Magnetic materials with tunable thermal, electrical, and dynamic properties

An experimental study of magnetocaloric, multiferroic, and spin-glass materials

Matthias Hudl
Abstract

This thesis concerns and combines the results of experimental studies of magnetocaloric, multiferroic and spin-glass materials, using SQUID magnetometry as the main characterization technique.

The magnetocaloric effect offers an interesting new technology for cooling and heating applications. The studies of magnetocaloric materials in this thesis are focused on experimental characterization of fundamental magnetic properties of Fe$_2$P-based materials. These are promising magnetocaloric materials with potential industrial use. It is found that the magnetocaloric properties of Fe$_2$P can be optimally tuned by substitution of manganese for iron and silicon for phosphorus. Furthermore, a simple device to measure the magnetocaloric effect in terms of the adiabatic temperature change was constructed.

Materials that simultaneously exhibit different types of ferroic order, for example magnetic and electrical order, are rare in nature. Among these multiferroic materials, those in which the ferroelectricity is magnetically-induced, or vice versa the magnetism is electrically-induced, are intensively studied due to a need for new functionalities in future data storage and logic devices. This thesis presents results on two materials: Co$_3$TeO$_6$ and Ba$_3$NbFe$_3$Si$_2$O$_{14}$, which belong to the group of magnetically-induced ferroelectrics and exhibit strong coupling between the magnetic and the electrical order parameter. Their ordering properties were studied using magnetic and electrical measurement techniques. The coupling between the magnetic and electronic degrees of freedom was investigated using high-field and low-temperature Raman spectroscopy.

Spin-glass materials exhibit complex magnetism and disorder. The influence of the spin dimensionality on the low and high magnetic field properties of spin glasses was investigated by studying model Heisenberg, XY and Ising spin-glass systems. Significant differences were found between the non-equilibrium dynamics and the hysteresis behavior of Heisenberg systems compared to those of XY and Ising spin glasses.

*Keywords*: Magnetocalorics, multiferroics, spin glasses, magnetization, polarization, spin-dimensionality
Dedicated to my mother(s).

Magnetes Geheimnis, erklär mir das!
Kein grösser Geheimnis als Lieb’ und Hass.

Johann Wolfgang von Goethe
1749-1832
MATTHIAS HUDL was born in 1981 in Jena, GDR. He earned a Dipl.-Phys. degree from Friedrich Schiller University Jena in 2007 and joined the Division of Solid State Physics at Uppsala University. Having a strong interest in fundamental science, his research has focused on magnetic materials. The thesis defence takes place on the 4th of April 2012.
This doctoral thesis is based on my research work at the Department of Engineering Sciences in the Division of Solid-State Physics at Uppsala University, Sweden. It was conducted during a 4-year Ph.D. education (2008-2012) under the supervision of Professor Per Nordblad and Docent Roland Mathieu.

This thesis is written in monographic style and presents a cumulative overview of my work, based primarily on scientific articles published in peer-reviewed journals and partly on unpublished results. A list of published articles can be found in the **List of Publications**. Throughout the thesis these articles are cited with their Roman numbers. For the reader’s convenience, a **List of Abbreviations** and a **List of Symbols** can be found in the end of this thesis.

The reason for writing the thesis in monographic style is mainly the fact that I had the opportunity to investigate three different classes of magnetic systems, namely magnetocaloric, magnetoelectric and spin-glass materials. Those three systems have a slightly different theoretical and experimental background and it seemed more appropriate to describe them separately. Furthermore, I had the intention to include unpublished results into my thesis which is unusual in case of a comprehensive summary thesis. During my Ph.D. work I had the opportunity to synthesize and characterize different magnetic materials, as well as design and construct my own experimental characterization setups.

There are certainly many ways to carry out Ph.D. work. The approach of my work was to study functional materials in the field of magnetism and magnetic materials. The quest for new functional materials requires a fundamental understanding of the nature and origin of functionalities and properties. In the case of magnetic materials, not only the magnetic states can be functionalized but also the spin degrees of freedom (magnetism) can be coupled to charge, orbital and lattice ones. Strongly correlated electron systems, such as, for exam-
ple, transition-metal oxides, display such interplay between their degrees of freedom.

The first functionality that was studied in this thesis is based on the existence of different magnetic states in the considered materials, and the phase transitions between these states. All magnetic materials are indeed magnetocaloric materials, yielding magnetic field-induced temperature changes related to the magnetic ordering. Electromagnetic laws include symmetry and reciprocity between magnetic ($M$) and electrical ($P$) polarizations. Indeed, the control of the electrical polarization could also be used in applications relevant to refrigeration, using the so-called electrocaloric effect.

The electrical polarization of materials, and its combination with magnetism, is actually very interesting. One can imagine new functionalities based on the use of both magnetic and electrical polarization of a material, or based on the control of one polarization by the other, if they are coupled as in magnetoelectric multiferroics. Different mechanisms for the combined existence of magnetic and electrical polarization in a given material, as well as its magnetization- or magnetic field-induced polarization are described. Since only few magnetoelectric multiferroics are usable in industrial applications, there is a great interest in finding new materials. I present several new materials with interesting magnetic, dielectric and magnetoelectric properties.

Spin-glass materials are very complex, out-of-equilibrium magnetic systems in their low-temperature, low-magnetic field phase. It is thus interesting to study the effect of both small and relatively large magnetic fields on the spin configuration. Magnetocaloric materials are mostly ferromagnets, and multiferroics antiferromagnets. However, spin-glass-like states often appear in these long-ranged magnetic materials, as a consequence of the chemical or magnetic disorder as well as geometrical frustration. It is thus of interest to investigate the effect of magnetic fields on these systems.

The outline of this thesis is as follows: Chapter 1 gives a short introduction to the field of magnetism and magnetic materials from a theoretical point of view. In chapter 2 the experimental techniques used in the studies of magnetism and magnetic materials described in this thesis are introduced. In the following three chapters experimental results relevant to the different scientific topics of this thesis are presented and discussed. A short introductory overview of each topic is included in these chapters. Chapter 3 is dedicated to the investigation of magnetocaloric materials, which can be found among ferromagnetic materials with high saturation magnetization and a tunable narrow phase transition with respect to temper-
nature. First, some theoretical and experimental fundamentals are reviewed and second the magnetocaloric properties of Fe$_2$P-based and other materials are discussed. Chapter 4 presents results from the study of magnetoelectric multiferroics, especially from those in which a complex magnetic structure (e.g. spin-spiral) gives rise to electrical polarization. Chapter 5 concerns the study of even more complex magnetic systems, namely spin-glass materials. Finally, chapter 6 summarizes the work presented in this thesis and gives a popular scientific summary in Swedish and German.

Parts of the experimental work presented in this thesis were obtained during visits to the Geophysical Laboratory of the Carnegie Institute of Washington, Washington D.C. (USA), CMRG at the Advanced Science Institute, RIKEN, Tokyo (Japan) and the HISKP/AG Fiebig at Bonn University, Bonn (Germany). Collaborators and colleagues are acknowledged in the Acknowledgements or listed as co-authors of the papers in the List of Publications.

The thesis was printed in black and white. A color version of this thesis is available online at http://uu.diva-portal.org/
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INTRODUCTION TO MAGNETISM AND MAGNETIC MATERIALS

This chapter is intended to give a short introduction to the field of magnetism and the magnetic materials studied in this thesis. Starting from a brief historical discourse a contemporary picture of magnetism is presented. Furthermore, fundamental concepts and terms used within this thesis are introduced. For a complete introduction we have to refer to common textbooks and compendia on magnetism listed in the references.

1.1 A brief history of electromagnetism

“The magnet’s mystery, explain that to me! No greater mystery than love and hate.” Magnetism is a phenomenon that has inspired mankind throughout the ages. An invisible “force” that is both attracting and repelling has sparked the human mind and led to useful applications, as early as the compass, already a 1000 years ago. Its traces can be followed back to the ancient cultures in Asia and Europe and even today the magnet’s mystery is not diminished. A schematic picture of a permanent magnet with north and south pole as well as field lines is shown in figure 1.1.

A more sophisticated understanding of magnetism was developed at the turn of the 18th century. In 1819 Hans Christian Oersted discovered that an electric current could influence a compass needle and hence that there is an inherent connection between electricity and magnetism. At about the same

\footnote{Johann Wolfgang von Goethe (1749-1832), German poet laureate and natural scientist [1]; see also Introduction to “Magnetism” by J. Stöhr and H. Siegmann}
1.1 A brief history of electromagnetism

André-Marie Ampère found that an electrical current produces a proportional magnetic field which is circulating in a closed-path around the current. Jean-Baptiste Biot and Félix Savart could give an equation for calculating the magnetic field from a current-carrying wire, known as the Biot-Savart Law. In 1830 Michael Faraday found that a time-varying magnetic flux induced a voltage in a conducting loop. All this experimental evidence created what is now known as electromagnetism.

