGa at low temperatures $T<T_M$ [4]
For several Ni\textsubscript{2}MnGa-based alloys, like Ni\textsubscript{2+\textgamma}Mn\textsubscript{1-\textgamma}Ga (\textgamma=0.18, 0.19) and Ni\textsubscript{2}Pd\textsubscript{0.18}Mn\textsubscript{0.82}Ga, another low-temperature structure was investigated [6], [7]. This structure consists of a mixture of an orthorhombic phase and a monoclinic one. The orthorhombic structure is a distorted Heusler L\textsubscript{21} structure. The monoclinic phase is a shuffling of a six-layer period of the (220) plane of the orthorhombic structure. The sequence of the shuffling is illustrated in Figure 2.8.

![Figure 2.8: Six-layer stacking of the (220) planes, forming the monoclinic phase [7]](image)

**Martensitic domains**

The structural change can also be interpreted as a sequence of 2 successive shears along (110) axes of the original cubic structure [8]. Since all (110) axes are equivalent, several combinations of shears can occur. Martensitic domains with different shear directions, and therefore different orientations of crystallographic axes, are called twins. However, the strain in these domains can have the same magnitude. With the formation of twins, the crystal structure increases its entropy, and therefore decreases its free energy. Domain walls separate the domains. These boundaries can be shifted by applied stress.
Chapter 2: Introduction to the martensitic phase transition

2.5 References

[1] Private communication with Professor Takeshi Kanomata, Tohoku Gakuin University, Tagajo, Japan


Chapter 3: Sample preparation

3 Sample preparation

3.1 Polycrystalline Samples

20g polycrystalline samples were prepared by melting the appropriate amounts of the constituent elements in an argon arc furnace. The elements were placed on top of each other, with the one with the highest melting point on top. After melting, the ingots were turned over and re-melted at least 3 more times, to ensure homogeneity. All ingots (except the Ni_{2.19}Mn_{0.81}Ga sample) were afterwards flop cast to obtain a sample shape appropriate for dilatometry and contactless resistance measurements.

Details about the constituent elements can be found in Table 3.1, details about the samples are displayed in Table 3.2.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>25</td>
<td>99.9</td>
<td>54.938</td>
<td>1517</td>
<td>2370</td>
<td>1.240</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Co</td>
<td>27</td>
<td>99.99</td>
<td>58.9332</td>
<td>1768</td>
<td>3143</td>
<td>1.253</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>28</td>
<td>99.9</td>
<td>58.70</td>
<td>1726</td>
<td>3005</td>
<td>1.246</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>29</td>
<td>99.9</td>
<td>63.546</td>
<td>1357</td>
<td>2868</td>
<td>1.278</td>
</tr>
<tr>
<td>Gallium</td>
<td>Ga</td>
<td>31</td>
<td>99.99</td>
<td>69.72</td>
<td>302.93</td>
<td>2676</td>
<td>1.221</td>
</tr>
<tr>
<td>Indium</td>
<td>In</td>
<td>49</td>
<td>99.9</td>
<td>114.82</td>
<td>429.32</td>
<td>2353</td>
<td>1.626</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>50</td>
<td>99.99</td>
<td>118.69</td>
<td>505.12</td>
<td>2543</td>
<td>1.405</td>
</tr>
</tbody>
</table>

The purities were obtained from the manufacturers; the other properties were taken from [1] and crosschecked with [2].

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight loss</th>
<th>Molar weight</th>
<th>Corrected molar weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni_{2.19}Mn_{0.81}Ga</td>
<td>1.17 %</td>
<td>242.773 g/mol</td>
<td>239.933 g/mol</td>
</tr>
<tr>
<td>Ni_{2}MnGa_{0.95}In_{0.05}</td>
<td>1.37 %</td>
<td>244.313 g/mol</td>
<td>240.966 g/mol</td>
</tr>
<tr>
<td>Ni_{2}MnGa_{0.95}Sn_{0.05}</td>
<td>0.98 %</td>
<td>244.507 g/mol</td>
<td>242.111 g/mol</td>
</tr>
<tr>
<td>Ni_{1.9}Cu_{0.1}MnGa</td>
<td>1.36 %</td>
<td>242.543 g/mol</td>
<td>239.244 g/mol</td>
</tr>
<tr>
<td>Ni_{1.9}Co_{0.1}MnGa</td>
<td>1.14 %</td>
<td>242.081 g/mol</td>
<td>239.321 g/mol</td>
</tr>
</tbody>
</table>
In Table 3.2 the molar mass was corrected for the weight loss, assuming the number of unit cells as constant, but the average number of atoms per unit cell is smaller than expected. After preparing the ingots, the samples were cut by spark erosion.

Ni$_{2.19}$Mn$_{0.81}$Ga sample: First, the ends of the ingot were cut-off. Afterwards a bar-shaped dilatometry specimen was cut, having the dimensions 4x4x20 mm. The end pieces and the small remnants were crushed to a fine powder of particle size < 63 µm.

Other samples: First, a flat disc (mass ≈ 1 g) for specific heat measurements was cut. Then a rod with diameter d ≈ 6 mm and length ≈ 18-30 mm with parallel end faces was prepared, for dilatometry and contactless resistance measurements. All flat surfaces were polished with papers of different grain sizes to obtain smooth surfaces (especially important for the specific heat specimen in order to get good thermal contact). The remnants were crushed in a hardened steel mortar and pestle to fine powder. During the crushing a few lumps of masses ≈ 5 mg were removed for SQUID measurements. The powder was sieved afterwards to obtain a powder with known grain size. For the subsequent X-ray powder diffraction measurements, powders with maximum particle sizes of 63 µm or 100 µm were used.

After initial X-ray scans, all samples (except the dilatometry stick of the Ni$_{2.19}$Mn$_{0.81}$Ga sample) were sealed under low-pressure argon atmosphere into a quartz tube. Then they were annealed in a furnace for 4 days at 800 °C before being slow cooled. The duration of this cooling process was approximately 10 hours.

### 3.2 Single-crystalline Samples

Table 3.3: Properties of the single-crystalline samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Orientation</th>
<th>Molar weight</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_2$MnGa</td>
<td>(110)</td>
<td>242.058 g/mol</td>
<td>5.3 mm</td>
</tr>
<tr>
<td>Ni$_2$MnGa</td>
<td>(100)</td>
<td>242.058 g/mol</td>
<td>4.25 mm</td>
</tr>
</tbody>
</table>

These samples were cut by spark erosion from a single crystal grown by the Bridgman method at the Institute of Materials Processing, Sendai, Japan by Dr. Matsumoto. After cleaning the surfaces with diluted nitric acid (approximately 10% acid), the orientation was confirmed by Laue backscattering pictures, using a XR-7 land diffraction cassette by Polaroid™.
3.3 References


4 Structure determination

4.1 Essentials of X-ray radiation

In order to obtain the structural details of a material the wavelength of the radiation (X-rays, electrons, neutrons) used in the observation must be smaller than the lattice parameter.

X-ray radiation is a high-energy part of the electromagnetic spectrum. It can be classified according to its wavelengths:

- X-rays with a wavelength between 0.12\,\text{Å} (Ångström, 1\,\text{Å} = 10^{-10}\,\text{m}) and 1.2\,\text{Å} are called "hard X-rays"
- X-rays with a wavelength between 1.2\,\text{Å} and 12\,\text{Å} are called "intermediate X-rays"
- X-rays with a wavelength between 12\,\text{Å} and 120\,\text{Å} are called "soft X-rays"

Since usual lattice parameters are of the order of a few Ångström, intermediate X-rays are most commonly used for structure analysis.

4.2 The production of X-ray radiation

X-rays are generated by the impact of energetic electrons on to a metallic surface. Between the cathode, which emits a flux of \( I_x \) electrons, and the metal anode an electric field of \( U_x \) is applied. In this field the electrons become accelerated to a final energy \( E_F = eU_x \). The anode material, \( I_x \) and \( U_x \) are parameters influencing the emitted radiation.

When the electrons hit the anode surface, they interact with the anode atoms. One result is the so-called Bremsstrahlung. This radiation is emitted due to the deceleration of the electrons in the electric field of the anode atoms. The Bremsstrahlung spectrum is a broad, continuous band of radiation. It shows a high-energy, low-wavelength limit, which is determined by the applied accelerating field. The limiting wavelength is emitted, when the electron loses its whole energy \( E_F \) during one interaction.

In addition, the interaction produces discrete emission lines, resulting from rearrangements of electrons in the electron shells of the anode atoms. The accelerated electrons can excite inner shell electrons beyond their ionisation energy. An outer electron falling into it will fill the resulting hole in the inner shell. The transitions are labelled by the two shells involved: If the lower shell is the K-shell (the inner most shell), the transition is a K-transition. If it’s an L-shell (the second shell), it’s an L-transition. The change of the principal quantum number of the falling electron adds a greek-letter index to the transition label. Thus, a change of unity is called an \( \alpha \)-transition, a change of two is a \( \beta \)-transition.
Summarising: a transition from shell L to shell K is a $K_{\alpha}$ transition. A transition from shell M to shell K is a $K_{\beta}$ transition.

The selection rules for these transitions are such, that the $K_{\alpha}$ lines are a close doublet with the stronger component $K_{\alpha 1}$ having approximately twice the intensity of the weaker $K_{\alpha 2}$ component [1]. The energies related to the shells depend on the material and its atomic number. Therefore, the lines are characteristics for the different materials.

### 4.3 General structure determination

The basic formula for the structure determination of a sample by diffraction is the Bragg law

$$\lambda = 2 \cdot d_{hkl} \cdot \sin(\theta),$$  \hspace{1cm} (4.1)

where $\lambda$ is the wavelength of the radiation, $d_{hkl}$ the separation of two neighbouring lattice planes with the Miller indices $(hkl)$ and $\theta$ the detection angle of the $(hkl)$ reflection. For cubic lattices $d_{hkl}$ can be calculated as

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$  \hspace{1cm} (4.2)

where $a$ is the lattice parameter.

For samples with cubic lattices equation (4.1) can be written as

$$\sin^2(\theta) = \frac{\lambda^2}{4 \cdot a^2} \cdot (h^2 + k^2 + l^2).$$  \hspace{1cm} (4.3)

The atomic scattering factor $f$ is a property of the single atom, depending on the atom, the wavelength of the incident beam, the type of radiation and the scattering angle. It describes how a single, free atom would scatter the incident beam.

The structure factor is the sum of all the waves scattered by the individual atoms of one unit cell. It is given by

$$F_{hkl} = \sum_{n=1}^{N} f_n \cdot e^{2\pi i (k u_n + k v_n + l w_n)},$$  \hspace{1cm} (4.4)

where the summation is carried out over all atoms of the unit cell. $(hkl)$ are again the Miller indices of the observed peak, $u_n, v_n, w_n$ are the positions of the $n^{th}$ atom in the unit cell and $f_n$ its atomic scattering factor. The exponential term describes constructive and destructive interference of the scattered waves of the individual atoms. The intensities $I$ of the reflections are related to the lattice and the associated basis, i.e. atoms, through the structure factor $F_{hkl}$: $I \propto |F_{hkl}|^2$. The structure factor describes therefore the influence of the general crystal structure, which is determined by the space group.
Chapter 4: Structure determination

4.4 Application to cubic Ni$_2$MnGa derivatives

As shown by Webster et al. [2], Ni$_2$MnGa is a Heusler alloy, which undergoes a structural phase transition from a high-temperature cubic L2$_1$ Heusler structure to a low-temperature tetragonal structure at a transition temperature $T_M = 202$K. The lattice parameter of the L2$_1$ structure for Ni$_2$MnGa is $a = 5.825$Å.

The Heusler L2$_1$ structure can be considered as four interpenetrating cubic fcc sublattices with atoms A, B, C and D at locations (0, 0, 0), ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) respectively. The structure factor is therefore

$$ F_{hkl} = 4 \cdot \left( f_A + f_B \cdot e^{i(h/2+k/2+l/2)} + f_C \cdot e^{i(h+k+l)} + f_D \cdot e^{i(3h/2+3k/2+3l/2)} \right). \quad (4.5) $$

In an ideal Ni$_2$MnGa sample the A and C sites are occupied by Ni, the B sites by Mn and the D sites by Ga. According to Webster [2] the structure factor is only non-zero for a limited number of lattice planes:

**Case 1:** $h$, $k$, $l$ all odd:

$$ F_{hkl} = 4 \cdot |f_{Mn} - f_{Ga}| $$

**Case 2:** $h$, $k$, $l$ all even and $h+k+l = 4n+2$:

$$ F_{hkl} = 4 \cdot 2 \cdot f_{Ni} - (f_{Mn} + f_{Ga}) $$

**Case 3:** $h$, $k$, $l$ all even and $h+k+l = 4n$:

$$ F_{hkl} = 4 \cdot 2 \cdot f_{Ni} + (f_{Mn} + f_{Ga}) $$

For any combination of $(hkl)$ not included in these sets of reflections the structure factor vanishes, independent of the scattering factors. However, for a crystal, where the B and the D sites are occupied randomly by Mn and Ga atoms, case 1 vanishes as well. For a completely disordered structure, even case 2 vanishes.

The reflections described by case 3 are called "principal reflections". They are independent of chemical order and occur at the same positions and with the same intensities in the patterns of both ordered and disordered alloys. Since the atomic scattering factors add (and atomic scattering factors being always positive for X-rays), the principal reflections have usually the highest intensities.
4.5 Application to non-cubic samples

The following paragraph deals with non-cubic lattices, because Ni$_{2.19}$Mn$_{0.81}$Ga does not crystallise in a cubic structure.