The electromagnetic interaction is one of the four fundamental forces in nature. The other three are the strong and the weak interaction describing intra-atomic processes in the atomic nucleus and the gravitation describing interaction of matter on cosmic length scales. Electromagnetic radiation, e.g. visible light, has its foundation in electromagnetism and acts on the length scale of an atom up to that of the universe. Finally, in 1864 James Clerk Maxwell formulated the fundamental theory that unifies magnetism, electricity and optics by one set of equations, the Maxwell equations:

\[
\nabla \cdot \mathbf{B} = 0, \quad (1.1) \\
\nabla \cdot \mathbf{D} = \rho, \quad (1.2) \\
\n\nabla \times \mathbf{H} = j + \frac{\delta \mathbf{D}}{\delta t}, \quad (1.3) \\
\n\nabla \times \mathbf{E} = -\frac{\delta \mathbf{B}}{\delta t}. \quad (1.4)
\]

In this set of equations both the electric field \( \mathbf{E} \) and electric displacement field \( \mathbf{D} \) as well as the magnetic induction \( \mathbf{B} \) and the magnetizing field \( \mathbf{H} \) are connected. It is evident that \( \mathbf{D} \) has its origin in the charge density \( \rho \) whereas \( \mathbf{H} \) is connected with the current density \( j \) and the time derivative of \( \mathbf{D} \). In the presence of matter one can define magnetization \( \mathbf{M} \) and polarization \( \mathbf{P} \). The material equations read (isotropic, linear case):

\[
\mathbf{B} = \mu_0 (\mathbf{H} + \mathbf{M}) = \mu \mathbf{H}, \quad (1.5) \\
\mathbf{D} = \varepsilon_0 \mathbf{E} + \mathbf{P} = \varepsilon \mathbf{E}. \quad (1.6)
\]

Many technical phenomena can be explained from this set of equations. However, the occurrence of ferromagnetism in some materials was still to be solved. A successful explanation required quantum mechanics, e.g. the concept of exchange interaction, which is a topic in section 1.5.

Magnetism today has grown out of its natural science context into a field with significant social and economical impact.
There are numerous excellent references on the history and science of magnetism, see for example Refs. [2–5].

1.2 Building blocks of solid state physics - electrons and phonons

In condensed matter physics, the description of most physical properties of materials are based on electrons and phonons. Therefore it is beneficial to recall some of the fundamental properties of these entities.

*Electrons* are elementary particles with both electric charge (-1.602 × 10⁻¹⁹ C) and spin moment (1/2 ℏ). The presence of the electron spin moment was discovered by G. ÜHLENBECK and S. GOUDSMIT as late as 1925. Electrons are fermions and obey the Pauli exclusion principle. The quantum state of an electron is described by a unique set of quantum numbers and the atomic states are arranged following Hund’s rules. An electron possesses a spin magnetic moment $S$ and an orbital magnetic moment $L$. These two moments are the origin of magnetism.

*Phonons* are collective excitations of lattice vibrations in a crystal and can be described as quasi-particles. Phonons as well as their interaction with electrons determine the thermal and electrical properties of a material. The propagation direction of a phonon is described by its wave vector $k$ and is connected to the phonon angular frequency $\omega$ through a dispersion relation, see figure 1.2. The slope of the dispersion relation $v = d\omega / dk$ determines the speed of propagation of a phonon (cf. speed of sound) in the lattice. Crystals with two or more atoms per unit cell exhibit two types of phonons: acoustic and optical phonons. Acoustic phonons are in-phase displacements of atoms from their equilibrium position in a crystal lattice whereas optical phonons are out-of-phase displacements. Longitudinal and transverse optical (acoustic) phonons are referred to as LO (LA) and TO (TA) phonons, respectively, see figure 1.2.

1.3 On the nature of magnetic materials

In the previous section it was stated that electrons exhibit a magnetic moment and that charged particles in motion are affected by a magnetic field. Therefore magnetism is inherent to all materials. A common way to experimentally distinguish different types of magnetism (or magnetic materials) is to measure the response of the material to the application of a magnetic field. That response can be characterized in terms of the
1.3 On the nature of magnetic materials

Figure 1.3: Several types of magnetic order: a) paramagnetic-, b) ferromagnetic-, c) antiferromagnetic-, d) canted antiferromagnetic-, e) ferrimagnetic-, and f) helical magnetic ordering.

magnetic susceptibility

\[ \chi = \left. \frac{dM}{dH} \right|_{H \to 0}. \]  

Depending on the magnetic field and temperature behavior of the magnetic susceptibility, different types of magnetic materials can be identified. In principle, one can distinguish two types of magnetic materials; those that exhibit collective magnetic interactions in the electron system and those with no such interactions. A fundamental understanding of the underlying processes which give rise to different types of magnetism can only be based on the concept of exchange interaction (see 1.5). Nevertheless, a sketch of the spin configuration for several types of ordered magnetic materials is shown in figure 1.3 and a short list of magnetic materials is introduced below.

Dia- and paramagnetism Diamagnetism is a property inherent to all materials. Diamagnetism is described by a rather small, temperature independent, negative susceptibility \( \chi \). Depending on the filling of the electron shells, materials can be dia- or paramagnetic. In the case of unpaired electrons the diamagnetic response is surmounted by a positive paramagnetic \( \chi \). Paramagnetism reflects the competition between the alignment of the unpaired magnetic moments due to the applied magnetic field and the disruption of that alignment due to thermal energy. The classical Curie paramagnetism obeys the famous \( \chi = C/T \) (Curie law) with the the Curie constant \( C = (N\mu_0\mu_{\text{eff}}^2)/3k_B \) and the effective magnetic moment \( \mu_{\text{eff}} \). Curie-Weiss paramagnetism describes a situation in which an additional exchange interaction is present, for example in the high-temperature paramagnetic phase of a ferromagnet. The Curie-Weiss susceptibility is described as \( \chi_{\text{CW}} = C/(T - \theta) \) with the characteristic Curie-Weiss temperature \( \theta \) which is >0 for a parallel alignment of the magnetic moments (ferromagnetic interaction) and <0 for an antiparallel alignment of the magnetic moments (antiferromagnetic interaction), c.f. Figure 1.4. Other types of paramagnetism are the Pauli paramagnetism, which is due to conduction electrons in metals and characterized by a small and temperature-independent \( \chi \) and Van Vleck paramagnetism due to the excitation of lower electron states.

Ferromagnetism Materials that possess a strong collective interaction of the electron system are commonly referred to as being magnetic. The collective interaction is a quantum mechanical phenomenon due to electronic exchange forces between the electron spins in the material and often reaches the order
of several 100 to 1000 T. In a ferromagnet these force tend to align the magnetic moments in parallel below a certain critical temperature, leading to a huge net magnetization. At room temperature there are only a few 3d and rare earth elements which show ferromagnetism: Fe, Ni, Co, and Gd. Characteristic of ferromagnetic materials are (1) spontaneous magnetization with long-range magnetic order below a critical temperature \( T_C \) and (2) the appearance of a magnetic hysteresis. Below the magnetic transition temperature \( T_C \), the parallel alignment of the spin system is divided into domains of parallel spins to diminish the magnetic energy. The magnetic ordering is governed by the growth of correlated magnetic moments referred to as domains. This growth process is hindered by the pinning of domain walls due to, for example, impurities and crystal defects giving rise to coercivity (see section 1.4). Ferromagnetic materials are particularly interesting in the field of magnetocaloric materials described in chapter 3.

**Antiferromagnetism and ferrimagnetism** In antiferromagnetic and ferrimagnetic materials the preferred alignment of the spin system is antiparallel. A theoretical description of such materials goes back to LOUIS NÉEL. The magnetic structure can be described by two magnetic sub-lattices \( A \) and \( B \) with antiparallel alignment relative to each other. This type of magnetic long-range ordering appears at the Néel temperature \( T_N \). In the case of equally strong magnetic sub-lattices \( A \) and \( B \), the system is an antiferromagnet, whereas for non-equal sub-lattices ferrimagnetism is encountered. A well-known example of such a ferrimagnetic material is Magnetite, \( \text{Fe}_3\text{O}_4 \) which crystallizes in the spinel structure and has a critical temperature of \( T_C \approx 850 \text{ K} \). Antiferromagnetism and ferrimagnetism are rather common features of many magnetic oxides. In particular, magnetoelectric and multiferroic materials studied in chapter 4 belong to the class of antiferromagnets.

**Helical magnetism and spiral magnetism** In some materials even more complex forms of magnetic ordering can occur due to the crystal structure, e.g. triangular or Kagomé lattices, and competing magnetic interactions. Such an ordering occurs in several oxide materials, e.g. some langasites. The general experimental appearance of such materials is that of an antiferromagnet. Competing interactions can lead to frustration, which can be measured by the parameter \( f = \theta_N / T_N > 1 \), cf. Figure 1.4. Materials with such properties have been studied in chapter 4.


1.4 Magnetic hysteresis

Spin-glass magnetism  An even more complex situation can be found in materials which combine both magnetic frustration and disorder in their spin system. In such a case no long-range magnetic ordering is possible and the material enters a new so-called spin glass state. Spin glass materials have interesting dynamical properties, for example aging, memory and rejuvenation. Such materials are the topic of the study presented in chapter 5 where a more detailed description is presented.

1.4 Magnetic hysteresis

The magnetic hysteresis, or just hysteresis, was independently studied by Emil Warburg [6] and James Ewing [7] in 1881. It describes a situation in which the response of the magnetic system, e. g. the magnetization, lags behind its "perturbation" the magnetic field. Hysteresis is common to ferromagnetic materials. A schematic picture of the magnetic hysteresis for a ferromagnet is shown in figure 1.5a. It is characterized by the saturation magnetization $M_s$, the remanent magnetization (remanence) $M_r$ and coercive field (coercivity) $H_C$. From a demagnetized state ($H = 0$ and $M = 0$) the curve follows the dashed line (virgin curve) up to $M = M_s$. A subsequent cycling of the magnetic field describes the hysteresis loop. The enclosed area $A$ represents the energy losses of one hysteresis cycle. In figure 1.5b the energy associated with the applied magnetic field and the energy needed to magnetize the materials are indicated and labelled $B$ and $C$, respectively. The parameters describing the hysteresis are not of intrinsic nature but are dependent on grain size, domain state, stresses, and temperature. Furthermore, the shape of the hysteresis loop depends strongly on the shape and anisotropy of the materials.

Comparison magnetic and electric materials

Hysteresis is a much more general phenomenon and can be found in nearly all branches of science, for example mechanics, electro-technics, biology, medicine and even economics. It is therefore no surprise that also electrical materials exhibit hysteresis behavior. An example for an electrical hysteresis is shown in figure 1.6.
1.5 Theoretical models of magnetism

1.5.1 Models of exchange interaction

The strong force responsible for the collective behavior in ordered magnetic materials is the exchange interaction. The concept exchange interaction was first introduced in 1926 by Werner Heisenberg and Paul A. M. Dirac and is based on quantum mechanics. In the wave description of quantum mechanics by Erwin Schrödinger (1926) the electron is described by a complex wave function $\Psi(r)$ and the energy of the system is given by the stationary Schrödinger equation

$$\mathcal{H}\Psi = \mathcal{E}\Psi,$$  (1.8)

with the Hamiltonian $\mathcal{H}$. The solutions of equation 1.8 are the eigenstates $\Psi(r)$ and the energy levels $\mathcal{E}$ of the system. The energy of a magnetic system is governed by its Hamiltonian, which is defined by the types of interaction

$$\mathcal{H} = \sum_i \mathcal{H}_i.$$  (1.9)

Heisenberg exchange interaction

The Heisenberg model describes the direct interatomic exchange between localized magnetic moments, for example in insulating materials. The general Heisenberg Hamiltonian is written as:

$$\mathcal{H} = -2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_0 \mu_B \sum_i \mathbf{H}_i \cdot \mathbf{S}_i,$$  (1.10)

where $J_{ij}$ is the exchange constant, $\mathbf{S}_i$ and $\mathbf{S}_j$ are the spins and $\mathbf{H}_i$ is the magnetic field acting on the spin $\mathbf{S}_i$. The first term in equation 1.10 is the exchange energy and the second term is the Zeeman energy. The exchange constant $J_{ij}$ corresponds to half of the energy difference between $\uparrow\uparrow$ and $\uparrow\downarrow$ [8]. For $J_{ij} > 0$ the interaction is ferromagnetic and becomes antiferromagnetic for $J_{ij} < 0$.

Superexchange interaction

Superexchange is an indirect exchange in which a nonmagnetic anion O mediates the magnetic interaction between two next-nearest neighbor magnetic cations M. In superexchange the electrons stay localized and the mechanism is typical for insulating oxide materials. The interaction can be described by the Heisenberg Hamiltonian (eq. 1.10). Whether the
interaction will be antiferromagnetic or ferromagnetic can be derived from the empirical Goodenough-Kanamori rules. For example, in simple cases, for bond angles M-O-M from $120^\circ$ to $180^\circ$ the exchange is strong and antiferromagnetic, whereas for a bond angle of $\sim 90^\circ$ the exchange is weak and ferromagnetic.

**Dzyaloshinskii-Moriya (DM) interaction**

The Dzyaloshinskii-Moriya (DM) interaction occurs in materials with low symmetry and reflects the spin-orbit coupling in which the crystal-field energy is minimized by a slightly non-collinear structure. The Hamiltonian is given by

$$\mathcal{H}_{DM} = -\frac{1}{2} \sum_{ij} D_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j$$ (1.11)

where $D_{ij}$ is the Dzyaloshinskii-Moriya vector which lies along a high symmetry axis. This type of interaction likes non-collinear spin states, due to the cross product. In the presence of superexchange the DM interaction is a higher-order effect and $|D/J| \approx 10^{-2}$ [5]. DM interaction is important for non-collinear material and spin glasses studied in chapter 4 and 5.

**Double exchange interaction**

In double exchange the interaction arises between magnetic ions with both localized and delocalized electrons. The electrons are itinerant and the electron movement is mediated by intermediate anions, e.g. oxygen. The double exchange mechanism is similar to superexchange but requires ions with mixed valence. It gives rise to magnetic exchange coupling as well as metallic conductivity.

**RKKY interaction**

The Ruderman-Kittel-Kasuya-Yosida (short RKKY) interaction was first proposed by Ruderman and Kittel as a coupling mechanism to explain an indirect exchange of the nuclear atomic spins with conduction electrons via the hyperfine interaction. Later it was extended by Kasuya and Yosida to describe the interaction of localized d or f shell electron spins in a metal via the polarization of conduction electron spins. The exchange interaction constant $J$ can be described as

$$J \sim \frac{\cos(2k_F r + \theta)}{k_F r^3}$$ (1.12)
and results in a damped oscillation giving rise to antiferromagnetic \((J < 0)\) and ferromagnetic \((J > 0)\) interaction, compare figure 1.7. RKKY is particular interesting for diluted magnetic system, e.g. canonical spin glasses such as Cu(Mn).

**Dipole-dipole interaction**

Magnetic dipol-dipol interaction is a direct anisotropic long-range coupling between two dipoles. The Hamiltonian can be described by

\[
\mathcal{H}_{DD} \propto \frac{1}{r_{ij}^3} \left( (\mathbf{m}_i \cdot \mathbf{e}_{ij}) (\mathbf{m}_j \cdot \mathbf{e}_{ij}) - \mathbf{m}_i \cdot \mathbf{m}_j \right),
\]

with \(\mathbf{e}_{ij}\) being a unit vector along the connecting line between two dipoles \(\mathbf{m}_i\) and \(\mathbf{m}_j\) at the distance \(r_{ij}\). Dipolar coupling occurs in molecules as well as in nanoparticle and spin-glass systems.

### 1.5.2 Models of magnetic anisotropy

Magnetic anisotropy describes a situation in which a preferred direction or axis in a magnetic system is present and determines the direction of the magnetic moments in a domain. The axis along a magnetic system that needs the least magnetic field to reach its saturation value is usually called easy axis. Different sources that can give rise to magnetic anisotropy:

1. **Shape anisotropy**, which is a non-intrinsic property depending on the sample shape and its associated demagnetization field. The internal magnetic field is given by \(\mathbf{H}_{\text{int}} = \mathbf{H}_{\text{ext}} - N\mathbf{M}\) where \(N\) is the demagnetization factor \((N_z=1/3\) for a sphere and \(N_z=0; N_{x,y}=1/2\) for a long cylinder along the \(z\)-direction). 

2. **Magneto-crystalline anisotropy** depends on the crystal symmetry and derives from the crystal-field interaction and spin-orbit coupling.

3. **Induced anisotropy** in which the preferred magnetization direction is in-printed by applied stress or external magnetic fields. Magneto-crystalline anisotropy can be described by the anisotropy energy \(E_a\). Conventional expressions for the anisotropy energy \((2^{\text{nd}}\) order) in different symmetries, for example cubic, uniaxial and unidirectional are:

\[
\begin{align*}
E_a^{\text{cubic}} &= K_1 (a_1^2a_2^2 + a_2^2a_3^2 + a_3^2a_1^2) + K_2 (a_1^2a_2^2a_3^2) \\
E_a^{\text{uniaxial}} &= K_1 \sin^2 \theta + K_2 \sin^4 \theta \\
E_a^{\text{unidirect.}} &= K_1 \cos \theta
\end{align*}
\]
1.6 Magnetic phase transitions

A phase transition is the transformation of a thermodynamic system from one phase or state of matter to another. Phase transitions are described by an order parameter Φ, see figure 1.9. A symmetry breaking when undergoing a phase transition is described by a non-zero order parameter. For a magnetic phase transition this order parameter is the spontaneous magnetization \( M \). In general, a magnetic phase transition is defined at the onset of a finite value of the order parameter (magnetization) as a function of a control parameter (temperature). In practice, the phase transition occurs at the inflection point of the magnetization vs. temperature curve recorded in a low magnetic field \( (H \rightarrow 0) \). Phase transitions are usually caused by interatomic interactions.

An initial classification scheme for phase transitions, given by Paul Ehrenfest, labeled phase transitions by the lowest derivative of the free energy which is discontinuous at the transition. First-order phase transitions are discontinuous in the first derivative of the thermodynamic free energy with a thermodynamic variable. Second-order phase transitions are continuous in the first derivative but exhibit discontinuity in the second derivative of free energy. In a modern classification scheme, phase transitions are defined differently [9]. First-order phase transitions involve latent heat, which is the amount of energy absorbed or released during such a transition, while the system temperature stays constant. Second-order phase transitions are continuous phase transitions which have no associated latent heat.

1.7 Symmetry and magnetism

“C’est la dissymétrie, qui crée le phénomène.”\(^2\) - Symmetry plays a key role in the understanding of nature and hence in the physics of magnetism. An introduction on the topic "Symmetry and magnetism" can be found in the book by R. Birss [11].

There are 32 crystallographic point groups describing the symmetry properties of a crystal system, cf. figure 1.10. These

\[ \text{where } K_1 \text{ and } K_2 \text{ are the anisotropy constants, } \theta \text{ is the angle between the magnetization and the anisotropy axis and } \alpha_i \text{ is the direction cosinus of the magnetization in a polar coordinate system (} \alpha_1 = \sin \theta \cos \phi, \alpha_2 = \sin \theta \sin \phi, \text{ and } \alpha_3 = \cos \theta \).
Table 1.1: Point group symmetry operations.