In an orthorhombic structure, all angles are rectangular, and all 3 lattice parameters are different. Assuming these lattice parameters are a, b and c, eq. (4.1) can be written as

$$\sin^2(\theta) = \frac{\lambda^2}{4 \cdot a^2} \cdot h^2 + \frac{\lambda^2}{4 \cdot b^2} \cdot k^2 + \frac{\lambda^2}{4 \cdot c^2} \cdot l^2.$$  (4.6)

A tetragonal structure is a special case of an orthorhombic structure, where two of the three lattice parameters are equal. Equation (4.1) can therefore be written as

$$\sin^2(\theta) = \frac{\lambda^2}{4 \cdot a^2} \cdot (h^2 + k^2) + \frac{\lambda^2}{4 \cdot c^2} \cdot l^2.$$  (4.7)

The equivalent formula for hexagonal lattices is

$$\sin^2(\theta) = \frac{\lambda^2}{3 \cdot a^2} \cdot (h^2 + h \cdot k + k^2) + \frac{\lambda^2}{4 \cdot c^2} \cdot l^2.$$  (4.8)

4.6 Determination of the lattice parameter

The formulas (4.3), (4.6), (4.7) and (4.8), depending on the crystal structure, are used to calculate the lattice parameters of the materials investigated. By measuring the diffraction angles $2\theta$ for a number of reflections, a lattice parameter for each reflection can be calculated. Computing the mean values of these lattice parameters and its standard deviations leads to the lattice parameters and its error margins given later in the chapter.

4.7 Experimental set-up

The measurements are based on the powder diffractometry method, and were made using standard Philips X-ray equipment with Cu K$_\alpha$ radiation. A broad focus PW2 103/100 copper radiation tube was used in conjunction with a PW 1050/25 goniometer. A proportional detector PW 1965/20/30 was fixed on the diffractometer axis and was moved around it at constant angular velocity. The X-ray system was controlled by a PC, using the software package Sietronics PW1050 diffraction automation SIE 122D.

The X-ray tube, with a supply voltage $U_x = 40kV$ and a supply current of $I_x = 20mA$, produced the Cu K$_{\alpha 1}$ K$_{\alpha 2}$ doublet, with wavelengths $\lambda_{\alpha 1} = 1.540562\AA$ and $\lambda_{\alpha 2} = 1.544390\AA$. The use of this doublet results in a splitting of the diffraction peaks, especially for high diffraction angles. The K$_\beta$ component was suppressed by the use of a nickel filter. Since the sample was mounted on an aluminium holder, the diffraction peaks of the aluminium had to be taken into account. Aluminium has a known space group F m -3 m (face-centred cubic) and a lattice parameter of $a = 4.0488\AA$, according to [3].
4.8 Results

4.8.1 Influence of heat treatment on X-ray patterns

The influence of heat treatment on the X-ray patterns of the investigated samples was briefly studied. The powder was scanned quickly (speed = 1 °/min and step size = 0.05 °) after crushing and before annealing. This was mainly done to discover obvious lattice anomalies. Afterwards all powder samples were annealed for 4 days at 800 °C and slowly cooled. The main scans were performed more accurately (using a speed = 0.1 °/min and step size = 0.05 °). For this section, a quick reference scan (speed = 1 °/min and step size = 0.05 °) of the Ni_{1.9}Cu_{0.1}MnGa sample was carried out. The following discussion will be limited to the Ni_{1.9}Cu_{0.1}MnGa and the Ni_{2.19}Mn_{0.81}Ga sample. The other samples show behaviours similar to the Ni_{1.9}Cu_{0.1}MnGa sample.

In order to compare the different patterns, the influence of the equipment on the measurement has to be considered. The integrated counting rate is a constant, only dependent on the parameters of the X-ray equipment, like efficiency of the tube, efficiency of the monochromators and the detection system. These parameters were not changed during all measurements.

The results are displayed for the Ni_{2.19}Mn_{0.81}Ga sample in Figure 4.1a (before annealing) and in Figure 4.1b (after annealing). The results for the Ni_{1.9}Cu_{0.1}MnGa sample are shown in Figure 4.2a (before annealing) and in Figure 4.2b (after annealing). For both samples, a sharpening of the peaks is observed due to the annealing. Since the integrated counting rate must be constant, the peak intensities are in general higher after the annealing than they were before. For the Ni_{2.19}Mn_{0.81}Ga sample, peaks, which were single broad peaks before the annealing, split into several narrow peaks. This sharpening is due to the relief of stress produced by smashing the samples into powder. While the stress is still applied, the lattice parameters are not well defined. They vary in a finite interval. Since the diffraction angle is correlated to the lattice parameter by the Bragg law, eq. (4.1), this leads to a finite interval of diffraction angles for every set of lattice planes. This gives rise to broad peaks.

The annealing allows the atoms to rearrange into its equilibrium lattice. The required energy is provided by the thermal excitation energy. In the absence of stress, the interval of the lattice parameter, and of the diffraction angles, is much smaller, resulting in sharper peaks.

The peaks caused by the aluminium holder do not change.
Figure 4.1a: X-Ray pattern for Ni$_{2.19}$Mn$_{0.81}$Ga before annealing

Figure 4.1b: X-Ray pattern for Ni$_{2.19}$Mn$_{0.81}$Ga after annealing
Figure 4.2a: X-Ray pattern for Ni$_{1.9}$Cu$_{0.1}$MnGa before annealing

Figure 4.2b: X-Ray pattern for Ni$_{1.9}$Cu$_{0.1}$MnGa after annealing
4.8.2 Structure determination for cubic samples

Figure 4.3: X-Ray pattern for $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$ with lattice plane indices

Figure 4.4: X-Ray pattern for $\text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05}$
Chapter 4: Structure determination

Figure 4.5: X-Ray pattern for Ni$_{1.5}$Cu$_{0.1}$MnGa

Figure 4.6: X-Ray pattern for Ni$_{1.5}$Co$_{0.1}$MnGa
The diffraction patterns show similar peaks, leading to the assumption that all the above listed samples have the same crystal structure. This structure could be identified as the L2₁ cubic Heusler structure with the space group Fm -3 m, shown in Figure 2.6. The only differences occur in the lattice parameters, given in Table 4.1:

**Table 4.1: Lattice parameters for cubic samples**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₂MnGa₀.₉₅In₀.₀₅</td>
<td>5.8420</td>
<td>0.0021</td>
<td>5.7426</td>
</tr>
<tr>
<td>Ni₂MnGa₀.₉₅Sn₀.₀₅</td>
<td>5.8416</td>
<td>0.0025</td>
<td>5.7299</td>
</tr>
<tr>
<td>Ni₁₀.₉₅Cu₁₀.₃MnGa</td>
<td>5.8402</td>
<td>0.0024</td>
<td>5.7225</td>
</tr>
<tr>
<td>Ni₁₀.₉₅Co₀.₁MnGa</td>
<td>5.8255</td>
<td>0.0015</td>
<td>5.7211</td>
</tr>
</tbody>
</table>

The lattice parameters of the samples investigated show an obvious feature: Only the lattice parameter of the Ni₁₀.₉₅Co₀.₁MnGa sample is consistent with the reference value \( a = 5.825 \, \text{Å} \), given by [2]. All other lattice parameters are rather consistent with a lattice parameter of \( a = 5.841 \, \text{Å} \), roughly \( \Delta a = 0.016 \, \text{Å} \) larger than the reference value. This discrepancy is one order of magnitude larger than the experimental error.

To study the qualitative behaviour a theoretical lattice parameter was calculated, utilising the (111) direction in the Heusler structure with the given atomic radii. This direction has the advantage to contain each atom at least once. The calculated lattice parameters are of the same order as the measured ones and show the same trend, but they are systematically 1.7-2.0 % smaller than the measured values (see Table 4.1). This reflects the rough assumptions that lead to these values. Especially an accurate determination of atomic radii...
is difficult and usually depends on the definition of an atomic radius. A usual definition is: the half of the smallest possible distance between two atoms of the same kind in the ground state. This definition was used to determine the above-mentioned atomic radii. However, the values are still hard to achieve. In addition, the crystal lattice consists rather of ions, dispensing electrons into the conduction band, than of atoms, as assumed above.
4.8.3 Structure determination for the Ni$_{2.19}$Mn$_{0.81}$Ga sample

The structure of Ni$_{2.19}$Mn$_{0.81}$Ga was investigated by Inoue et. al.[4], who determined a mixture of an orthorhombic phase and a monoclinic phase. The orthorhombic phase is a distorted Heusler structure with \( a = 6.09223 \) Å, \( b = 5.75111 \) Å, \( c = 5.48279 \) Å (the Heusler structure is displayed in Figure 2.6). The monoclinic phase is a shuffling of a six-layer period of the (220) plane of the orthorhombic structure (shown in Figure 2.8) with \( a = 4.24601 \) Å, \( b = 5.46336 \) Å, \( c = 12.6780 \) Å, \( \beta = 99.2356 \) °. In private communication [5]Dr. Inoue pointed out the dependency of the shuffling period as well as the martensitic transition temperature on the grain size. Since the data by [4] were obtained by neutron diffraction using rough powder, in contrast to the fine powder used in recent X-ray diffraction measurements, variations can be expected.

Using the provided information [4], the expected diffraction angles for the orthorhombic phase of the Ni$_{2.19}$Mn$_{0.81}$Ga sample investigated were calculated first. The related peaks in the diffraction pattern were indexed, as shown in Figure 4.7. The lattice parameters were calculated as described in Section 4.6. The results are: \( a = 6.108 \pm 0.027 \) Å, \( b = 5.802 \pm 0.013 \) Å, \( c = 5.542 \pm 0.026 \) Å. Since all main peaks can be associated to reflections of the orthorhombic phase, the fraction of the monoclinic phase is expected to be small compared with the orthorhombic phase.

Figure 4.7: X-Ray pattern for Ni$_{2.19}$Mn$_{0.81}$Ga with lattice plane indices
4.9 References


Chapter 5: Magnetism and Magnetisation measurements

5 Magnetism and Magnetisation measurements

5.1 Theory of Ferromagnetism

Since the investigated samples are all ferromagnetic in the observed temperature range, the discussion about the theory of magnetism will be limited to ferromagnetism.

As proved by [1], the magnetic moment in $X_2MnZ$ Heusler alloys is almost totally localised at the Mn sites, unless $X = Co$, where a minor moment is localised at the Co sites as well. Therefore, the magnetic properties have to be described using a localised model.

5.1.1 Localised Ferromagnetism

In atoms, magnetic moments are formed by the interaction of the intrinsic magnetic moments, caused by the electron spins and the distribution of the electrons into the different orbitals of the atom.

These atomic magnetic moments may interact with each other. This interaction can be described as the overlap of two or more orbitals of neighbouring atoms. The overlap integral is related to the exchange energy gained by the system. If the exchange energy is positive, the magnetic moments become aligned parallel. This results in a macroscopic magnetisation of the sample. The alignment is enhanced by an external magnetic field. The atomic moments will than try to align parallel to the external field. Even after removing the external field, the moments will stay aligned.

In order to increase the entropy of the ferromagnetic system and to decrease its free energy, the sample forms regions, called domains, where the moments are aligned parallel. However, the moments in neighbouring domains are not parallel. The mechanism of domain building therefore decreases the overall magnetisation of the sample. Bloch walls separate the domains. The application of an external field shifts the Bloch walls. Domains with moments parallel to the field grow at the expense of domains with other orientations. This gives rise to an increased magnetisation of the sample.

If a ferromagnet is heated above its critical temperature (called Curie temperature $T_C$), the thermal energy will exceed the exchange energy. The moments become disordered. The ferromagnet transforms into a paramagnet, where the atomic moments are still existing, but no longer correlated.

The temperature behaviour of the magnetisation can be described by mean field theory, where every spin interacts with a mean of the other spins. This leads to magnetisation curves, like displayed in Figure 5.1. In this figure, the reduced magnetisation $\mu(T)/\mu(T=0K)$ as a function of the reduced temperature $T/T_c$ is shown.
In an applied magnetic field, the magnetisation stays larger than zero, even for temperatures above the Curie temperature. In this case, the external field provides the energy to keep a part of the moments aligned, even if the thermal energy exceeds the exchange energy.

Depending on the crystal structure of the material, there are special axes, along which the moments can be aligned already in small magnetic fields. These axes are called "easy axes". For Heusler alloys in the Heusler cubic L2₁ structure, the easy axes are the (111) directions (8 equivalent axes). For the tetragonal structure of the martensitic phase of Ni₂MnGa, the easy axes are along the c-axis [2]. Hence, 2 equivalent axes exist. As a result, the probability, that a randomly chosen direction is nearly along one of the easy axes, is much higher in the cubic structure than in the tetragonal structure. As the observed samples undergo a structural phase transition from a high-temperature cubic structure to a low-temperature tetragonal one, the average amount of domains with moments nearly parallel to the observation direction is decreased. The magnetisation of the sample is expected to drop.

Figure 5.1: Spontaneous magnetisation, as obtained from mean field theory

![Graph showing spontaneous magnetisation](image)
5.1.2 Indirect Exchange Interaction

While the localised ferromagnetism, as described above, requires the overlap of electronic wavefunctions, ferromagnetic systems without overlap are reported, for example ferromagnetic Heusler alloys containing manganese. The general formula is $X_2\text{Mn}Z$, where $X$ is a transition metal from the latter part of a transition series, and $Z$ a non-transition metal containing only sp-valence electrons. Webster [1] has confirmed that for most Heusler alloys containing Mn essentially the whole magnetic moment is confined to the Mn sites, with amplitude of $\mu \approx 4\mu_B$. The only exceptions are alloys containing cobalt, where the moment is shared with the Co atoms. Since the Heusler alloys crystallising in the $L2_1$ Heusler structure, the distance between 2 manganese atoms is $\frac{a}{\sqrt{2}} \approx 4.2\text{Å}$. The overlap of the d-orbitals, which carry the magnetic moment in the manganese atoms, is negligible, because of d-orbitals being highly localised.

For describing the magnetism in such localised systems, the RKKY theory (named after Ruderman, Kittel, Kasuya and Yosida) was developed. This theory describes the magnetic ordering with an indirect exchange interaction between the localised magnetic moments, transmitted by the polarisation of conduction band electrons. The conduction electrons become polarised in the field of one atom. The polarisation depends on the electronic configuration of the first atom, including the spin distribution. The conduction electrons carry this polarisation to the next atom, whose electrons interact with the conduction electrons and their polarisation. Since the different electronic wavevectors interfere, there are areas of constructive interference and areas with destructive interference. Therefore, there are areas with positive and areas with negative exchange energy, depending on the distance and on the Fermi wavevector. The dependence is damped oscillatory, with a wavelength proportional to the inverse of the Fermi wavevector, and amplitude proportional to $k_F \cdot \cos(2 \cdot k_F \cdot r + 2 \cdot \delta)$, $\delta$ being a phase shift caused by the scattering. For a free electron Fermi gas, the Fermi wavevector is a function of the electron density only: $k_F = \sqrt{3} \cdot \pi^2 \cdot n$. The electron density alters therefore the periodicity of the exchange energy and its amplitude, and hence the magnetic ordering behaviour.

Different extensions and applications were introduced. Calculations, especially for Heusler alloys, were done by Blandin & Campbell [3], Malmstroem, Geldart & Blomberg [4], Price [5] and Kuebler, Williams & Sommers [6].
5.2 Arrott Plots

Two important magnetic properties of a ferromagnetic material are its Curie temperature and its magnetic moment per formula unit. In principle, both properties can be obtained from isotherms, where the magnetisation is measured as a function of the applied magnetic field, if the magnetisation approaches saturation at high fields. Since accurate determination of the magnetic moment per formula unit and the Curie temperature are not easy using isotherms, the easier to handle Arrott plots were derived.

Arrott plots are plots of $M^2$ versus $\mu_0H/M$, based on a Landau description of the magnetisation. In this Landau description the free energy takes the form

$$F = F_0 + \frac{1}{2} A \cdot M^2 + \frac{1}{4} B \cdot M^4 - \mu_0 \cdot \vec{M} \cdot \vec{H},$$  \hspace{1cm} (5.1)

where $F_0$ describes the magnetisation-independent contributions [7]. The term $\vec{M} \cdot \vec{H}$ describes the interaction between the magnetisation $M$ and the external magnetic field $H$. In this expansion, only even terms are present, due to the time-reversal symmetry. $A$ and $B$ are the coefficients of the series expansion. The coefficient $A$ is temperature dependent and can be identified with the inverse susceptibility. $B$ is taken to be temperature independent. Minimising the free energy with respect to $M$ for a given external field $H$ results in

$$M^2 = \frac{1}{B} \cdot \frac{\mu_0 \cdot H^2}{M} - \frac{A}{B}. \hspace{1cm} (5.2)$$

The graphical representations of eq. (5.2) are the Arrott plots. The term $A/B$ can be interpreted as the squared spontaneous magnetisation. This term, evaluated for different temperatures, leads to the graphs of ordered moment per formula unit given later in this chapter.

According to (5.2) Arrott plots should be straight lines. In practice, the graphs are slightly curved. In this case, only the linear part should be taken into consideration. By linear interpolation to $B = 0T$ the spontaneous magnetisation can be determined. Reasons for the nonlinearity can be interactions between magnetic domains, spin fluctuations, spin rotations, inhomogeneities in the composition or impurities. Especially for the investigated materials, the influence of the internal anisotropy field is not negligible. This topic was discussed in detail by [8].
5.3 The Superconducting Quantum Interference Device (SQUID)

A Superconducting QUantum Interference Device (SQUID) was used to investigate the magnetic properties of the Ni$_2$MnGa derivatives, by measuring the magnetisation as a function of temperature and applied magnetic field. With these data, and using the Arrott plots described in section 5.2, the spontaneous magnetisation (respectively the ordered moment per formula unit) and the Curie temperature can be determined.

With a resolution of $10^{-8}$ e.m.u. ($10^{-11}$ JT$^{-1}$) the SQUID is the most accurate method to measure magnetisations. This high accuracy allows samples with very small magnetic moments to be investigated. Since the samples under investigation are ferromagnetic, the sample size was decreased. The SQUID magnetometer is a device made especially to investigate the magnetic properties of samples over a broad range of temperatures (1.9K - 400K) and magnetic fields (maximum field $B_{\text{max}} = 5.5$T, reversible). It consists of a superconducting solenoid, a SQUID detector system, a liquid helium Dewar, a temperature control module and PC remote control. The system, including the control and analysis software, was built by Quantum Design$^\text{TM}$.

The SQUID detection system consists of the SQUID sensing loops (a highly balanced second-derivative coil set, to pick up the signal induced by the solenoid into the sample), a superconducting transformer with an RFI shield (to guide the signal to the SQUID sensor, while shielding it against external radio-frequency sources) and the SQUID sensor.

The SQUID sensor itself is a superconducting ring including a Josephson junction. A Josephson junction is a small gap within the ring, formed by an insulator. This gap is small enough for Cooper pairs to tunnel through it. The overlap of the Cooper pair wavefunctions on both sides of the junction leads to interference. The phase $\xi$ of the interference depends on the magnetic flux $\Phi$ trapped within the superconducting sensor ring

$$\xi = 2\pi n - \frac{2\pi \phi}{\Phi_0},$$

(5.3)

where $n$ is an integer number, and $\Phi_0 = \frac{\hbar}{2e}$ is the flux quantum. The charge involved in the flux quantum is $2e$, the charge of one Cooper pair, which consists of 2 electrons. While measuring the interference phase, the magnetic flux can be calculated and hence the magnetisation.

Further information about theory and applications of SQUIDs can be obtained from the literature ([9], [10], [11]).
5.4 Magnetisation measurements: Results

The properties of the SQUID samples are displayed in Table 5.1. The specimen masses are chosen to be small, in order not to saturate the SQUID sensor. In general, powder and lumps can be used as specimen. However, the usage of lumps makes the samples easier to handle.

Table 5.1: Properties of the SQUID samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight</th>
<th>Molar weight</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$<em>{2.19}$Mn$</em>{0.81}$Ga</td>
<td>3.98 mg</td>
<td>242.773</td>
<td>Lump</td>
</tr>
<tr>
<td>Ni$<em>{2}$MnGa$</em>{0.95}$In$_{0.05}$</td>
<td>5.14 mg</td>
<td>244.313</td>
<td>Powder</td>
</tr>
<tr>
<td>Ni$<em>{2}$MnGa$</em>{0.95}$Sn$_{0.05}$</td>
<td>1.71 mg</td>
<td>244.507</td>
<td>Lump</td>
</tr>
<tr>
<td>Ni$<em>{1.9}$Cu$</em>{0.1}$MnGa</td>
<td>4.69 mg</td>
<td>242.543</td>
<td>Lump</td>
</tr>
<tr>
<td>Ni$<em>{1.9}$Co$</em>{0.1}$MnGa</td>
<td>4.86 mg</td>
<td>242.081</td>
<td>Lump</td>
</tr>
</tbody>
</table>

The measurements where performed in the same way for all samples. First, a temperature scan at a moderate magnetic field (0.1T) was performed, in order to find any transitions. Secondly, isotherms (field scans at certain temperatures) were performed, with special focus on temperatures within the transition regions. In the end, further temperature scans at different fields were realised.

In this section, the results for Ni$_{2}$MnGa$_{0.95}$Sn$_{0.05}$ will be discussed in detail only. The behaviour of the other samples is similar, and only differences will be mentioned. The section will finish with a comparison between all samples, and a discussion, comparing the data with theoretical approaches.
5.4.1 \( \text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05} \)

As shown in Figure 5.2 the magnetisation of the \( \text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05} \) sample exhibits a broad transition, centred around 100K. At a field of 1000 gauss the transition occurs over roughly 60K, with a hysteresis of approximately 20K. For higher fields the transition becomes even broader, with a decrease in amplitude at high fields (1T and 1.5T). The transition vanishes at a field of 2T.

As mentioned above, the martensitic phase transition is accompanied by a change in the number of easy axes of the system. This change in the number of easy axes is accompanied by a change in the magnetisation, since the fraction of domains with easy axis nearly parallel to the magnetic field direction changes. In the discussed cubic-to-tetragonal transformation, the magnetisation is expected to drop as the system cools through the transition. This drop is observed in low fields.

For high fields the magnetic energy forces the moments to align parallel to the field, independent of the direction of the easy axes. Therefore, the magnetisation measurement is not longer sensitive to the structural change. However, it can be shown (i.e. with diffraction experiments) that the structural change still occurs.

**Figure 5.2: Temperature scans for \( \text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05} \) at various applied fields**
The high field data show the usual behaviour of a ferromagnet, with a slow decrease in the magnetisation with increasing temperature towards the Curie temperature.

Another feature is the heating and cooling data not merging for the martensitic phase (this feature is more obvious in data shown further on). The reason could be that some martensitic domains in the polycrystalline sample realign in a new way while cooling through the transition. This hypothesis is supported by the fact, that usually the cooling data (as they are obtained after the heating data) have higher magnetisation values. This would mean that in the beginning at low temperatures the domains are not perfectly aligned. During the cooling process, domains can now stay aligned to a higher degree parallel to the magnetic field in order to minimise the free energy of the system.

Figure 5.3: Isotherms for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ at various temperatures

The change in the number of easy axes is observable in Figure 5.3. Up to 90K the graphs nearly merge to one graph, saturating only in high fields above 2T. The scans at 105K and 120K are saturated easier and are separated from the first set. The scans at even higher temperatures (T $\geq$ 135K) are nearly saturated in small fields (of the order of 0.4T to 0.6T). These scans merge for fields up to 0.2T, and split afterwards due to the decrease of the magnetisation towards the Curie temperature.
Chapter 5: Magnetism and Magnetisation measurements

Figure 5.4: Arrott plots for \( \text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05} \) at various temperatures

Since there are sets of isotherms with varying low-field behaviour, similar sets occur in the Arrott plots as well. In the cubic phase, the curvature for low fields is due to domain rotation: the spins in the domains rotate in order to minimise the free energy of the system by increasing the entropy. This leads to a decreasing magnetisation. In the martensitic phase, the influence of the internal anisotropy field in the sample exceeds the domain rotation effect, resulting in a bending of the Arrott plots up to even higher magnetic fields. Therefore, only the high field data were used to obtain the spontaneous magnetisation by interpolating these data linearly to \( H = 0 \)T. The temperature dependence of the ordered moment per formula unit is shown in Figure 5.5.
The ordered magnetic moment per formula unit in units of $\mu_B$ (Bohr magneton) can be computed from the previous data. This description eases comparisons between different samples and can be deemed to be the natural unit of the magnetic moment, since the Bohr magneton is the magnetic moment of a free electron. The conversion is given by

$$M[\mu_B] = M[e.m.u.] \cdot \frac{molar \ mass[\text{g/mol}]}{mass[\text{g}]} \cdot \mu_B[J/T] \cdot N_A[1/\text{mol}]$$

The error of the moment is dominated by the errors in the molar mass and the mass of the samples. The error in the molar mass is systematic and associated with the weight loss. The corrected molar weight was already calculated in section 3.1. The mass error can be calculated from the accuracy of the balance, which is $\Delta m = 0.02\text{mg}$. The mass error is therefore in the range of 0.4% (for $\text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05}$) to 1% (for $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$). The other error contributions are negligible, due to the high accuracy of the SQUID. This yields an average error of the magnetic moment of the order of magnitude of $\Delta M = \pm 0.02\mu_B$. The magnetic moment per formula unit (equal to the ordered moment / f.u. at $T = 0\text{K}$) can be calculated by a polynomial fit for the low-temperature data. For this sample follows

$$\mu_{00} = 3.989 \pm 0.047\mu_B.$$  The temperature range of the SQUID was not able to cover the Curie temperature. A significant decrease in the magnetisation is shown in Figure 5.5. However, an estimation of the Curie temperature would still be too inaccurate.
5.4.2 \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \)

Figure 5.6: Temperature scans for \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) at various applied fields

Figure 5.7: Isotherms for \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) at various temperatures
The transition, centred on 185K, is easily to observe. In a field of 1000 gauss the transition occurs over roughly 45K, with a hysteresis of approximately 20K. The transition becomes slightly sharper (roughly 40K) at 5000 gauss, and nearly vanishes at 1T. The transition is not as distinct as for the $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$ sample.

Unlike in $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$, for this material the isotherms do not merge that closely, suggesting that the magnetisation is more temperature dependent than for $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$. However, no strong temperature dependence of the magnetisation is found in Figure 5.6, apart from two small jumps, which probably result from spontaneous reorientation of domains. A possible explanation is that after one field scan (which starts with the smallest field and increases the magnetic field up to the maximum field, followed by switching off the field) few powder grains stay magnetised along the magnetic field direction. Therefore, for the next temperature there is still some magnetisation remaining from the last scan. This process repeats for every scan, accumulating some amount of spontaneous magnetisation resulting in a less pronounced merging of the data.

The Curie temperature is again not reached, but the magnetic moment per formula unit could be measured to be $\mu_{00} = 3.917 \pm 0.015 \mu_B$. 