<table>
<thead>
<tr>
<th>Symmetry operation</th>
<th>Schönflies notation</th>
<th>Hermann-Mauguin notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>E</td>
<td>1</td>
</tr>
<tr>
<td>Inversion</td>
<td>I</td>
<td>( \bar{1} )</td>
</tr>
<tr>
<td>Mirror plane</td>
<td>( \sigma )</td>
<td>( m )</td>
</tr>
<tr>
<td>Rotation axis</td>
<td>( C_n )</td>
<td>( n ) (= 2, 3, 4 and 6)</td>
</tr>
<tr>
<td>Rotation-inversion</td>
<td>-</td>
<td>( \bar{n} ) (= 3, 4, and 6)</td>
</tr>
<tr>
<td>Rotation-reflection</td>
<td>( S_n )</td>
<td>-</td>
</tr>
<tr>
<td>Time reversal</td>
<td></td>
<td>( 1', m', \ldots )</td>
</tr>
</tbody>
</table>

Point groups describe the symmetry of atoms arranged in 14 Bravais lattices which belong to 7 lattice systems (triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic). The combination of all these symmetry operations results in a total of 230 unique space groups describing all possible crystal symmetries. After including time reversal to account for the magnetic symmetry there are 1651 magnetic space groups in 3 dimensions.

From Neumann’s principle it follows that crystal symmetry and the physical properties of a crystalline solid are not independent. Neumann’s principle states that the invariant symmetry elements of the crystal are also invariant symmetry elements of the physical properties. The symmetry of any physical property of a crystalline material is constricted to the point group symmetry of the crystal and has to transform under the same symmetry elements. A symmetry-related description of physical properties of a material can be achieved using a tensor formalism. One has to distinguish between polar tensors and axial tensors. A tensor of rank \( N \) transforms as

\[
T'_{ijk\ldots} = |a|a_{il}a_{jm}a_{kn}\ldots T_{lmn\ldots} \quad (1.14)
\]

where every tensor component has \( N \) subscripts. The determinant of the direction cosines matrix is \( |a| = +1 \) or -1 depending on whether the chirality for an axial tensor changes under a transformation or not. For a polar tensor \( |a| = +1 \). The rank \( N \) describes the directions involved in the measurement of the particular physical properties.

Temperature or specific heat for example, are scalar properties and are described by a zero rank polar tensor. The electrical polarization and pyroelectricity for instance are vectorial properties and comply with a first rank polar tensor. It follows that these properties disappear in all point groups with inversion symmetry and hence in all centro-symmetric materials. In
other words the electrical polarization breaks inversion symmetry. The magnetic moment and magnetic field on the other hand are first rank axial tensors and do not break inversion symmetry but do break time reversal symmetry.

![Figure 1.10](image)

**Figure 1.10:** Stereographic projections of the three monoclinic point groups a-c) and two of the five trigonal point groups d-e). Adapted from Reference [12].
In this Chapter, experimental characterization methods for studying magnetism and magnetic materials are reviewed. A multitude of techniques can be employed to obtain a profound understanding of the physics behind condensed matter magnetism. Different methods starting from X-ray diffraction (crystal structure), via SQUID magnetometry (magnetic properties) to optical spectroscopy are described.

2.1 Synthesis of magnetic samples

All experimental studies on functional materials depend on high-quality samples and before the first measurement to determine intrinsic properties can be performed a “good” sample has to be synthesized. As a fellow Ph.D. student pointed out lately, “any turkey can measure magnetic properties, the true insight is in knowing what samples to make” [13]. I would like to add “..., the true insight is in knowing what samples to make and how to achieve the highest possible quality”.

2.1.1 Sample preparation using the drop synthesis method

The drop synthesis method [14, 15] is a suitable technique for synthesizing compounds consisting of volatile materials with a low melting temperature, such as phosphorus. Volatile materials are added by dropping them into a melt of non-volatile materials. The dropping process causes the melt to enclose the volatile elements, hence evaporation can be minimized and an
2.1.1 Sample preparation using the drop synthesis method

An instantaneous reaction occurs. The synthesis process is done using an induction furnace. A schematic drawing of the setup is shown in figure 2.1. In the following description the numbers (#1-10) correspond to those in figure 2.1. In an induction furnace, electrically conductive materials are heated above their melting point by the eddy currents induced by applying a high-frequency magnetic field. The non-volatile raw materials (#10 in figure 2.1) are placed in an Al₂O₃ crucible (#8) and heated by an induction coil (#9) under ~400 mbar Argon atmosphere until a glowing melt is formed. The temperature of the melts is measured using a pyrometer (not shown in figure 2.1).

When a stable melt is established the volatile materials (#3), initially placed in a horizontal glass tube (#5), are dropped into the melt. The synthesis weight for the drop synthesis technique can be varied between 5 and 50 g. Within this thesis the Fe₂P-based magnetocaloric materials presented in chapter 3 and the Cu(Mn) spin glass presented in chapter 5 were synthesized using this method.

Synthesis of Fe₂P-based materials

The (Fe,Mn)₂(P,Si) samples were synthesized in an Ar atmosphere of 40 kPa by the drop synthesis method described above. This synthesis “road” has been described for Fe₂P by Stig Rundqvist [14]. The synthesis temperature was chosen to be 1300-1350 °C. Temperature measurements are done using a pyrometer. Since the pyrometer estimates the temperature on the surface of the melt a correction factor should be applied. The real temperature might therefore be 50-100 °C higher. To estimate suitable synthesis parameters for a particular system, the temperature phase diagram can be used. For a synthesis involving 4 elements, no phase diagrams are available and synthesis conditions need to be optimized empirically. Stoichiometric amounts of iron (Leico Industries, purity 99.995%, surface oxides were reduced in H₂-gas), manganese (Institute of Physics, Polish Academy of Sciences, purity 99.999%), phosphorus (Cerac, purity 99.999%) and silicon (Highways International, purity 99.999%) were used as raw materials. A synthesis weight of 15 - 20 g was found to be optimal for the synthesis because the synthesis temperature is more stable compared to smaller weights and the synthesis duration is still short enough to avoid disruptions of the Al₂O₃ crucible.

After the drop synthesis, the samples were crushed, pressed into pellets, sealed in evacuated fused silica tubes and heat treated. The temperature protocol for the heat treatments was to first sinter the sample at 1373 K for 1 hour and then to anneal the sample at 1073 K for about 65 hours. The annealing
process is necessary to homogenize the raw synthesized material. As reported by CARLSSON ET AL. [15], high homogeneity of pure non-stoichiometric Fe$_2$P samples requires a very efficient quenching technique to avoid phase segregation. Hence, whether the sample is quenched or slowly cooled after heat treatment is crucial for the structural and magnetic properties. Subsequent to the annealing process the samples were therefore water quenched. An X-ray powder diffraction (XRD) pattern for FeMnP$_{0.5}$Si$_{0.5}$ after annealing and quenching is shown in figure 2.2. The synthesis of polycrystalline (Fe,Mn)$_2$(P, Si) samples presented in this thesis was mainly performed by VIKTOR HÖGLIN and partly by myself.

Figure 2.1: Induction furnace for the drop synthesis method. (1) viewing window, (2) gas inlet, (3) volatile elements (e.g. Mn, P), (4) soft magnetic iron pusher, (5) Pyrex glass container, (6) silica funnel, (7) silica tube, (8) alumina-oxid crucible, (9) RF work coil, (10) non-volatile elements (e.g. Fe, Si), (11) vacuum connection. Taken from Reference [15].
2.1.2 Arc melting

Using the drop synthesis method one can obtain samples with very low amounts of impurities and good reproducibility. Another advantage of the drop synthesis method is the rather short synthesis time (order of 1 hour) compared with ball milling, which may require the order of 100 hours or more [16].

2.1.2 Arc melting

The arc melting method is a simple technique for synthesizing compounds consisting of non-volatile elements. The raw materials are placed on a Cu seat and melted in inert atmosphere using an electric arc. Within this thesis polycrystalline FeNiCr samples were synthesized by JONAS ÅNGSTRÖM and MARTIN SAHLBERG using the arc melting technique.

Figure 2.2: Room temperature XRD pattern for FeMnP$_{0.5}$Si$_{0.5}$ after annealing and quenching. Adapted from Paper II.
2.1.3 Single crystal growth using the floating zone method

The floating zone method (or zone melting) is a synthesis technique suitable for the preparation of single crystalline samples with high purity. The zone melting method was developed in 1952 by William Gardner Pfann at Bell Labs to control the impurity level of semiconductors [18]. The floating zone process works as follows (see also figure 2.3). A solid rod of a stoichiometric mixture of the desired material is prepared. A narrow region of that feed rod is melted under controlled atmosphere and brought in contact with an oriented seed crystal at the bottom. The seed crystal is used to initiate a defined orientation of crystal growth. The seed crystal and feed rod are set to rotate in opposite directions and the whole arrangement is pulled through a heater, which in the case of an imaging furnace consists of two halogen lamps facing each other. The segregation coefficient, the ratio of the amount of an impurity in the solid phase to the amount in the liquid phase, is usually smaller than one. Impurities will hence stay in the liquid phase and will be first segregated at the end of the crystal. Furthermore, there is no physical contact of the molten material to any kind of crucible which is an advantage of the technique and assures high purity of the synthesized samples. A limitation of the technique is that the materials need to melt congruently.