**Figure 5.8: Magnetic moment per formula unit of $\text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05}$**

![Graph showing magnetic moment per formula unit as a function of temperature. The graph shows a decrease in magnetic moment with increasing temperature, with a transition at around 185K.](image-url)
5.4.3 \( \text{Ni}_{1.9}\text{Co}_{0.1}\text{MnGa} \)

Figure 5.9: Temperature scans for \( \text{Ni}_{1.9}\text{Co}_{0.1}\text{MnGa} \) at various applied fields

Figure 5.10: Isotherms for \( \text{Ni}_{1.9}\text{Co}_{0.1}\text{MnGa} \) at various temperatures
Figure 5.11: Magnetic moment per formula unit of Ni_{1.9}Co_{0.1}MnGa

In a field of 1000 gauss the transition is clearly visible and centred around 170K, with a temperature range over which the transition occurs (transition width) of approximately 40K and a hysteresis of not more than 5K. The transition is quite sharp (with a width of approximately 20K) for a field of 6000 gauss and vanishes in a field of 1.5T. The isotherms merge for temperatures up to 150K and fields up to 2T. These isotherms are difficult to saturate, suggesting high anisotropy of the system. For temperatures higher than 160K the isotherms saturate in low fields, indicating lower anisotropy, while the saturation magnetisation decreases towards the Curie temperature. The $T = 160$K isotherm is in between these two cases. The Curie temperature is again not reached. The magnetic moment per formula unit could be measured to be $\mu_{00} = 3.959 \pm 0.016 \mu_B$. 
5.4.4 Ni$_{1.9}$Cu$_{0.1}$MnGa

Figure 5.12: Temperature scan at 1000 gauss for Ni$_{1.9}$Cu$_{0.1}$MnGa

Figure 5.13: Field scans for Ni$_{1.9}$Cu$_{0.1}$MnGa at various temperatures
Figure 5.13a: Isotherms for Ni$_{1.9}$Cu$_{0.1}$MnGa at various temperatures (detail)

Figure 5.14: Magnetic moment per formula unit of Ni$_{1.9}$Cu$_{0.1}$MnGa
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In the temperature scan (Figure 5.12), no evidence for a transition was observed. The drop for high temperatures ($T > 250\,\text{K}$) is the approach towards the Curie temperature.

However, looking in detail at the field scans (Figure 5.13a) the same merging phenomenon as described above is visible. The isotherms for $T = 5\,\text{K}$ and $T = 50\,\text{K}$ coincide, suggesting high anisotropy. For $T \geq 150\,\text{K}$ the isotherms saturate for much smaller fields, revealing smaller anisotropy. The $T = 100\,\text{K}$ isotherm is an intermediate case. Nevertheless, in comparison with the above-mentioned samples, the anisotropy behaviour is less evident and less pronounced, but existent.

The magnetic moment per formula unit was determined to be $\mu_{\text{eff}} = 3.940 \pm 0.017\,\mu_\text{B}$.

5.4.5 $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$

![Temperature scans for $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$ at various applied fields](image)

Figure 5.15: Temperature scans for $\text{Ni}_{2.19}\text{Mn}_{0.81}\text{Ga}$ at various applied fields
Figure 5.16: Isotherms for Ni$_{2.19}$Mn$_{0.81}$Ga at various temperatures

Figure 5.17: Arrott plots for Ni$_{2.19}$Mn$_{0.81}$Ga at various temperatures
For this composition, a match of the Curie temperature with the martensitic transition temperature was previously observed [12]. One transition is obvious. It appears around 350K. This value is consistent with the Curie temperature obtained from the ordered moment per formula unit. Therefore, at least a contribution from the magnetic transition is expected. The small increase of the 1000 gauss heating data, while approaching the transition, can be an indication of the martensitic transition, as well as the pronounced hysteresis of the data, which seems to occur slightly below $T_C$, approximately at 325K. Width and hysteresis are strongly field-dependent. For 1000 gauss, the heating and cooling data are only poorly comparable. The fact of both datasets not merging at low temperatures is an indication of the system having passed a structural transition and the different domains staying aligned parallel to the field to a higher degree for the cooling process. Over the whole range of measured temperatures, the isotherms are not saturated (Figure 5.16), which indicates a high anisotropy. High anisotropy is expected rather in the martensitic phase than in the austenitic phase. On the other hand, the Arrott plots obtained from these field scans are curved for temperatures up to 320K/330K only, which coincides with the observed hysteresis loop. This indicates the martensitic transition temperature being smaller (by approximately 25K) than the Curie temperature.
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The ordered moment per formula unit (Figure 5.18) shows the usual behaviour of a ferromagnet reaching its Curie temperature. The Curie temperature can be determined to be \( T_C = 352 \text{K} \). The magnetic moment per formula unit was determined to be \( \mu_{\text{00}} = 3.076 \pm 0.015 \mu_B \).

5.4.6 Comparison

The magnetic properties are quite different, even while comparing materials with as little as 5% exchange in composition. This reflects the strong influence of these properties on the materials parameters, as will be discussed in the next section.

Table 5.2: Properties of the observed materials concerning transition properties (for \( H = 1000 \text{ gauss measurements} \)) and magnetic moment per formula unit

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \mu_{\text{00}} (T = 0 \text{ K}) ) [( \mu_B )]</th>
<th>Centre of transition [K]</th>
<th>Transition width [K]</th>
<th>Hysteresis [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}<em>2\text{Mn}</em>{0.81}\text{Ga} )</td>
<td>3.076 ± 0.015</td>
<td>325</td>
<td>25 (heating)</td>
<td>n.a.</td>
</tr>
<tr>
<td>( \text{Ni}<em>2\text{MnGa}</em>{0.95}\text{In}_{0.05} )</td>
<td>3.917 ± 0.015</td>
<td>185</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>( \text{Ni}<em>2\text{MnGa}</em>{0.95}\text{Sn}_{0.05} )</td>
<td>3.989 ± 0.047</td>
<td>100</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td>( \text{Ni}<em>{0.9}\text{Co}</em>{0.1}\text{MnGa} )</td>
<td>3.959 ± 0.016</td>
<td>170</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>( \text{Ni}<em>{0.9}\text{Cu}</em>{0.1}\text{MnGa} )</td>
<td>3.940 ± 0.017</td>
<td>≈100 (field scans)</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>( \text{Ni}_2\text{MnGa} ) [13]</td>
<td>4.17 ± 0.3</td>
<td>202</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Properties of the completely substituted materials \[14\]

<table>
<thead>
<tr>
<th>Composition</th>
<th>( T_C )</th>
<th>( \mu_{\text{00}} (T = 0 \text{ K}) ) [( \mu_B )]</th>
<th>Structure</th>
<th>a</th>
<th>( \mu_{\text{Mn}} )</th>
<th>( \mu_{\text{Ni}/\text{Co}/\text{Cu}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ni}_2\text{MnGa} )</td>
<td>374</td>
<td>4.17</td>
<td>( \text{L}_2^1 )</td>
<td>5.825</td>
<td>4.17 &lt;0.3</td>
<td></td>
</tr>
<tr>
<td>( \text{Ni}_2\text{MnIn} )</td>
<td>314</td>
<td>4.43</td>
<td>( \text{L}_2^1 )</td>
<td>6.069</td>
<td>4.40 &lt;0.3</td>
<td></td>
</tr>
<tr>
<td>( \text{Ni}_2\text{MnSn} )</td>
<td>360</td>
<td>4.22</td>
<td>( \text{L}_2^1 )</td>
<td>6.053</td>
<td>4.05 &lt;0.3</td>
<td></td>
</tr>
<tr>
<td>( \text{Co}_2\text{MnGa} )</td>
<td>694</td>
<td>4.05</td>
<td>( \text{L}_2^1 )</td>
<td>5.770</td>
<td>3.01 0.52</td>
<td></td>
</tr>
<tr>
<td>( \text{Cu}_2\text{MnGa} )</td>
<td>No data available</td>
<td></td>
<td>No data available</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A structural phase transition was observed for \( \text{Ni}_2\text{MnGa} \) only.
Chapter 5: Magnetism and Magnetisation measurements

Curie temperature

For Ni$_{2.19}$Mn$_{0.81}$Ga only, the Curie temperature was within the temperature range of the SQUID. It could be determined to be $T_C = 352 \text{K}$.

For the other compositions, the Curie temperatures could not be determined directly. However, by comparing the high temperature data for the different samples a qualitative estimate of $T_C$ was possible. From Figure 5.19a a sequence of Curie temperatures for the materials investigated can be predicted:

$T_C(Ni_{1.9}Co_{0.1}MnGa) > T_C(Ni_{1.9}Cu_{0.1}MnGa) > T_C(Ni_2MnGa_{0.95}Sn_{0.05}) > T_C(Ni_2MnGa_{0.95}In_{0.05})$.

This sequence is supported by the data of the completely substituted materials, shown in Table 5.3.

Magnetisation

![Figure 5.19: Ordered moment per formula unit of the different materials](image-url)

Figure 5.19: Ordered moment per formula unit of the different materials
Figure 5.19a: Ordered moment per formula unit of the different materials (except Ni$_{2.19}$Mn$_{0.81}$Ga)

Figure 5.19b: Reduced ordered moment per formula unit of the different materials
Chapter 5: Magnetism and Magnetisation measurements

The reduced ordered moment per formula unit, defined as $\mu(T)/\mu_{100}$, is plotted in Figure 5.19b as a function of reduced temperature, defined as $T/T_C$. A linear dependence for the Curie temperature between pure Ni$_2$MnGa and the completely substituted materials (Table 5.3) was assumed.

In general, all obtained data of the materials measured are smaller than the moment per formula unit of pure Ni$_2$MnGa, as reported by [13].

- Ni$_{2.19}$Mn$_{0.81}$Ga: Since the amount of manganese, at which site most of the magnetic moment is localised, is drastically reduced, enhancing the content of nickel, where only a small moment is localised, a huge decrease in the moment per formula unit was expected and observed. The moment per formula unit of Ni$_{2.19}$Mn$_{0.81}$Ga is approximately 78% of the moment per formula unit of the other materials. This is consistent with the decrease of Mn content by 19%, and reflects the predominant location of magnetic moment at the Mn sites.

- Ni$_2$MnGa$_{0.95}$In$_{0.05}$ and Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$: The moment per formula unit for Ni$_2$MnGa$_{0.95}$In$_{0.05}$ is smaller than for the Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ sample, in contrast to the data for the totally substituted materials Ni$_2$MnIn and Ni$_2$MnSn (Table 5.3). While changing from In to Sn, two parameters change: the lattice parameter decreases slightly, and the sp-conduction electron concentration increases.

- Ni$_{1.9}$Co$_{0.1}$MnGa and Ni$_{1.9}$Cu$_{0.1}$MnGa: The moment per formula unit for the Ni$_{1.9}$Co$_{0.1}$MnGa is larger than for the Ni$_{1.9}$Cu$_{0.1}$MnGa sample. While changing from Co to Cu, two parameters change: the lattice parameter increases, and the d-conduction electron density increases.

Properties of the martensitic transition

For all materials investigated, a martensitic transformation was observed. For Ni$_{2.19}$Mn$_{0.81}$Ga the Curie temperature and the martensitic transformation temperature merge at temperatures around 325K [12]. This result was verified to a certain extent by the experiments performed for this thesis. The merge is within the temperature range $320K<T_{M,C}<355K$, probably with $T_M$ slightly smaller than $T_C$.

The transition properties for the other materials are altered. The transition temperature $T_M$ drops, slightly for Ni$_{1.9}$Co$_{0.1}$MnGa and Ni$_2$MnGa$_{0.95}$In$_{0.05}$ ($T_M \approx 175K$), drastically for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ ($T_M \approx 100K$). For Ni$_{1.9}$Cu$_{0.1}$MnGa a transition is only indirectly observed, suggesting a drastic drop ($T_M \approx 100K$) compared with Ni$_2$MnGa. The temperature range, over which the transitions occur, and the hysteresis were usually high.
5.5 Discussion

Magnetic properties

The magnetic moments per formula unit of the materials investigated differ from the properties of Ni$_2$MnGa, as reported by [13]. This fact is probably caused by the polycrystalline structure of the samples. Firstly, interactions with grain and domain boundaries can prohibit the ideal alignment of the magnetic moments parallel to the field. Secondly, the c-axis, which is the easy axis of the magnetisation in the martensitic phase, has different orientations with respect to the observation axis in each domain and each powder grain, while the measured magnetisation is an average over all grains.

A parameter appropriate to describe the stability of the ferromagnetic state is the coupling strength. It is proportional to the Curie temperature and determined by several competing processes:

- The influence of the indirect exchange interaction has to be considered: With increasing electron density the oscillation frequency and the amplitude of the coupling strength increase.
- The lattice parameter determines the position of the coupling moments within the oscillations of the indirect exchange interaction coupling strength.
- An increase in the lattice parameter results in a narrowing of the conduction bands with symmetry along the extending lattice parameter, due to the decreasing overlap of the wavefunctions. This band narrowing leads to an overall increase of the density of states in these bands. A high density of states at the Fermi energy results in a higher coupling strength.

The above-mentioned effects have to be taken into account to analyse the magnetic properties observed.

- Ni$_2$MnGa$_{0.95}$In$_{0.05}$ → Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$:
  - By substituting In with Sn, the lattice parameter decreases slightly, which should lead to a decrease in the Curie temperature (due to the band broadening) and a shift within the coupling strength oscillations.
  - Both effects are expected to be small, because the change in the lattice parameter is small.
  - Simultaneously the sp-conduction electron density increases. While In dispenses 3 electrons to the sp-conduction band, Sn dispenses 4 electrons to this band. This could cause the increasing Curie temperature either by increasing the amplitude of the coupling strength or by stretching the coupling strength oscillations to reach a
higher value (indicating the coupling strength being on the spatial increasing branch of the oscillation for Ni$_2$MnGa$_{0.95}$In$_{0.05}$).

- **Ni$_{1.9}$Co$_{0.1}$MnGa → Ni$_{1.9}$Cu$_{0.1}$MnGa:**
  - By substituting Co with Cu, the lattice parameter increases, which should lead to an increase in the Curie temperature, due to the band narrowing, and a shift within the coupling strength oscillations.
  - Nevertheless, both effects should have only a minor influence.
  - Simultaneously the d-conduction electron density is increased. This could cause the decreasing Curie temperature by stretching the coupling strength oscillations to reach a lower value, indicating the coupling strength being on the spatial decreasing branch of the oscillation for Ni$_{1.9}$Co$_{0.1}$MnGa.