Synthesis of the \( \text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14} \) langasite

The floating zone method is a standard technique for growing large high-quality single crystals suitable in terms of studying the intrinsic material properties. The synthesis process for the \( \text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14} \) langasite is briefly described. First, a stoichiometric mixture of the desired elements is prepared using \( \text{BaCO}_3, \text{Nb}_2\text{O}_5, \text{SiO}_2 \) and \( \text{Fe}_2\text{O}_3 \) as precursors. Then the mixture is calcinated in \( \text{O}_2 \) atmosphere for 24 h at 1100°C,

\[
3 \cdot \text{BaCO}_3 + \frac{1}{2} \cdot \text{Nb}_2\text{O}_5 + 2 \cdot \text{SiO}_2 + \frac{3}{2} \cdot \text{Fe}_2\text{O}_3 \\
\rightarrow \text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14} + 3 \cdot \text{CO}_2.
\]

Subsequently, a rod of suitable size (length \( \sim 100 \text{ mm} \), diameter \( \sim 6 \text{ mm} \)) is prepared and sintered. Finally, the floating zone synthesis is performed as described above using an imaging furnace. The XRD patterns of several samples of \( \text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14} \) synthesized via the floating zone technique are shown in figure 2.4. The impurity phase in some of the samples is visible from the inset of figure 2.4 is \( \text{Ba}_2\text{FeNbO}_6 \).
2.2 Structural characterization methods

The Ba$_3$NbFe$_3$Si$_2$O$_{14}$ langasite samples are studied in chapter 4 of this thesis and have been synthesized by AKIKO KIKKAWA and myself at RIKEN, Tokyo (Japan).

2.2 Structural characterization methods

X-ray diffraction (XRD)

X-ray diffraction is the most fundamental and commonly used method to determine the structural and phase properties of crystalline samples. The basic principle of X-ray powder diffraction is illustrated in figure 2.5. The diffraction patterns can be analyzed in terms of Bragg’s law: $2d \cdot \sin \theta = n \cdot \lambda$. The phase analysis and crystal structure characterizations of the samples in this thesis were mostly performed using X-ray powder diffraction (XRD) with a Bruker D8 diffractometer equipped with a Vantec position sensitive detector (PSD, 4 degree opening) using Cu Ka$_1$ radiation, $\lambda = 1.540598$ Å.

For a quantitative analysis of the powder diffraction pattern from a crystalline material, the pattern has to be refined. This can be done by the Rietveld method [19] using the software FULLPROF [20]. Rietveld refinement uses a least
square algorithm to minimize the difference between the observed data and a calculated profile. From such refinements all essential crystallographic data can be derived and impurity phases quantified.

For the orientation of the single crystalline $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ samples, the Laue method was used. A Laue picture for an oriented $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ crystal is seen in figure 2.6.

**Figure 2.5:** Schematic diagram for a X-ray powder diffraction (XRD) experiment. Adapted from BRUNDLE ET AL. [21]

**Scanning electron microscopy (SEM)**

The surface homogeneity and stoichiometry of a sample can be probed using an Electron Probe Micro-Analyzer (EPMA). This technique enables quantitative chemical analysis and imaging of minerals down to a size of minimum 5 $\mu$m. Measurements using a CAMECA SX50 - equipped with three wave length dispersive crystal spectrometers (WDS), secondary (SE) and backscattered (BSE) electron detectors - were performed within this thesis.
2.3 Magnetic characterization methods

The main part of the experimental work in this thesis is based on macroscopic magnetic measurements using DC magnetization or AC-susceptibility techniques. Magnetic measurements probe the magnetic state (see chapter 1.3) of the measured species. In DC measurements the magnetic moment $m$ induced in the sample is recorded in emu [cgs] or Am$^2$ [SI]. For a specific sample of known mass (volume) the magnetization $M$ in emu/g (emu/cm$^3$) [cgs] or Am$^2$/kg (A/m) [SI] can be obtained (1 Am$^2$/kg = 1 emu/g). Both quantities $m$ and $M$ depend on temperature $T$, magnetic field $H$, time $t$ and pressure $p$. The characterization of the magnetic properties of a magnetic material depends on a thorough control of these parameters during the measurements. The type of magnetism of the studied material is manifested by the responses obtained. The most common way of probing the type of magnetism is to measure a hysteresis loop at constant temperature. When measuring the magnetic response as a function of temperature and magnetic field, not only these parameters but also the employed cooling protocol is important.

There are a number of different cooling protocols:

- **Zero-field-cooled (ZFC) magnetization measurement**: The sample is cooled in zero magnetic field and the magnetization is recorded in a magnetic field during reheating.

- **Field-cooled (FC) magnetization measurement**: The sample is cooled in an applied magnetic field and the magnetization is recorded while it is cooling or on reheating.

- **Thermoremanent magnetization (TRM) measurement**: The sample is cooled in an applied magnetic field and the magnetization is recorded in zero magnetic field under reheating.

- **Isothermal-remanent magnetization (IRM) measurement**: The sample is cooled in zero magnetic field and the magnetic response is measured on reheating in zero magnetic. During the initial cooling a stop is made at $T_{IRM}$ and a magnetic field is applied for the duration of the stop.

Figure 2.7 shows $M/H$ of a Cu(Mn) spin glass measured using the different protocols described above (a weak field has been used).
In DC magnetic measurements the sample is magnetized by a constant magnetic field, while AC magnetic measurements use an oscillating magnetic field. For small magnetic fields $H_{AC}$ with frequency $\omega$, the AC magnetization is given to $M_{AC} = (dM/dH) \cdot H_{AC} \sin(\omega t)$. The AC susceptibility $\chi = dM/dH$ has two components, an in-phase component $\chi' = \chi \cos \phi$ and an out-of-phase component $\chi'' = \chi \sin \phi$ ($\chi = \sqrt{\chi'^2 + \chi''^2}$) [22].

For the study of the time dependence and the dynamics of the magnetic properties, it is important to be familiar with the observation time of the used technique. In AC measurements, the observation time is $\sim 1/\omega$. An overview of the experimental observation times for the several experimental techniques is given in Table 2.1.

As mentioned, $M = f(T, H, t, p, ...)$ and during a magnetic measurement usually one parameter is varied while other parameters are fixed. To be able to interpret and understand magnetic measurements, it is beneficial to review the influence of temperature and magnetic field on the magnetization. In Figure 2.8 an example of the relation between the magnetic field and temperature dependence of the ZFC and FC magnetization of an arbitrary bulk ferromagnetic material is described.

Figure 2.8 a) to c) show magnetization as a function of temperature $M = f(T, H = const.)$ for three different applied magnetic fields ($H_1 > 0$, $H_2 > H_1$ and $H_3 >> H_1$). It is evident that with increasing applied field the probed sample is getting closer to its saturated state and hence the difference between ZFC and FC magnetization vanishes. In addition, the magnetization value at a constant temperature increases. In Figure 2.8 d) to f) the magnetization as a function of magnetic field $M = f(T = const., H)$ for three different temperatures $T_1 > 0$, $T_2 > T_1$ and $T_3 >> T_1$) is shown. With increasing temperature (d) $\rightarrow$ (e)) both the saturation magnetization and coercivity field decrease.

**Table 2.1:** Characteristic observation times of several experimental techniques for magnetic measurements.

<table>
<thead>
<tr>
<th>Experimental technique</th>
<th>Observation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>DC magnetization</td>
<td>$10^{-1} - 10^6$ s</td>
</tr>
<tr>
<td>AC magnetization</td>
<td>$10^{-6} - 10^2$ s</td>
</tr>
<tr>
<td>Mössbauer spectroscopy</td>
<td>$10^{-9} - 10^{-7}$ s</td>
</tr>
<tr>
<td>Ferromagnetic resonance</td>
<td>$10^{-9}$ s</td>
</tr>
<tr>
<td>Neutron scattering</td>
<td>$10^{-12} - 10^{-8}$ s</td>
</tr>
</tbody>
</table>
In figure 2.8 f) the ferromagnetic sample is in a paramagnetic state.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.8.png}
\caption{Schematic picture of magnetization vs. temperature for a ferromagnetic sample after ZFC and FC protocols a) to c) and the corresponding hysteresis loops d) to f). The vertical dashed lines a1, a2 and a3 in figure a) correspond to the vertical dashed line 1a in figure d), 2a in figure e) and 3a in figure f), respectively. (b1 = 1b, c2 = 2c, etc.)}
\end{figure}
Quantum Design MPMS and PPMS

Most characterization experiments have been performed using commercial equipments from Quantum Design, Inc. Magnetic measurements are commonly collected using the magnetic property measurement system (MPMS). The MPMS is a superconducting quantum interference device (SQUID) magnetometer and provides temperature control from 2 - 400 K (with furnace 300 K to 800 K) and magnetic fields of 5 or 7 T. Magnetic measurements using a vibrating sample magnetometer (VSM) as well as specific heat, resistance, and Hall-effect measurements can be performed using the physical properties measurement system (PPMS). The accessible magnetic field is 9 T (Uppsala) and 14 T (RIKEN, Japan). The PPMS system has also been used as a base to provide temperature and magnetic field control for custom-made experimental set-ups: for $\Delta T$ measurements, Raman spectroscopy and magnetoelectric measurements (RIKEN, Japan).