In this case, the change of the localised moment, which is significant at the Co sites, but insignificant at the Cu sites, is of importance and explains the drop in the magnetic moment per formula unit. This probably influences the Curie temperature too.

Further systematic doping experiments or pressure-dependent magnetisation measurements could determine the position within the coupling strength oscillations.

The above interpretation is based on the indirect exchange interaction between localised moments. This model cannot describe any changes in the magnetic moment per formula unit (or even non-integer values of it), except by changing the initial localised moment. This change is only expected for the Ni$_{1.9}$Co$_{0.1}$MnGa sample, since only for Co-containing compositions the magnetic moment is not completely localised at the Mn sites [1]. Hence, other effects have to be taken into account, such as a transfer of moment and itinerant magnetism effects.
Properties of the martensitic transition

The large temperature ranges, over which the transitions occur, and the large hysteresis, are most likely caused by the polycrystalline nature of the samples. Inner strains at grain and domain boundaries can alter the transition temperature locally and produce constraints for the reverse transformation. In addition spatial composition fluctuations can occur. Several precautions were undertaken to eliminate these effects, such as repeated re-melting of the sample ingots and annealing. The high success of the annealing is displayed in section 4.8.1. However, the above-mentioned effects can still influence the properties of the martensitic transition.

As shown by Brown et. al. [15] the martensitic phase transition in NbMnGa is driven by a band Jahn-Teller effect. The transformation is cubic-to-tetragonal, with c/a = 0.94 in the tetragonal phase. This transformation broadens the conduction band extending towards the c-axis ($d_c$), and decreases the density of states in this band. According to Fujii et. al. [16] the density of states has a peak near the Fermi energy for NbMnGa. This peak makes the band Jahn-Teller distortion for the martensitic transition more effective. Hurd [17] observed a shift of the Fermi energy towards higher energies in the system Ni$_2$MnX, where X follows the sequence In → Sn → Sb, due to the increased conduction electron density, leaving the above-mentioned peak occupied below the Fermi energy.

While Ni$_2$MnGa$_{0.95}$In$_{0.05}$ has approximately the same transition temperature as Ni$_2$MnGa, Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ has a much lower transition temperature. This indicates, Ni$_2$MnGa$_{0.95}$In$_{0.05}$ having a band structure and Fermi energy comparable to the properties of Ni$_2$MnGa. By substituting In by Sn the electron density increases and the Fermi energy is shifted away from the peak in the band structure, making the Jahn-Teller distortion less effective, resulting in a lower transition temperature. The observed trend is in good agreement with the work done by Bargawi [18], who observed a linear dependence between transition temperature and the degree of substitution for Ga → In and Ga → Sn in Ni$_2$MnGa. $T_M$ decreased twice as fast for Ni$_2$MnGa$_{1-x}$Sn$_x$ than for Ni$_2$MnGa$_{1-x}$In$_x$ with increasing substitution x.

Similar effects are probably responsible for the decreasing transition temperature for Ni$_{1.9}$Co$_{0.1}$MnGa → Ni$_{1.9}$Cu$_{0.1}$MnGa.

Recapitulating, it can be stated, that the obtained results strongly suggest the conduction electron density being the dominant factor for the alteration of the magnetic properties and the properties of the martensitic phase transition in the materials investigated.
5.6 References

Chapter 6: Dilatometry measurements

6 Dilatometry measurements

One of the properties, which describe a material's microscopic structure, is its lattice parameter. This microscopic property is related to the macroscopic sample length. Changes in the sample length may be caused by a change in temperature (thermal expansion) or a change in an applied magnetic field (magnetostriction). These changes can be observed by using a dilatometer. Dilatometers with the best resolution \( dL/L_0 \) are based on the three terminal capacitance technique. For this system a resolution of the order of \( dL/L_0 = 10^{-10} \) can be achieved. Other techniques, such as optical methods \( (dL/L_0 = 10^{-7} - 10^{-8}) \), X-ray diffraction methods \( (dL/L_0 = 10^{-6}) \) or inductive methods \( (dL/L_0 = 10^{-6}) \), provide more limited resolutions [1].

The dilatometer used in the study reported here was designed, calibrated and tested by Jonathan W. Taylor during his PhD work at the Physics Department of Loughborough University. In the present thesis only the essential details of the dilatometry system are given. Further details can be obtained from Jonathan W. Taylor's thesis [2].

6.1 Theory of Thermal Expansion

The inter-atomic potential of atoms in a crystal lattice consists of various contributions, such as the mutual repulsion of the positive ion cores, the screening of the cores by the electrons and the influence of the formation and occupation of the energy bands.

For \( T > 0K \) the atoms vibrate around their equilibrium positions and the potential can be developed in a power series around the equilibrium positions. It can be shown, that a harmonic approximation leads to zero thermal expansion at all temperatures [3], which of course is not consistent with observations. Therefore, at least the cubic term in the series has to be taken into account. This term describes the anharmonicity of the atomic vibrations and leads to non-zero thermal expansion. However, a more general approach arises from thermodynamics. The equilibrium state of the system is defined by its minimum free energy. The free energy consists of various contributions, which include the static lattice, lattice vibrations (phonons), electrons, magnetic ions and other degrees of freedom, which lead to martensitic phase transformations. The last aspect is the central point in this thesis, and its theory was already discussed in Chapter 2.
In thermodynamics the linear thermal expansion coefficient can be described as

\[ a = \left( \frac{\partial \ln(L)}{\partial T} \right)_p = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_p \]  

(6.1)

Another common definition is

\[ a^* = \frac{1}{L_0} \left( \frac{\partial L}{\partial T} \right)_p \]  

(6.2)

where \( L_0 \) is a reference length at some reference temperature (usually room temperature).

In this thesis, definition (6.2) will be used, and \( L_0 \) will be the reference sample length at room temperature. In addition the strain parameter

\[ \eta = \frac{dL}{L_0} \]  

(6.3)

will be used as indicator for the transition behaviour.

The linear thermal expansion coefficient can be written as

\[ a^* = \frac{\partial \eta}{\partial T} \]  

(6.4)

The most commonly used thermodynamic approach is the Debye theory, which can be applied to thermal expansion and to specific heat. Although the model is rather simple, it can describe the behaviour of a wide range of materials quite accurately. The following explanations are based on [3].

The central assumption of the Debye theory is a linear dependence of the phonon frequency on the wave vector with a maximum cut-off frequency \( \omega_D \). With this cut-off frequency the Debye temperature can be defined as

\[ \Theta_D = \frac{\hbar \cdot \omega_D}{k_B} \]  

(6.5)

In this model, the Debye frequency and the Debye temperature are properties of the material and does not depend on temperature. The energy of the phonons follows a Planck black body radiation law.
The specific heat determined by this model is given as

\[ c_v(T) = 9 \cdot n \cdot k_B \cdot \left( \frac{T}{\Theta_D} \right)^3 \cdot \int_0^{\Theta_D/T} x^4 \cdot e^x \cdot \frac{dx}{(e^x - 1)^2}, \]  
(6.6)

with a low-temperature relation, valid for \( T < \Theta_D/10 \)

\[ c_v(T) = \frac{12 \cdot \pi^4}{5} \cdot n \cdot k_B \cdot \left( \frac{T}{\Theta_D} \right)^3, \]  
(6.7)

and a high-temperature (\( T \gg \Theta_D \)) limit equal to the classic Dulong-Petit law

\[ c_v(T) = 3 \cdot n \cdot k_B. \]  
(6.8)

The Debye model of the thermal expansion is an extension of the specific heat description and uses the relations deduced for the specific heat. In this model, two additional parameters determine the thermal expansion coefficient: the bulk modulus \( B \) and the Grüneneisen parameter \( \gamma \).

The bulk modulus \( B \) represents the inverse compressibility, and is defined as

\[ B = -V \cdot \frac{\partial P}{\partial V}, \]  
(6.9)

where \( P \) is the pressure and \( V \) the volume of the system. It is only weakly temperature dependent.

The Grüneneisen parameter \( \gamma_{ks} \) for one phonon mode, described by the wavevector \( k \) and the polarisation \( s \), can be defined as the change in the phonon spectrum in response to a volume change

\[ \gamma_{ks} = -\frac{V}{\omega_s(k)} \cdot \frac{\partial \omega_s(k)}{\partial V}. \]  
(6.10)

The overall Grüneneisen parameter \( \gamma \) can now be defined as the weighted average of all contributions of the different modes

\[ \gamma = \frac{\sum_{k,s} \gamma_{ks} \cdot c_{ns}(k)}{\sum_{k,s} c_{ns}(k)}. \]  
(6.11)

The Grüneneisen parameter can be interpreted to be a measure of the anharmonicity of the vibrational modes in the crystal. Thus, the thermal expansion coefficient described by the Debye model becomes

\[ \alpha = \frac{\gamma \cdot c_v}{3 \cdot B}. \]  
(6.12)
In real solids, the Grüneisen parameter depends on the actual phonon distribution, and thus on the temperature. However, assuming the Grüneisen parameter $\gamma$ and the bulk modulus $B$ depend only weakly on temperature, the general temperature dependence of the thermal expansion coefficient is expected to be similar to the specific heat, with the limits presented in eq. (6.7) and eq. (6.8).

For metals, eq. (6.12) must be modified to include the electronic contribution

$$\alpha = \frac{1}{3 \cdot B} \left( \gamma \cdot c_v^{\text{ion}} + \frac{2}{3} \cdot c_v^{\text{el}} \right).$$

(6.13)

The electronic contribution is small, and is only observable at low temperatures ($T \leq 10K$), where the ionic and the electronic contributions are of the same order. Within the scope of this thesis, no measurements were performed in this temperature range.

### 6.2 Theory of Magnetostriction

In general, it can be distinguished between external and internal variables. External variables, like temperature, external magnetic field and external stress, are fixed by the experimental conditions. Internal variables are degrees of freedom of the system, such as magnetisation and internal strain. The free energy of a system includes contributions of both types of variables. A change in an external variable will cause a response of the system, in order to minimise the modified free energy. This response will be realised by changing one or more internal variables.

Within the scope of this thesis, different phenomena were observed. The response of the magnetisation depending on temperature and external magnetic field was already described in Chapter 5. The response of the internal strain depending on temperature is called thermal expansion and is described in detail in Section 6.1. The response of the internal strain depending on an external magnetic field is called magnetostriction.
6.3 The Dilatometry System

The dilatometer consists of:

- A three-terminal capacitance bridge system described in section 6.6.3.
- A 7T superconducting solenoid with a variable temperature insert (VTI) for the temperature range between 1.5K and 300K, and a sample stick. The cryomagnet was built by Oxford Instruments™, who also provided a 60A superconducting magnet power supply. The temperature in the VTI is controlled by an Oxford Instruments™ 3120 temperature controller.
- A Lakeshore, model 340, cryogenic temperature controller is used to fix the sample temperature. The three-term temperature control was optimised by Jonathan W. Taylor [2].
- Remote control via a PC controlled IEEE 488.2 interface bus and a 96-channel ISA digital (TTL) I/O card.
- A vacuum system.

For further details see the thesis by Jonathan W. Taylor [2].

6.4 Types of Dilatometers

There are two different techniques to measure the dilatation of a sample: either measuring the length change directly by using an absolute dilatometer (for instance, with interferometric methods), or by measuring the dilatation of the sample relative to the sample environment (sample cell) and eliminate the expansion effect of the sample cell afterwards.

The use of a relative dilatometer has two major advantages compared with an absolute dilatometer: the heating and the thermal isolation are much easier to realise. In addition, relative dilatometers allow a greater flexibility of sample size and shape [2]. On the other hand, a relative dilatometer must be accurately calibrated. Usually a relative dilatometer is made of one specific, well-characterised material to eliminate differential expansion arising from the use of different materials. The data for the expansion of the sample cell's material must be available. These data can be parameterised using a polynomial fit and used in the data analysis routine. Measuring the thermal expansion of a sample, which is made of the same material as the sample cell, should lead to no signal at all.
6.5 Temperature Stability

The three-term temperature control consists of a proportional term, an integral term and a differential term to control the output of the heater. The temperature approaches the set temperature in damped oscillating time dependence. The 3 parameters of the different controller terms determine the oscillation period, the time constant of the damping, and hence the temperature stability behaviour.

![Proportional term only](image1)

**Figure 6.1: Proportional term only**

![Proportional and integral term](image2)

**Figure 6.2: Proportional and integral term**

![Proportional, integral and differential term](image3)

**Figure 6.3: Proportional, integral and differential term**

The temperature stability is of major importance for magnetostriction measurements only, when the field dependence of the strain is studied for a fixed temperature. For these measurements, a strict distinction between temperature-induced and field-induced effects is needed.

The measurements were performed by ramping the field from 0T up to 6.5T and down to 0T again. For the magnetostriction measurements of the single crystal in the (100) orientation the temperature showed dependencies like those displayed in Figure 6.4. For the measurements in the (110) orientation the temperature was stabilised to a higher degree, with dependencies like those displayed in Figure 6.5.
Chapter 6: Dilatometry measurements

Figure 6.4: Temperature dependence of the field scans at 197K, (100) orientation

Figure 6.5: Temperature dependence of the field scans at 197K, (100) orientation
6.6 Capacitance Systems

6.6.1 Theory

Theoretical arguments in this section follow the work done by Pott [4].

In general, the capacitance of a capacitor is determined by the equation:

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{A}{d} \]  

\( (6.14) \)

For circular capacitor plates eq. (6.14) is equal to

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{d}. \]  

\( (6.15) \)

\( \varepsilon_0 \) is the dielectric constant, \( \varepsilon_r \) is the relative permittivity of the material between the plates, \( d \) is the electrode separation of the two capacitor plates and \( r \) their radius.

Differentiating this equation with respect to the electrode separation leads to

\[ \frac{\delta C}{\delta d} = -\varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{d^2}. \]  

\( (6.16) \)

Thus, for small electrode separations a given sample elongation results in a larger (and more accurately detectable) capacitance change, than by using a large electrode separation. This leads to an increased accuracy in the determination of length changes.

Some corrections for this ideal capacitor have to be considered:

1) At the edges of the capacitor plates, the electric field becomes inhomogeneous.

Grounded guard rings are required to minimise this effect. Due to the guard rings, the formula for the capacitance has to be refined. The new formula is:

\[ C = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{d} \left[ 1 + \frac{\varepsilon_r \cdot d}{\varepsilon_r \cdot d + 0.22 \cdot \frac{w}{r}} \right]. \]  

\( (6.17) \)

with \( \varepsilon_r \) being the relative permittivity of the insulation space between the guard ring and the plate, and \( w \) the annular separation between the electrode and the guard ring.

This formula considers only terms of the order of \( w/r \). Since this equation varies only weakly with \( d \), the correction can be treated as a constant \( \zeta \).
2) The plates can be tilted or have a rough surface. In this case, the plate separation is no longer well defined, but varies in the interval \([d-a, d+a]\). In this case, \(d\) can be calculated as

\[
d = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{C_{\text{exp}}} \left[ 1 + \left( \frac{C_{\text{exp}}}{C_{\text{max}}} \right)^2 \right],
\]  

(6.18)

where \(C_{\text{max}} = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{a}\).

\[
C_{\text{max}} = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot r^2}{a}.
\]  

(6.19)

is the maximum capacitance, when the plates are almost closed.

3) Since the capacitor plates expand as the temperature increases, the plate’s radius, and therefore the effective plate area changes. This is accompanied by a change in capacitance. Knowing the thermal expansion data of the plate’s material, this effect can be corrected. The revised formula for the plate separation is

\[
d = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot (r_0 - \Delta r(T))^2}{C_{\text{exp}}},
\]  

(6.20)

4) Since the dilatometer is of a relative type, the dilatation of the sample cell must be known and taken into account for the data analysis. Standard data for the sample cell’s material must be available.

Consideration of all these corrections leads to the formula

\[
d = \varepsilon_0 \cdot \varepsilon_r \cdot \frac{\pi \cdot (r_0 - \Delta r(T))^2}{C_{\text{exp}}} \cdot \zeta \left[ 1 + \left( \frac{C_{\text{exp}}}{C_{\text{max}}} \right)^2 \right],
\]  

(6.21)

where all contributions can be measured and calculated.
6.6.2 Experiment
Experimental details are taken from the thesis by Jonathan W. Taylor [2].
The dilatometer's sample cell and the capacitor plates are made of High Conductivity Oxygen Free Copper (HCOF Cu). This material was chosen for two reasons:
- Its high thermal conductivity improves the temperature stability of the system.
- Established standard calibration data, provided by Kroeger & Swenson [5], are available.

The calibration of the system was performed with a sample taken from the same batch of HCOF Cu, from which the sample cell was made. Therefore, the relative dilatation to the sample cell should be zero. Thus, any measured dilatation arises from the contributions of non-copper constituents. The observed data are consistent with Stycast 1285GT epoxy resin (which was used to produce the guard-ringed lower electrode) thermal expansion data, as measured by Swenson [6].

The standard data, provided by Kroeger and Swenson [5], were fitted by a 7th order polynomial. The coefficients obtained in the fit are used to analyse the raw experimental data and to obtain the absolute sample dilatation.

Some experimental details:

1) The electrode separations used are of the order of 200 to 300 μm only.

2) An annular guard ring around the negatively charged electrode reduces fringing effects. The parameters are: \( w = 0.24 \text{ mm}, \epsilon_s = 6.3 \) (for Stycast epoxy at 1000 Hz), \( r = 10 \text{ mm} \). For a typical electrode separation of \( d = 200 \text{ μm} \) the correction factor is \( \zeta = 1.023 \), equal to a correction of 2.3 % (eq.(6.17)).

3) The maximum capacitance was measured to be \( C_{\text{max}} = 120 \text{ pF} \). For a typical experimental capacitance \( C_{\text{exp}} = 10 \text{ pF} \) the tilting correction term is of the order of 0.7 % (eq.(6.18)).

4) Evaluating the standard data by Kroeger and Swenson the correction for the plate's expansion can be calculated. The biggest contribution occurs at low temperatures. For \( T = 1.5K \) the correction is of the order of 0.7 % (eq.(6.20)).

All the above-mentioned corrections are included in the data analysis routine, which is part of the data acquisition program written by Jonathan W. Taylor [2].
6.6.3 The Transformer Ratio Arm Bridge and the Three Terminal Capacitance Technique

These techniques were developed and improved by Thompson in the early 1960’s. It allows measuring capacitances with a high precision. A simple transformer ratio arm bridge is analogous to a Wheatstone bridge. A variable capacitance is compared with the capacitance, which is to measure. The known capacitor is tuned until the bridge is balanced. Unfortunately, the accuracy achievable with this system is insufficient (usually not better than 0.1 %). The transformer ratio arm bridge increases the sensitivity immensely. It consists of a primary coil and two secondary coils, one exciting the standard part of the bridge, the other exciting the experimental arm. The bridge can be balanced by a tuneable capacitor. This capacitor bank (a 1616 Precision Capacitance Bridge by General Radio™) provides capacitances up to 90 pF with an accuracy of 1aF. The balancing is either done manually or by an auto-balancing routine included in the data acquisition program by Jonathan W. Taylor [2]. The zero position is detected by the use of a lock-in amplifier SR 510 manufactured by Stanford Research Systems™.

6.7 Properties of Dilatometry Specimen

Table 6.1: Properties of dilatometry samples

<table>
<thead>
<tr>
<th>#</th>
<th>Sample</th>
<th>Sample length</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni₂MnGa (110) orientation</td>
<td>5.3 mm</td>
</tr>
<tr>
<td>2</td>
<td>Ni₂MnGa (100) orientation</td>
<td>4.25 mm</td>
</tr>
<tr>
<td>3</td>
<td>Ni₂MnGa₀.₉₅In₀.₀₅ (rod-shaped)</td>
<td>18.8 mm</td>
</tr>
<tr>
<td>4</td>
<td>Ni₂MnGa₀.₉₅In₀.₀₅ (bar-shaped)</td>
<td>4.0 mm</td>
</tr>
<tr>
<td>5</td>
<td>Ni₂MnGa₀.₉₅Sn₀.₀₅</td>
<td>29.5 mm</td>
</tr>
</tbody>
</table>

Samples #1, #2 and #4 are specimen in the form of a parallelepiped with the end faces cut parallel. Sample #3 and #5 are rod-shaped specimen with circular cross section and parallel end faces.

Since the transformation is expected to consist of 2 successive shears along the (110) directions of the cubic lattice, the dependence of the transition properties on the orientation is investigated for the single-crystalline specimen. The observation axis is along the shear direction for the (110) orientation (sample #1), and perpendicular or with an angle of 45° to the shear direction for the (100) orientation (sample #2).
6.8 Dilatometry Measurements: Single-crystalline specimen

6.8.1 \textit{Ni}_2\textit{MnGa} single crystal, (110) orientation

The system can be run in two modes:

- Controlled: - for heating only
  - temperature of sample and sample cell are stabilised, before a measurement is carried out
  - advantage: system is definitely in equilibrium
  - disadvantages: no dynamics observable, takes a lot of time

- Ramped: - for heating and cooling
  - the system will be heated or cooled, while the measurements are taken
  - for cooling simply the heaters are switched off and the system cools down naturally
  - advantages: reveals dynamics, small temperature steps, fast measurement
  - disadvantage: system not necessarily in equilibrium

The ramping mode has another disadvantage. Since the temperature sensors, as well as the heaters, are at top and bottom of the sample cell, and not attached to the sample itself, a high temperature gradient between top and bottom of the sample cell can occur (the temperature given refers to the bottom sensor), especially for fast ramping. This creates a temperature profile over the sample too, decreasing the reliability of the data. Since the sample is much smaller than the sample cell, the temperature gradient across the sample is smaller than the temperature gradient across the sample cell. The influence of this temperature gradient on measurements, as well as its shape and dependence on the temperature history, was not investigated in the past.

In the controlled mode, the sample cell is stabilised with a temperature gradient across the sample cell of 10K. For the measurements described here the cell gradient was kept as small as possible. All measurements with a cell gradient larger than 15K were discarded.
Table 6.2: Parameters for all dilatometry runs on Ni$_2$MnGa, (110) orientation

<table>
<thead>
<tr>
<th>Run</th>
<th>Type</th>
<th>Transition temperature</th>
<th>Maximum cell gradient</th>
<th>Cell gradient at transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Controlled heating</td>
<td>197K</td>
<td>28K</td>
<td>23K</td>
</tr>
<tr>
<td>2</td>
<td>Ramped heating</td>
<td>207K</td>
<td>37K</td>
<td>29K</td>
</tr>
<tr>
<td>3</td>
<td>Ramped heating</td>
<td>201.4K</td>
<td>11K</td>
<td>6.6K</td>
</tr>
<tr>
<td>4</td>
<td>Controlled heating</td>
<td>201.8K</td>
<td>14K</td>
<td>12K</td>
</tr>
<tr>
<td>5</td>
<td>Natural cooling</td>
<td>194.5K</td>
<td>2.2K</td>
<td>2K</td>
</tr>
<tr>
<td>6</td>
<td>Ramped heating</td>
<td>200.8K</td>
<td>±2.3K</td>
<td>±0.05K</td>
</tr>
</tbody>
</table>

Table 6.2 verifies the influence of the cell gradient on the transition temperature. There is an obvious increase of the transition temperature with increasing cell gradient. It indicates the average temperature of the sample being different from the temperature displayed. This justifies discarding the data with high cell gradients. Further on, run 1 and run 2 will be neglected. The strain parameter $\eta = \frac{dL}{L_0}$ will be taken as an indicator for the behaviour of the system.

Figure 6.6: Strain parameters for different runs for Ni$_2$MnGa, (110) orientation
Comparing the different heating runs, one aspect is remarkable: the general appearance of the curves does not depend on the run being controlled or ramped (especially comparing run 3 and run 4). Therefore, mainly ramped measurements were subsequently performed. Later in this section, the results of the different runs will be discussed in detail.

Several details can be seen in Figure 6.6, characterising the temperature behaviour of the strain:

- Precursor: At temperatures close to the transition temperature, for heating at temperatures slightly below $T_M$, for cooling slightly above $T_M$, a small decrease of the strain can be observed over a small temperature range. This is probably caused by the lattice softening, suggested by Murray [10].
- Jump: The strain can change rapidly during the transition, with a time scale shorter than the detection time.
- Step: While the temperature passes through the transition, the strain can change gradually without showing jumps. The temperature dependence can change during the transition, being nearly constant for certain temperatures, showing kinks or similar aspects. This phenomenon either suggests the existence of metastable intermediate states, or is a sign for a stepwise slip of the lattice planes.
- Overshoot: At temperatures close to the transition temperature, for heating at temperatures slightly above $T_M$, for cooling slightly below $T_M$, the strain can establish an unstable state for a short time, before relaxing back to a stable value.

In Table 6.3 selected characteristics of the different runs on Ni$_2$MnGa in the (110) orientation are displayed.

<table>
<thead>
<tr>
<th>Run</th>
<th>Transition temperature</th>
<th>Transition range</th>
<th>Change in strain (% of strain change)</th>
<th>Do steps exist? Number</th>
<th>Do precursors exist? Length, depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>201.4K</td>
<td>3.0K</td>
<td>1.020 %</td>
<td>Yes, 2 (18.6 %, 57.2 %)</td>
<td>Yes, 1.24K, 0.065 %</td>
</tr>
<tr>
<td>4</td>
<td>201.8K</td>
<td>3.6K</td>
<td>0.925 %</td>
<td>Yes, 2 (45.8 %, 78.9 %)</td>
<td>Yes, 1.37K, 0.0566 %</td>
</tr>
<tr>
<td>5</td>
<td>194.5K</td>
<td>1.3K</td>
<td>0.860 %</td>
<td>Yes, 1 (38.9 %)</td>
<td>No, but overshoot</td>
</tr>
<tr>
<td>6</td>
<td>200.8K</td>
<td>2.9K</td>
<td>0.265 %</td>
<td>Yes, 1 (83.3 %)</td>
<td>No</td>
</tr>
</tbody>
</table>
Figure 6.7: Strain in run 3, (110) orientation

Figure 6.8: Strain in run 4, (110) orientation
Figure 6.9: Strain in run 5, (110) orientation

Figure 6.10: Strain in run 6, (110) orientation
As mentioned above, the general behaviour does not seem to depend strongly on the type of data acquisition technique. Run 3 and run 4 appear similar, with the same order of strain change and a comparable precursor effect. In comparison, run 3 and run 6 are looking quite different: run 6 has a smaller strain change and does not show any precursor effects. The only cooling run (run 5) shows a pronounced step. The transition overshoots first, and relaxes back to a metastable state afterwards. The strain remains in this state over a range of almost 0.9K, before transforming into the finally stable state. This transition again overshoots. Smaller, less pronounced steps are visible in all graphs, demonstrating either the transformation of individual martensitic domains or the incomplete and stepwise slip of the lattice planes. The strain values of the steps vary between the different runs. Therefore it can be concluded, that the shears have to overcome an activation energy, which depends on the thermal history of the sample. For different runs, the strain does not recover the values far away from the transition, probably caused by incomplete transformation.