SQUID magnetometry

Measurements of magnetic quantities are usually based on the determination of the magnetic flux. One of the most sensitive instruments for measuring magnetic flux is the superconducting quantum interference device (SQUID) magnetometer [23]. This device uses the quantization of magnetic flux in superconducting materials with Josephson junctions to measure magnetic fields with a resolution of $10^{-15}$ T or better. In the MPMS, the sample is transported through the detection coils, which are configured as a second-order (second-derivative) gradiometer to reduce noise and background drifts [24]. The change in the magnetic flux density produced by the dipole field of the sample is measured. SQUID magnetometry is a standard technique used to measure macroscopic magnetic properties. Magnetization data as function of temperature, time and magnetic field are required to study magnetic materials. For example, in the case of magnetocaloric materials the isothermal magnetic entropy change $\Delta S_M$ can be calculated from knowledge of $\mathbf{M} = f(T, \mathbf{H})$.

Additionally, to the MPMS a home-built low magnetic-field SQUID magnetometer [25] was used for the study of spin glass materials. In this set-up small fields ($1 \text{mOe} < H < 50 \text{ Oe}$) can be switched within a millisecond. A sketch of the layout for that magnetometer is shown in figure 2.9. The design provides good thermal stability and very low magnetic background due to niobium and Mu-metal shielding.
2.3 Magnetic characterization methods

Figure 2.9: Schematic drawing of the Uppsala home-built SQUID magnetometer [25]. Courtesy of Bengt Göteesson.

Mössbauer spectroscopy

Mössbauer spectroscopy is based on the resonant emission and absorption of gamma rays in solids and was discovered by Rudolf Mössbauer in 1957. For performing resonant emission and absorption measurements the $\gamma$-photon source needs to match the probed element, e.g. $^{57}$Fe can be studied using $^{57}$Co $\gamma$-decay. Therefore Mössbauer spectroscopy is an element-specific method. The technique has been applied in
a wide variety of scientific fields and it can be used to gain knowledge about many properties, such as chemical bonding, magnetic properties, and oxidation states. The hyperfine interaction denotes any interaction between nuclei and electrons, and can be described as an effective field, called the hyperfine field, yielding information about the magnetic moments of the measured element. In the present study, Mössbauer, absorption spectra were recorded in the constant acceleration mode with a $^{57}$CoRh source. Information about the site occupancy and magnetic moments for Fe was obtained.

**Optical second-harmonic generation (SHG)**

Second-harmonic generation (SHG) is an experimental technique that can probe the symmetry properties of a magneto-electric material. The SHG signal is coupled to both the magnetic and the electrical properties of the material. Furthermore, the technique makes it possible to get spatially resolved data and hence a map of the domain structure. In the electric dipole approximation of, nonlinear optical SHG, the coupling of incident light $E(\omega)$ with frequency $\omega$ to the induced polarization $P(2\omega)$ in the material at frequency $2\omega$, can be described by $P_i(2\omega) = \epsilon_0 \chi_{ijk} E_j(\omega) E_k(\omega)$, [26]. The symmetry of the material defines the set of non-zero tensor components $\chi_{ijk}$. In the case of inversion symmetry all tensor components $\chi_{ijk}$ are equal to zero and no SHG signal can be observed. The SHG data shown in this thesis were measured in collaboration with VERA CAROLUS using a magnetic-field and low-temperature SHG set-up.

**Neutron diffraction measurements**

Neutron diffraction is a non-destructive technique for determining the atomic positions in a crystalline material. Since neutrons carry a magnetic moment, their diffraction is sensitive to the magnetic ordering of the atoms investigated. For ferromagnetic order, where the magnetic and the crystal lattice coincide, the magnetic contribution is observed as a change in the intensity of the magnetic Bragg peaks. Due to the great penetration depth and direct interaction with the nucleus, neutron diffraction is suited to analyzing materials containing atoms with widely varying atomic number.

**2.4 Heat capacity measurements**

Heat capacity [J/K] (specific heat capacity [J/kgK]) is of fundamental interest since it shows the caloric properties of a ma-
2.4 Heat capacity measurements

Material. It represents the ability of a material to absorb or store heat. The heat capacity is defined by

\[ C = \frac{\delta Q}{dT} = T \frac{dS}{dT}, \]  \hspace{1cm} (2.1)

as the ratio between the amount of heat \( \delta Q \) added to a material, and the corresponding increase in its temperature \( dT \). The heat capacity is therefore connected to the change in entropy \( dS \). The heat capacity contains electronic, lattice and magnetic contributions and can be expressed in a power series

\[ \frac{C}{T} = \gamma + \beta T^2 + \beta_5 T^4 + \beta_7 T^6 + \ldots + \eta T^p, \]  \hspace{1cm} (2.2)

where \( p \) depends on the type and dimensionality of magnetism. At the phase transition the heat capacity shows critical behavior and \( C_M \propto |t|^{-\alpha} \), with \( t = (T - T_N)/T_N \). An example for the different contributions, namely lattice and magnetic, to the molar specific heat of MnF\(_2\) is shown in figure 2.10. A common technique used to measure heat capacity is the relaxation method, where a heat pulse is applied to a material and the relaxation of the temperature of the material is measured. This method is favorable for low temperature measurements since relaxation times are short. At room temperature, where relaxation times are longer, this method is very time consuming. An alternative could be to use a microcalorimeter where the amount of sample is reduced to the micro- or even nanoscale and relaxation times are shorter.

![Figure 2.10: Molar specific heat of MnF\(_2\) showing the magnetic phase transition evident from a lambda-shaped kink. Underneath the specific heat of the lattice system not undergoing a phase transition is shown. Taken from Reference [27].](image)
2.5 Dielectric measurements

Measurements of the relative dielectric constant (or relative permittivity) $\varepsilon_r$ and the electrical polarization $P$ give important information on the electrical properties of functional materials. The dielectric constant $\varepsilon = \varepsilon' + i\varepsilon''$ ($D = \varepsilon E$) is a complex number with a real part $\varepsilon'$ and an imaginary part $\varepsilon''$ representing losses. The real part of the dielectric constant describes the ability of the electric material to store energy. The dimensionless relative dielectric constant is defined by the ratio $\varepsilon_r = C/C_0 (= \varepsilon/\varepsilon_0)$ between capacitance $C$ of the material and the capacitance $C_0$ of vacuum. The capacitance per area $C_A$ for a linear dielectric with uniform charge density $\sigma$ can be calculated from

$$C_A = \frac{\sigma}{V} = \frac{\varepsilon_0 \varepsilon}{d}, \quad (2.3)$$

with voltage $V$ and thickness $d$. Measurements of the relative dielectric constant are done on samples with capacitor geometry using a four-wire measurement set-up. The capacitance is measured using an impedance analyzer or LCR meter and the relative dielectric constant can be calculated.

The induced electrical dipole moment is given by $p = \alpha \varepsilon_0 E$ and is related to the electrical polarization $P = \sum p_i \approx n p = \chi \varepsilon_0 E$; ($D = P + \varepsilon_0 E$). The polarization of a material appears as a surface charge density $\sigma_n = P \cdot n_s$, with the surface normal vector $n_s$. The polarization can obtained by pyroelectric current measurements. A sketch of the experimental set-up is shown in figure 2.11. The sample is prepared as a thin plate typically 100 $\mu$m - 500 $\mu$m thick and electrodes are applied to both sides. Then the sample can be cooled under applied electrical- or magnetic field (“poling”). During this process the direction of the electrical field is given by the capacitor geometry whereas the direction of the magnetic field can be adjusted freely (see figure 2.11a). After cooling, the pyroelectric current can be measured as a function of time during reheating. Integration over time yields the electrical polarization $P$.

2.6 Raman spectroscopy

Inelastic light-scattering spectroscopy has become an important tool for studying the physical properties of functional materials. It can be used to give information about different kinds of excitations, such as magnetic exictation (magnons), and can probe the coupling between these excitations. An introduction to the field can for example be found in the book ”Light Scattering in Magnetic Solids” by M. COTTAM and D. LOCKWOOD [28].
2.6 Raman spectroscopy

The Raman effect was experimentally discovered by C. V. Raman in 1928 [29] after being theoretical prediction by A. Smekal in 1923 [30]. The effect is an inelastic light scattering process $\omega_0 \rightarrow \omega_0 + \omega_R$ in which the frequency of the incident light $\omega_0$ is shifted by $\omega_R = -\omega_S$ (Stokes) or $\omega_R = +\omega_{AS}$ (anti-Stokes), cf. figure 2.12. $\omega_R$ corresponds to the eigenfrequency of a vibrational or rotational mode of the substance. In a classic picture the Raman effect can be described by a modulation of the incident light with the eigenfrequency of the substance. The oscillating dipole moment is $\mu = \alpha E = \alpha E_0 \cos(\omega_0 t)$ and the polarizability $\alpha$ reads $\alpha = \alpha_0 + \alpha_1 \sin(\omega_R t)$. It follows that Raman lines only occur if the polarizability $\alpha$ is changed during the scattering process. It is possible to distinguish between spontaneous Raman scattering and induced Raman scattering in which the intensity of the Stokes lines increase exponentially with the incident light. The intensity of Raman scattered light is given by

$$I_S \sim I_0 L \left( \frac{d\alpha}{dq} \right)^2 \left( \frac{1}{\lambda} \right)^4,$$

(2.4)

with the wavelength $\lambda$, the intensity $I_0$ of the incident light, the optical path in the sample $L$, and the change of polarizability $d\alpha/dq$. The typical Raman shift for lattice vibrations in a crystalline solid is of the order 100 - 1000 cm$^{-1}$ and the life time of a scattering process is $\tau < 10^{-14}$ s. A detailed introduction to the home-built experimental setup used for measuring Raman spectroscopy under an applied magnetic field, low temperatures and high pressure can be found in appendix A.2.