6.8.2 Ni₂MnGa single crystal, (100) orientation

Table 6.4: Parameters for all dilatometry runs on Ni₂MnGa, (100) orientation

<table>
<thead>
<tr>
<th>Run</th>
<th>Type</th>
<th>Transition temperature</th>
<th>Maximum cell gradient</th>
<th>Cell gradient at transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural cooling</td>
<td>192.2K</td>
<td>5K</td>
<td>4.2K</td>
</tr>
<tr>
<td>2</td>
<td>Controlled heating</td>
<td>198.5±0.5K</td>
<td>27K</td>
<td>27K</td>
</tr>
<tr>
<td>3</td>
<td>Ramped heating</td>
<td>198.35K</td>
<td>26K</td>
<td>23K</td>
</tr>
<tr>
<td>4</td>
<td>Ramped heating</td>
<td>201.38K</td>
<td>4.4K</td>
<td>4.4K</td>
</tr>
<tr>
<td>5</td>
<td>Natural cooling</td>
<td>192.25K</td>
<td>3.4K</td>
<td>2.6K</td>
</tr>
<tr>
<td>6</td>
<td>Natural cooling</td>
<td>192K</td>
<td>9K</td>
<td>8K</td>
</tr>
<tr>
<td>7</td>
<td>Controlled heating</td>
<td>197.55±0.05K</td>
<td>10K</td>
<td>9.6K</td>
</tr>
<tr>
<td>8</td>
<td>Ramped heating</td>
<td>196.91K</td>
<td>2.2K</td>
<td>1.1K</td>
</tr>
</tbody>
</table>

Table 6.4 indicates again the dependence of the transition temperature on the cell gradient. The only exception is run 4. Run 2 and run 3 have high cell gradients and will be neglected further on.
Chapter 6: Dilatometry measurements

Figure 6.11: Strain for different runs on Ni$_2$MnGa, (100) orientation (heating)

Due to a unique fault in the bridge auto-balancing routine, the absolute values for the strain in run 7 were written wrong.

Figure 6.12: Strain for different runs on Ni$_2$MnGa, (100) orientation (cooling)
Table 6.5: Parameters for selected dilatometry runs on Ni$_2$MnGa, (100) orientation

<table>
<thead>
<tr>
<th>Run</th>
<th>Transition temperature</th>
<th>Transition range</th>
<th>Change in strain</th>
<th>Do steps exist? Number (% of strain change)</th>
<th>Do precursors exist? Length, depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>192.2K</td>
<td>0.25K</td>
<td>0.505 %</td>
<td>Yes, 1 (58 %)</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>201.38K</td>
<td>0.01K</td>
<td>0.840 %</td>
<td>No</td>
<td>No, but overshoot</td>
</tr>
<tr>
<td>5</td>
<td>192.25K</td>
<td>0.26K</td>
<td>0.600 %</td>
<td>Yes, 1 (51.1 %)</td>
<td>No</td>
</tr>
<tr>
<td>6</td>
<td>192K</td>
<td>0.35K</td>
<td>0.620 %</td>
<td>Yes, 2 (68.4 %, 87.6 %)</td>
<td>No</td>
</tr>
<tr>
<td>8</td>
<td>196.91K</td>
<td>0.01K</td>
<td>0.845 %</td>
<td>No</td>
<td>Yes, 0.55K, 0.0050 %</td>
</tr>
</tbody>
</table>

Figure 6.13: Strain in run 4, (100) orientation
Figure 6.14: Strain in run 8, (100) orientation

Figure 6.15: Strain in run 1, (100) orientation
Figure 6.16: Strain in run 5, (100) orientation

Figure 6.17: Strain in run 6, (100) orientation
A few characteristics of the runs in (100) orientation:

- There is a significant difference between the heating and cooling measurements concerning the transition width. This width is more than an order of magnitude larger for cooling.
- The changes in strain are all of the same order, with the heating data always slightly higher than for the cooling runs.
- Precursor effects are visible for heating only.
- Steps occur for cooling only, but with different magnitudes.

In comparison with the (110) orientation data, the following points are worth mentioning:

- The transition width is one to two orders of magnitude larger for the (110) orientation than it is for the (100) orientation.
- The strain changes within existing precursors are one order of magnitude larger (and occur over a slightly larger temperature interval) for the (110) orientation.
- The observed steps in the transition are less pronounced for the (100) orientation.
- The change in strain is usually smaller for cooling data than for heating data.
- Only two runs show overshoots (run 5 in (110) orientation [cooling] and run 3 in (100) orientation [heating]). In both cases, the actual transitions are faster than the data acquisition. The existence of overshooting is expected to be universal, but its detection depends on the measuring speed and the relaxation time.
6.9 Discussion: Dilatometry of single-crystalline specimen

For single-crystalline specimen of shape-memory alloys, dilatometry measurements provide several advantages, such as the investigation of the transformation dynamics. The maximum achievable strain can be calculated from the change in the lattice parameter: 

\[ \Delta a_c = 5.825 \text{ Å (cubic phase)}, \ a_t = 5.920 \text{ Å and } c_t = 5.566 \text{ Å (tetragonal phase)}. \]

For the (110) direction the maximum achievable strain is 

\[ \frac{dL/L_0}{\Delta a_c} = \frac{\sqrt{a_t^2 + c_t^2}}{(\sqrt{2} \cdot a_c)} - 1 = -1.36\%. \]

The maximum achievable strain along the initial cubic axes (100) orientation is 

\[ \frac{dL/L_0}{\Delta a_c} = \frac{c_t}{a_c} - 1 = -4.45\%. \]

This maximum can be achieved by measuring an untwinned single crystal with the c-axis of the martensitic phase along the observation axis. With a tetragonal a-axis along the observation axis a strain of +1.63% is achievable. Untwinned specimen can be investigated using stress-biased samples [7]. As stress induces a partial martensitic transformation of the sample, as shown by [10], this technique has serious drawbacks. The maximum strain observed in the presented measurements was 1.02%. This value is smaller than the maximum achievable value, due to twinning effects. Following the model by Batterman & Bateman [14], the martensitic transformation can be described as a sequence of 2 shears along different (110) directions of the austenitic cubic structure, resulting in a tetragonal structure. This structure can be described also as shrinkage along one of the cubic axes (which becomes the c-axis of the tetragonal structure) and an elongation along the two remaining cubic axes (becoming the a-axes of the tetragonal structure), with c/a=0.94 [8]. Since all (110) orientations are equal, in both cases, the formation of twins has to be taken into account.

The calculated maximum strain for the (100) orientations depends strongly on the orientation of the martensitic domains, including elongation and shrinkage, while the calculated maximum strain for the (110) orientations depends equally on both tetragonal lattice parameters. Hence, the impact of the twinning is much stronger for measurements along the cubic (100) axes than along the (110) directions. As the length change due to the transformation is larger for the (110) orientation than for the (100) orientation (even though the maximum achievable strain for the (110) orientation is smaller than for the (100) orientation), a strong twinning of the sample can be assumed.

This strong twinning can explain the observed steps too. A step occurs when a large domain transforms. Since the domain boundaries of one domain represent constraints for the transformation process of this domain, the domain surrounding influences the transition behaviour. Since these constraints differ for different domains, the domains are not expected to transform all at once. This explains the finite transition temperature range.
6.10 Dilatometry measurements: Polycrystalline specimen

6.10.1 Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ polycrystalline sample

According to previous measurements on Ni$_2$MnGa polycrystals [2][2], no pronounced steps were expected. Instead, a local minimum at the transition temperature or just a change in slope was observed ([2], [9]). This can be understood in terms of the atomic potential. In the cubic phase, the atomic potential is the same along all crystal axes. Hence, the linear thermal expansion coefficient $\alpha = \frac{\partial (dL/L_0)}{\partial T}$ is the same for all directions. The volume expansion coefficient $\beta = \frac{\partial (dV/V_0)}{\partial T}$ is simply $\beta = 3\alpha$. The martensitic transformation changes the atomic potential and establishes a preferred direction along the c-axis, which results in two different thermal expansion coefficients parallel ($\alpha_||$) and perpendicular ($\alpha_\perp$) to the c-axis. The measured thermal expansion coefficient is a mixture of $\alpha_||$ and $\alpha_\perp$, due to the polycrystalline nature of the specimen.

In the magnetisation measurements, described in section 5.4.1, a magnetic transition around 100K was found, which was thought to be a concomitant phenomenon to the structural transformation. Special attention was therefore paid on this region. Due to internal changes of parameters, data acquisition for heating cannot be performed continuously across the temperature of 100K. Separate data sets were taken below and above 100K. Since in the beginning of a measurement the heater has to settle to a constant heat output, the system is not in equilibrium and the first data points have to be discarded. The data were obtained by measuring the linear thermal expansion along the axis of the rod.

Since no obvious features in the strain data (Figure 6.18, Figure 6.19) were visible, the derivative with respect to the temperature was calculated to reveal the above-mentioned change in slope. The derivatives are displayed in Figure 6.20 and Figure 6.21, for heating and cooling respectively. Due to the problems with data acquisition, the heating data around 100K are not continuous. However, no reproducible jumps were observed. The first data have to be discarded, due to the system not being in equilibrium. The two peaks in the derivative of the first cooling run are not reproduced in further measurements. The step at 154K occurs only in the derivatives of the cooling runs #2 and #3, but is not reproduced in run #1 or during heating. The area around 100K shows no signs of any transition.
Figure 6.18: Strain in heating runs for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$

Figure 6.19: Strain in cooling runs for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$
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Figure 6.20: Thermal derivative of the strain in heating runs for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$

Figure 6.21: Thermal derivative of the strain in cooling runs for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$
6.10.2 \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) polycrystalline rod-shaped sample

In the magnetisation measurements, described in section 5.4.2, a transition around 170K was found, which is probably a consequence of the structural phase transformation.

The data were obtained measuring the linear thermal expansion along the axis of the rod.

A large number of measurements were performed, especially around the expected transition temperature of \( T = 170 \text{K} \). The obtained data are displayed in Figure 6.22 for heating and in Figure 6.23 for the cooling runs. These data show a smooth increase with temperature, without any obvious jumps, changes in slope or other remarkable features. In order to reveal these expected features, the derivative of the strain with respect to temperature was calculated. The results are shown in Figure 6.24 and Figure 6.25, for heating and cooling runs respectively. Like for the \( \text{Ni}_2\text{MnGa}_{0.95}\text{Sn}_{0.05} \) sample, the derivative data show irreproducible jumps, peaks and spikes. However, the general appearance is rather a smooth rise. No systematic, reproducible step, as would have been expected to appear at the martensitic transition temperature, is observed.

![Figure 6.22: Strain in heating runs for Ni2MnGa0.95In0.05 (rod-shaped specimen)](image-url)
Figure 6.23: Strain in cooling runs for $\text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05}$ (rod-shaped specimen)

Figure 6.24: Thermal derivative of the strain in heating runs for rod-shaped $\text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05}$ specimen
Figure 6.25: Thermal derivative of the strain in cooling runs for rod-shaped Ni$_2$MnGa$_{0.95}$In$_{0.05}$ specimen
6.10.3 Ni$_2$MnGa$_{0.95}$In$_{0.05}$, polycrystalline bar-shaped sample

At this point, characteristics about the preparation and the appearance of the samples have to be mentioned.

After melting the constituents to form an ingot, the ingot was placed on top of a water-cooled mould in the form of a hollow copper cylinder. On re-melting the ingot, the melt dropped in the mould and rapidly solidified. This solidification process is obviously fastest at the wall of the mould. On breaking one of the rods, it revealed some inner, star-like structure with characteristics of dendrite growth (Figure 6.26). Obviously there is a strong anisotropic structure in the sample.

![Figure 6.26: Sketch of the rod cross-section](image)

Since the martensitic transition did not leave any observable anomalies in the dilatometry results using the original rod-shaped specimens, it was decided to investigate the thermal expansion perpendicular to the rod axis, respectively along the axis of the star-like substructure. For this purpose, a small, bar-shaped sample was cut from the cross-section of the rod (Figure 6.27).

![Figure 6.27: Sketch of the bar-shaped sample](image)

Unfortunately, the cross-section of the rod has a diameter of only 6.3 mm. In order to get sufficiently large and flat end-faces, the length of the resulting sample was only 4 mm. This length is close to the limit of the dilatometer system. The data are therefore expected to contain some noise.
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Figure 6.28: Strain in heating runs for \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) (bar-shaped specimen)

Figure 6.29: Strain in cooling runs for \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) (bar-shaped specimen)

The strain data do not merge very closely, due to the small sample length. Some jumps occur, especially in the cooling run #1. These jumps are not reproduced in further measurements and are probably caused by the special sample design.
Nevertheless, a general change in slope can be seen. Further information can be obtained by plotting the derivative of the strain with respect to the temperature. The irreproducible jumps are causing unphysical spikes.

Figure 6.30: Thermal derivative of the strain in heating runs for bar-shaped \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) specimen

Figure 6.30a: Thermal derivative of the strain in heating runs for bar-shaped \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) specimen (detail)
Figure 6.31: Thermal derivative of the strain in cooling runs for bar-shaped \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) specimen

Figure 6.31a: Thermal derivative of the strain in cooling runs for bar-shaped \( \text{Ni}_2\text{MnGa}_{0.95}\text{In}_{0.05} \) specimen (detail)
30
28
SZ'
26
24...
~
22
b ..... 20
...
18
16
14
12
10

150
155
160
165
170
175
180
185
190
195
200

Figure 6.31b: Thermal derivative of the strain in cooling runs for bar-shaped
Ni$_2$MnGa$_{0.95}$In$_{0.05}$ specimen (detail, cleared from noise)

Even though the data of the derivatives are quite noisy, the existence of an increase in the
derivative around 175K is clearly visible. This temperature coincides with the transition
temperature observed by the magnetisation measurements, described in Chapter 5.4.2.
The temperature range over which the transition occurs is difficult to determine, due to the
noise. Nevertheless, it seems to be smaller than the width obtained in the magnetisation
measurements. The most remarkable aspect is the absence of any signs of hysteresis.
However, the transitions can be expected to have the same origin.