Pressure is a natural variable, as is temperature. For material science the most interesting pressure ranges from ambient pressure to the order of 3 GPa. High pressure experiments are usually performed using piston pressure cells or diamond anvil pressure cells (DAC). Piston pressure cells are suitable for transport and magnetic measurements in a pressure range up to about 1 GPa. The use of DACs allows pressures in the order of 10 - 100 GPa and the possibility of performing optical measurements, for example Raman spectroscopy.
This Chapter is devoted to the study of magnetocaloric materials, which are particular interesting for heating and cooling applications. First, a short introduction to the topic is given and the theoretical background is presented. Second, results on the characterization of promising magnetocaloric materials are surveyed. Finally, our results are summarized and a future perspective is given.

3.1 Introduction to magnetocaloric materials

A main challenge for today’s research is to solve the world’s energy issue. This can be accomplished by developing new or improving established energy sources as well as reducing our energy consumption. Refrigeration and air-conditioning systems are major and increasing consumers of electric energy worldwide. Novel refrigeration and air-conditioning systems based on the magnetocaloric effect have the potential to be more energy effective and environmental friendly than current gas compression/expansion based systems [31].

The magnetocaloric effect (MCE) is known as the temperature change in a magnetic material when it is subjected to a change in the magnetic field. The effect was discovered in pure iron by E. Warburg in 1881 [6] and theoretically described by P. Weiss & A. Piccard in 1918 [32]. In 1926-27 P. Debye and W. Giauque proposed adiabatic demagnetization of paramagnetic salts in order to reach temperatures far below 1 K [33], [34].

In general, thermomagnetic energy transformation and magnetic refrigeration/heating has great potential and certain advantages [35]. For instance, the cooling/heating power per
3.2 Fundamentals of magnetocaloric materials

3.2.1 Principle of the magnetocaloric effect

The origin of the magnetocaloric effect is the coupling between the spin system biased by the applied magnetic field and the lattice vibrations of the material. In general, all magnetic materials exhibit magnetocaloric effects. The maximum magnetocaloric effect for materials undergoing a para- to ferromagnetic phase transition is around the transition temperature. For paramagnetic materials the maximum is at low temperatures.

A magnetic-refrigerator working cycle can be used to obtain a basic understanding of the magnetocaloric effect and is presented in figure 3.1. Initially, the magnetic moments are oriented randomly (I) and the magnetocaloric material is at temperature $T(I) = T_0$. By applying a magnetic field the magnetic moments are aligned (II), which results in heating of the magnetic material to $T(II) > T_0$. (The heating or cooling of the magnetocaloric material under application or removal of a magnetic field is discussed in detail in chapter 3.2.1.) Next, the magnetic field is kept constant and heat is removed from the magnetocaloric material to its surroundings by a heat-transfer unit volume for a solid magnetic material is much larger than for a gaseous medium used in conventional gas compression-expansion-based cooling/heating techniques. This is due to the density of a solid being higher compared to a gaseous medium. Additionally, a magnetic cycle can reach close to 100% Carnot efficiency over a very broad temperature range from a few K to several 100 K.

Apart from the utilization of magnetocaloric materials in magnetic refrigeration, other applications such as air conditioning, power generation or power transformation are conceivable uses and have been discussed in literature [35–37]. Another interesting aspect in the study of the magnetocaloric effect and magnetocaloric materials is a fundamental understanding and characterization of magnetic phase transitions (see e.g. Ref. [38] and section 3.5).

All magnetocaloric applications rely on the quality and performance of the magnetocaloric material used. A study of these materials with focus on a profound understanding of the underlying processes is therefore crucial and an important motivation of this work. This thesis presents a study on magnetocaloric materials based on Fe$_2$P iron phosphide compounds and a comparison of the magnetic and magnetocaloric properties of geological and synthetic samples of melanostibite.
medium, until $T(III) \approx T_0$. The magnetic field is then removed and the magnetic moments randomize (IV), leading to cooling of the magnetic material to $T(IV) < T_0$. Finally, heat from the system to be cooled is extracted using a heat-transfer medium.

**General thermodynamic approach**

The concept of entropy can be used to understand the temperature changes which arise in magnetocaloric materials. In statistical physics the entropy $S$ is defined as a measure of the accessible phase space volume under certain macroscopic conditions. Therefore, it represents the number of accessible states of the system. The larger the entropy of a system, the more uncertain the microscopic state, the less information is known about the system, and the greater its microscopic disorder.

The total entropy, $S_{tot}$, of a magnetic material can be divided into three main parts: (1) the magnetic entropy part, $S_M$, due to degrees of freedom in the electron spin system; (2) the lattice entropy part, $S_{lat}$, due to lattice vibrations (phonons) in the system; and (3) the electronic entropy part, $S_{elec}$, due to free (conduction) electrons in the system [8]. In general, all contributions to the total entropy are functions of temperature $T$, field $H$, and pressure $p$. By assuming constant pressure and ignoring the influence of the magnetic field on the lattice- and electronic entropy part the total entropy reads

$$S_{tot}(H, T) = S_M(H, T) + S_{lat}(T) + S_{elec}(T). \quad (3.1)$$

For an adiabatic process the total entropy of the system remains constant ($S_{tot} = \text{const}$). An applied magnetic field results in a finite magnetization which reduces the magnetic entropy part. Since the process is driven under adiabatic conditions the lattice- and electronic entropy part increases. In figure 3.2, the total entropy $S = S_{tot}$ is shown schematically as a function of temperature. Increasing the magnetic field from $H_1$ to $H_2$ reduces the magnetic entropy by $\Delta S_M$ and increases the temperature by $\Delta T_{ad}$. The equations to calculate $\Delta T_{ad}$ and $\Delta S_M$ can be derived from thermodynamical relations, as shown e.g. in the book by TISHIN AND SPICHKIN [40], and the equations read:

$$\Delta T_{ad} = -\mu_0 \int_{H_1}^{H_2} \frac{T}{C_{H,P}} \left( \frac{\partial M}{\partial T} \right)_{H,P} dH, \quad (3.2)$$

and

$$\Delta S_M = \mu_0 \int_{H_1}^{H_2} \left( \frac{\partial M}{\partial T} \right)_{H,P} dH. \quad (3.3)$$
3.2.2 Magnetic phase transitions

The entropy $S$ is connected to the specific heat via

$$dS = \frac{\delta Q}{T}, \quad (3.4)$$

and

$$C_x = \left(\frac{\delta Q}{dT}\right)_x \frac{\delta Q=TdS}{x} \Rightarrow C_x = T \left(\frac{\partial S}{\partial T}\right)_x. \quad (3.5)$$

The magnetization (for systems with a para- to ferromagnetic phase transition) decreases with increasing temperature, producing a negative derivative of the magnetization with respect to the temperature $\left(\frac{\partial M}{\partial T}\right)$). This results in a negative magnetic entropy change and a positive adiabatic temperature change. From equation 3.2 one can conclude that the adiabatic temperature change and thereby the MCE is larger for

- a large change of the magnetic field $H_i \approx 0 \ll H_f$,
- a large $\left|\frac{\partial M}{\partial T}\right|$ which is given in the vicinity of a sharp phase transition,
- a small specific heat $C_{H,P}$ and higher $T$.

In certain magnetic systems with inverse transition, for example from a ferromagnetic to an antiferromagnetic state, the inverse magnetocaloric effect is observed. In that case the magnetic material exhibits a positive magnetic entropy change and a negative adiabatic temperature change when applying a magnetic field.

3.2.2 First and second order magnetic phase transitions

In first-order magneto-structural phase transitions (FOMT), the magnetic and the crystal sublattice couple and both undergo a transition, meaning that atoms are shifted during the transformation. This is evident in FOMT materials by a hysteresis effect, shown in figure 3.3, as a difference in magnetization vs. temperature data measured on cooling and heating. For a second-order magnetic phase transition (SOMT), only the spin system is changed under the phase transition, and direct and indirect $\Delta T_{ad}$ measurements are usually in very good agreement [31], see section 3.2.4.

In terms of evaluating the nature of a magnetic phase transition by means of magnetic measurements, a technique proposed by A. Arrott [41, 42] can be used. The field dependence of the magnetization is expressed as a power series
Magnetocaloric materials

Figure 3.5: Relationship between a) magnetization $M$, b) specific heat $C$, and c) magnetic entropy change $\Delta S_M$, adiabatic temperature change $\Delta T_{ad}$.