6.11 Discussion: Dilatometry of polycrystalline specimen

The martensitic transition for the bar-shaped Ni$_2$MnGa$_{0.95}$In$_{0.05}$ specimen is observed at
approximately the same temperature, as the previous magnetisation measurements suggest.
In general, the technique of thermal expansion measurements seems to have serious
drawbacks while investigating polycrystalline samples. It should not be used as the only
indicator to determine the properties of the martensitic transition of shape memory alloys.
The results strongly depend on the sample design. Verification using SQUID equipment is
highly recommended.
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6.12 Magnetostriction Measurements: Single-crystalline specimen

Two types of measurements were performed: temperature scans through the transition at various fields, and field scans at various temperatures close to the transition temperature. According to previous measurements, the magnetisation saturates in fields above 2T. Therefore, fields of 0T (no magnetisation), 1T (intermediate state) and 2T (saturation magnetisation) were chosen to perform temperature scans under applied magnetic fields.

6.12.1 Temperature scans, (110) orientation

The results are shown in Figure 6.32 and Figure 6.33, for heating and cooling. The magnetic field alters the transition temperature. The heating data suffer from uneven cell gradients and are therefore rather unreliable. As the cooling runs had all the same cell gradient, the observed small decrease of the transition temperature with increasing applied field is expected to be a real effect. The transition is quite broad (over a range of roughly 4K). This range is independent of the applied field. Hysteresis of approximately 7K is observed. Steps are observed in the heating data only, without showing any field dependence or reproducibility.

Figure 6.32: Temperature scans during heating, (110) orientation
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6.12.2 Temperature scans, (100) orientation

Figure 6.34: Temperature scans during heating, (100) orientation
The applied magnetic field alters the transition. Especially the temperature range, over which the transition occurs, is field dependent. While the transition is rather sharp for no applied field (in particular the heating data), it becomes broader with increasing field. No systematic shift of the transition temperature with applied field is observed. Since the cell gradients are comparable for all runs, the cell gradient does not provide an explanation. Distinct steps within the transition are observed with varying magnitudes.
6.12.3 Field scans, (110) orientation

The field scans were performed ramping the magnetic field from 0T up to 6.5T, and down to 0T again. During this ramping the measurements were taken in time intervals of approximately 4 seconds. The temperature scans were performed in a row, starting with the lowest temperature. The temperature stability for these measurements was already discussed in section 6.5. The calculated strain \( \frac{dL}{L_0} \) is based on the actual extension in comparison with the extension at 0T. \( L_0 \) is the sample length at room temperature. A positive strain indicates an elongation of the sample. The field scans were carried out at the following temperatures: 188K, 197K, 201K, 204K and 215K. The expected transition temperature is \( T \approx 200K - 206K \).

For a temperature of \( T=188K \) (Figure 6.36) the magnetostrictive behaviour is very distinct. Up- and down-sweep have the same characteristics. An overall elongation of the sample is observed, with a sharp maximum for fields around 0.3T.

At \( T = 197K \) (Figure 6.37) the magnetostrictive behaviour is similar to the 188K measurement. Both scans seem to be below the transition temperature. This is supported by the temperature scans, discussed in section 6.12.1. The magnitude of the maximum is slightly higher than for the 188K scan.

The scans at \( T = 201K \) (Figure 6.38) and \( T = 204K \) show roughly the same characteristics. Up- and down-sweep show in both cases significantly different behaviour. The effects in the 201K scan are of a higher magnitude than for the 204K scan.

The measurement at \( T = 215K \) (Figure 6.) shows only very small field dependence, nearly 2 orders of magnitude smaller than observed in the previous scans.
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Figure 6.36: Field scans at 188K, (110) orientation

Figure 6.37: Field scans at 197K, (110) orientation
Figure 6.38: Field scans at 201K, (110) orientation

Figure 6.39: Field scans at 204K, (110) orientation
Figure 6.40: Field scans at 215K, (110) orientation
6.12.4 Field scans, (100), orientation

The field scans were carried out at the following temperatures: 183K, 197K, 198K and 210K. The expected transition temperature is $T \approx 196.5K - 199K$.

A pronounced, reversible transition is observed for $T=183K$ (Figure 6.41), with the down-sweep transition being sharper than the up-sweep transition. Slight differences between the two runs are visible, probably caused by martensitic domain formation or due to hysteresis effects.

The largest observed transformation caused by applied fields, with a maximum sample elongation of almost 0.6%, is observed at $T = 197K$ (Figure 6.42). Kinks are visible in both sweeps, possibly indicating a step-wise slip of the lattice planes during the martensitic transformation. Only slight oscillations can be seen, indicating a very small influence of the temperature oscillations on the behaviour. Therefore, the transition can be seen as being purely field-induced. The shape is similar to the 183K scan. This indicates that this scan is still slightly below the transition temperature.

For the last scans (at $T = 198K$, displayed in Figure 6.43, and at $T = 210K$, displayed in Figure 6.44) a transition is not obvious. The oscillations in the up-sweep data are caused by the above-mentioned temperature oscillations. The small increase at low fields for the down-sweep may be an indication for magnetostrictive effects.

The observed data suggest a sample shrinkage for measurements in the austenitic phase, and a sample elongation in the martensitic phase.
Figure 6.41: Field scans at 183K, (100) orientation

Figure 6.42: Field scans at 197K, (100) orientation
Figure 6.43: Field scans at 198K, (100) orientation

Figure 6.44: Field scans at 210K, (100) orientation
6.13 Discussion Magnetostriction

Knowing the lattice parameters of the different phases, the maximum achievable strain can be calculated: \[ \frac{dL}{L_0} \big|_{\text{max}} = \alpha / c_{-1} = -6.36\% \] for the tetragonal phase. This refers to an untwinned specimen in the martensitic phase with one of its a-axes along the observation axis, being transformed into an untwinned martensitic specimen with its c-axis along the observation axis. Usually the observed strain will be much smaller, due to incomplete transformation and the existence of martensitic twins. For the cubic (austenitic) phase, only a negligible magnetostrictive strain is predicted.

From the present measurements, it can be estimated that magnetostrictive effects are most distinct at temperatures close to the transition temperature. The magnitude of the magnetostriction increases while the temperature approaches the transition temperature. The magnitude far away from the transition is higher in the martensitic phase than in the austenitic phase, as expected. Except for the highest temperatures (well within the cubic Heusler phase), all field scans show an elongation of the sample due to the applied magnetic field. To illustrate this behaviour, the maximum magnetostrictive strain as a function of the run temperature for each run is plotted in Figure 6.45 and Figure 6.46.

![Figure 6.45: Maximum strain vs. temperature for Ni$_2$MnGa, (110) orientation](image-url)
Figure 6.46: Maximum strain vs. temperature for Ni$_2$MnGa, (100) orientation

The magnetic hysteresis effects seem to be more distinct in the transition region too. There are qualitative differences concerning the field dependencies (shape and magnitude) between scans below and above the transition temperature. In the near-transition measurements of the (110) orientated crystal, the martensitic domains reorient during the down-sweep of the magnetic field. Close to the transition temperature the domain configuration seems to become very sensitive to external influences, supporting a lattice softening near the transition, as proposed by [10].

It has been shown previously ([11], [12]), that twin-boundary motion, driven by an applied magnetic field, results in magnetic-field-induced strains in ferromagnetic shape memory alloys by favouring domains with the magnetisation along the external field. This motion is caused by the Zeeman energy difference between adjacent twins. Typical time scales for boundary motions can be up to several hours, as reported by [13]. The data, which were obtained within the scope of this thesis, suggest an enhanced mobility of the twin boundaries in the vicinity of the martensitic transition temperature. In some cases (Figure 6.38, ), the boundary motion can even lead to the formation of a new zero-field configuration, with the free energy of the system reaching a new minimum.
Huge magnetostriction is apparently limited to the martensitic phase, and the close surrounding of the transition temperature, where the existence of twin boundaries is expected.

Another explanation for the strain enhancement around the transition temperature is the magnetic-field-induced martensitic transformation. Assuming, the transition temperature decreases with increasing field, as the temperature scans for the (110) orientation suggest, for temperatures near the transition an increasing magnetic field can induce a partial tetragonal-to-cubic transition by lowering the transition temperature below the actual temperature. In this case, the transition-induced change in the lattice parameters causes the observed magnetic-field-induced strains.
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6.14 References

Chapter 7: Conclusion

7 Conclusion

This study has been aimed at exploring the way in which the structural phase transition takes place in the ferromagnetic Heusler alloy Ni$_2$MnGa. For this purpose, parts of the constituents were replaced by other elements: Ni was partially substituted by Co or Cu, Ga was partially substituted by In or Sn. The measurements included structure determination by X-ray powder diffraction, magnetisation measurements using a SQUID, and dilatometry measurements. In addition, dilatometry measurements and magnetostriction measurements on stoichiometric Ni$_2$MnGa single crystals were performed.

The chemical and magnetic structure of Ni$_2$MnGa has been investigated in detail by other workers. It was confirmed that at room temperature Ni$_2$MnGa is highly ordered in the cubic L$_2^1$ Heusler structure with a lattice parameter of $a = 5.825$ Å. The alloy is ferromagnetic with a Curie temperature of $T_C = 376$K and a magnetic moment per formula unit $\mu_{00} = 4.17$ $\mu_B$. On cooling below $T_M = 202$K it undergoes a martensitic transformation from the cubic L$_2^1$ structure to a tetragonal phase with $a = 5.920$ Å and $c = 5.660$ Å.

Polycrystalline samples with compositions Ni$_2$MnGa$_{0.95}$In$_{0.05}$, Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$, Ni$_{1.9}$Co$_{0.1}$MnGa, Ni$_{1.9}$Cu$_{0.1}$MnGa and Ni$_{2.19}$Mn$_{0.81}$Ga were prepared by repeated re-melting in an argon arc furnace. The crystal structure of the Ni$_{2.19}$Mn$_{0.81}$Ga sample was found to be orthorhombic with lattice parameters $a = 6.108$ Å, $b = 5.802$ Å, $c = 5.542$ Å. The crystal structure of the other samples was found to be cubic Heusler L$_2^1$ structure, with lattice parameters as displayed in Table 4.1. The lattice parameters were found to be slightly higher than the reported value for Ni$_2$MnGa. This could be explained by the larger atomic radii of the substituents.

Magnetisation measurements carried out using a SQUID magnetometer within the temperature range from 5K to 350K and applied fields up to 5T on the polycrystalline samples indicated a ferromagnetically ordered state.

For the Ni$_{2.19}$Mn$_{0.81}$Ga specimen a Curie temperature of $T_C = 352$K was determined. Simultaneously signs of a structural phase transition at the same temperature were noticed, in agreement with previous research.

For the other samples, transitions in the magnetic behaviour were detected at temperatures below $T_M$(Ni$_2$MnGa) = 202K. For the Ni$_2$MnGa$_{0.95}$In$_{0.05}$ and the Ni$_{1.9}$Co$_{0.1}$MnGa samples, the detected transition occurred around $T_M \approx 175$K. For the Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$ and the
Ni$_{1.9}$Cu$_{0.1}$MnGa sample, the transition occurred around $T_M \approx 100$K. Since the most substantial difference between these two sets of materials is the higher electron density for the second one, where a huge decrease in the transition temperature is observed, a major impact of the electron density on the martensitic transition temperature can be concluded. The martensitic transition temperature is drastically lowered with increasing electron density.

The magnetic moment per formula unit for Ni$_{2.19}$Mn$_{0.81}$Ga ($\mu_{\text{eff}} = 3.076 \mu_B$) is approximately 78% of the magnetic moment per formula unit for the other samples ($\mu_{\text{eff}} = 3.917 - 3.989 \mu_B$). This reflects the strong localisation of magnetic moments on the Mn sites, as shown by previous investigations.

The dilatometry measurements of the polycrystalline samples verified the existence of the martensitic transition at $T_M \approx 170$K for Ni$_2$MnGa$_{0.95}$In$_{0.05}$, in good agreement with the magnetisation measurements. However, no transition was observed for Ni$_2$MnGa$_{0.95}$Sn$_{0.05}$. The observability of the martensitic transition for a polycrystalline sample, using a dilatometer depends strongly on the sample design and is highly sensitive on anisotropies in the sample.

The dilatometry properties of the single crystal specimen depend strongly on the orientation of the crystal with respect to the observation axis. The results of the dilatometry along the two orientations, (110) and (100) with respect to the high-temperature cubic Heusler phase, show significant differences in the transformation behaviour, stating the non-equivalence of these orientations during the martensitic transformation. This is in agreement with the two-shear-mechanism involving shears along the austenitic (110) direction. The effects of martensitic domain twinning were observed, resulting in a decrease of the measured strain change due to the transition for the (100) orientation in comparison to the (110) orientation, and explaining the occurrence of steps in the transition regions. The observed precursor effects can be explained with a lattice softening in the vicinity of the transition, as proposed previously.

This lattice softening, resulting in an enhanced mobility of twin boundaries, is supported by magnetostriction measurements on the same single crystals, where a huge increase of the maximum magnetic-field-induced strain close to the transition is noticed.
Summarising it can be seen, that the conduction electron density is the dominant factor influencing the martensitic transition in Ni$_2$MnGa system. The investigation of the properties using a SQUID magnetometer was found to be most effective.

Further doping experiments and pressure-dependent magnetisation measurements are recommended for a more detailed study. In addition, the determination of electron density and band structure by precise Hall effect measurements and spectroscopy or inelastic neutron scattering will provide additional information.