3.2.3 Magnetocaloric materials and applications

Magnetocaloric materials

What are the desired properties of a magnetocaloric material for possible applications? From the thermodynamic equations 3.2 and 3.3 in chapter 3.2.1, one can deduce, that to obtain a comparably large MCE, the phase transition from the paramagnetic to ferromagnetic phase - under an applied field of some Teslas - should occur in a narrow temperature range. In terms of the energy involved, it is preferable to have a material with high saturation magnetization (magnetic ions with high moments) in the ferromagnetic phase. Usually, materials undergoing a FOMT show higher $\Delta S_M$ values than materials undergoing a SOMT, but the measured $\Delta T_{ad}$ is of comparable size for applied fields up to 2 T (see figure 3.6). TISHIN [44] used a simple estimation based on Gibbs free energy to compare the contribution of exchange interaction energy, magnetoelastic interaction energy, anisotropy energy and magnetic Zeeman energy to the MCE in FOMT materials. He found that the main contribution to the magnetic entropy change in

$$H = (1/\chi) M + \beta M^3 + \gamma M^5 + \cdots.$$  
At the Curie point $T_C$ $(1/\chi) = 0$ is valid and the field dependence can be rewritten as $H = \beta M^3 + \gamma M^5 + \cdots$ which should result in straight lines in the “critical region” when the data are plotted as $M^2$ vs. $H/M$. In a more general approach, the equation of state can be expressed as

$$\left(\frac{H}{M}\right)^{1/\gamma} = \frac{T - T_C}{T_1} + \left(\frac{M}{M_1}\right)^{1/\beta}, \quad (3.6)$$

with $\gamma$, $\beta$, $T_1$, $M_1$ being a set of parameters which define the phase transition of the system being investigated. In a mean field approach $\gamma = 1$ and $\beta = 1/2$. By plotting the experimental $M(T,H)$ data using equation 3.6 the Curie temperature $T_C$ and the critical exponents can be determined. Nevertheless, the criterion is not unique and one can often find several combinations of possible values for the exponents $\gamma$ and $\beta$. Furthermore, there is a dependence on the chosen width of the “critical region”. Analyzing the slope of data plotted as $M^2$ vs. $H/M$ indicates the order of phase transition. A straight line with positive slope implies a second-order-continuous phase transition, whereas an S-shaped negative slope suggests a first-order-discontinuous phase transition (“Banerjee criterion”) [43], compare figure 3.27 and 3.36.
3.2.3 Magnetocaloric materials and applications

Figure 3.6: Comparison of the magnetic entropy change $\Delta S_M$ (left graph) and the adiabatic temperature change $\Delta T_{ad}$ (right graph) for some selected materials. Taken from Reference [31].

A FOMT material comes from the change in energy of the exchange interaction. The change is associated with a rearrangement of the band structure due to a change in the interatomic distances. Furthermore, such materials show a strong dependence of the Curie temperature with applied pressure. Hence materials with a strong dependence of the exchange parameters on the interatomic distance possess potentially good magnetocaloric properties.

Zerev et al. [45] theoretically estimated the maximal accessible $\Delta T_{ad}$ values to be $\Delta T_{ad} \approx 18 \text{ K/T}$. In comparison, gadolinium (Gd) metal shows a $\Delta T_{ad}$ of about (2.6-2.9) K/T and FeRh 6.5 K/T. In figure 3.5, the schematic behavior of the magnetocaloric effect near the magnetic phase transition for a FOMT material in a 1 T field is sketched. The inflection point of the magnetization data as a function of temperature corresponds to the peak in $\Delta S_M$ and $\Delta T_{ad}$. For increasing magnetic field, the inflection point is shifted towards higher temperatures. $\Delta S_M$ and $\Delta T_{ad}$ have their maximum slightly above the Curie temperature $T_C$.

Materials undergoing a magnetostructural transition with high values for $\Delta S_M$ are often referred to as “giant” magnetocaloric materials. In figure 3.6 a comparison of the adiabatic temperature change $\Delta T_{ad}$ and the magnetic entropy change $\Delta S_M$ for selected materials is shown. It is obvious from the $\Delta T_{ad}$ plot (figure 3.6: right graph) that in the magnetic field range up to about 2 T, the difference between the materials is marginal. For instance, if one compares MnAs to Gd for a magnetic field change of 2 T, then MnAs gives a 5 times higher
\( \Delta S_M \) than Gd; whereas \( \Delta T_{ad} \) is almost identical. Nevertheless, using only the peak value in \( \Delta S_M \) is not adequate to evaluate whether a magnetocaloric material is suitable for applications or not.

**Table 3.1:** Overview of selected magnetocaloric materials (PT: phase transition)

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure type</th>
<th>( T_{PT} ) (PT) (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>hcp</td>
<td>294 (SOMT)</td>
<td>[46]</td>
</tr>
<tr>
<td>Gd\textsubscript{5}(Si\textsubscript{2}Ge\textsubscript{2})</td>
<td>Sm\textsubscript{5}Ge\textsubscript{4}</td>
<td>276 (FOMT)</td>
<td>[47]</td>
</tr>
<tr>
<td>Fe\textsubscript{0.49}Rh\textsubscript{0.51}</td>
<td>CsCl</td>
<td>(~316) (FOMT)</td>
<td>[48]</td>
</tr>
<tr>
<td>MnAs</td>
<td>NiAs</td>
<td>318 (FOMT)</td>
<td>[31, 49]</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}As\textsubscript{x})</td>
<td>Fe\textsubscript{2}P</td>
<td>293 (FOMT)</td>
<td>[39, 50]</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}Ge\textsubscript{x})</td>
<td>Fe\textsubscript{2}P</td>
<td>288 (FOMT)</td>
<td>[51]</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}Si\textsubscript{x})</td>
<td>Fe\textsubscript{2}P</td>
<td>297 (FOMT)</td>
<td>[52]</td>
</tr>
<tr>
<td>La(Fe\textsubscript{0.89}Si\textsubscript{0.11})\textsubscript{13}H\textsubscript{1.3}</td>
<td>NaZn\textsubscript{13}</td>
<td>291 (FOMT)</td>
<td>[44, 53]</td>
</tr>
<tr>
<td>La\textsubscript{0.6}Ca\textsubscript{0.4}MnO\textsubscript{3}</td>
<td>CaTiO\textsubscript{3}</td>
<td>263 (SOMT)</td>
<td>[31, 54]</td>
</tr>
<tr>
<td>Ni\textsubscript{55.2}Mn\textsubscript{18.6}Ga\textsubscript{26.2}</td>
<td>BiF\textsubscript{3}</td>
<td>315 (FOMT)</td>
<td>[31, 55]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Material</th>
<th>( \Delta T_{ad} )  ( {\mu\Delta H} ) (K), (T)</th>
<th>( \Delta S_M )  ( {\mu\Delta H} ) (J/kgK), (T)</th>
<th>( T_{Hyst} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>5.7, {2}</td>
<td>-5, {2}</td>
<td>(~0)</td>
</tr>
<tr>
<td>Gd\textsubscript{5}(Si\textsubscript{2}Ge\textsubscript{2})</td>
<td>7.4, {2}</td>
<td>-14, {2}</td>
<td>2-14</td>
</tr>
<tr>
<td>Fe\textsubscript{0.49}Rh\textsubscript{0.51}</td>
<td>8.4, {2.1}</td>
<td>-11.7, {2.1}</td>
<td></td>
</tr>
<tr>
<td>MnAs</td>
<td>5, {2}</td>
<td>-30, {5}</td>
<td>6.5</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}As\textsubscript{x})</td>
<td>4.2, {1.45}</td>
<td>-14.5, {2}</td>
<td>4</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}Ge\textsubscript{x})</td>
<td>2.9, {1}</td>
<td>-20.3, {2}</td>
<td>1</td>
</tr>
<tr>
<td>MnFe(P\textsubscript{1-x}Si\textsubscript{x})</td>
<td>30, {2}</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>La(Fe\textsubscript{0.89}Si\textsubscript{0.11})\textsubscript{13}H\textsubscript{1.3}</td>
<td>6.9, {2}</td>
<td>-24, {2}</td>
<td></td>
</tr>
<tr>
<td>La\textsubscript{0.6}Ca\textsubscript{0.4}MnO\textsubscript{3}</td>
<td>2.1, {3}</td>
<td>-5, {3}</td>
<td></td>
</tr>
<tr>
<td>Ni\textsubscript{55.2}Mn\textsubscript{18.6}Ga\textsubscript{26.2}</td>
<td>1.5, {2}</td>
<td>-20.4, {5}</td>
<td>(~7)</td>
</tr>
</tbody>
</table>
A better parameter for comparing magnetocaloric materials is their refrigerant capacity (cooling capacity), $q$,

$$q = \int_{T_{Cold}}^{T_{Hot}} \Delta S_M(T) dT,$$  

(3.7)

where the temperature spans between the hot $T_{Hot}$ and the cold $T_{Cold}$ side, and the temperature dependence of $\Delta S_M(T)$ are considered. The refrigerant capacity is a measure of the amount of heat that can be transferred between the cold heat load and the warm heat sink in an ideal refrigeration cycle [31]; whereas the $\Delta T_{ad}$ indicates how much the temperature of the magnetocaloric material can be altered by changing the magnetic field. Both quantities need to be considered, when evaluating the applicability of a magnetocaloric material.

In table 3.1, an overview of some magnetocaloric materials is shown with focus on the room temperature range and high magnetocaloric properties.

Applications of magnetocaloric materials

In 1933, W. F. GIAUQUE and D. P. MACDOUGALL [56] used adiabatic demagnetization of gadolinium sulfate $\text{Gd}_2(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ to reach a minimal temperature of 0.25 K. This was one of the first practical application of the MCE.

A first magnetic refrigeration system was demonstrated in 1953-54 by S. COLLINS & F. ZIMMERMAN [57] and, independently, by HEER ET AL. [58]. In 1976, G. BROWN constructed the first room temperature magnetic refrigeration system reaching a no-load temperature difference of 47 K [59]. In 1998, ZIMM ET AL. presented an active magnetic regenerator (AMR) system with 500 W refrigeration capacity, a coefficient of performance $^1$ of 4 for a magnetic field change of 1.5 T and a temperature span of 12 K [60]. This cutting-edge prototype together with the discovery of the large magnetocaloric effect in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [47] and the use of permanent magnets to provide the magnetic field [61], made magnetic refrigeration a promising technology for commercial applications. Over the years, numerous possible applications for magnetocaloric materials have been discussed in the literature (for example magnetic heating, magnetic refrigeration or energy conversion [35–37]).

A major effort in research on magnetocaloric materials during the last two decades has been spent on room-temperature magnetic refrigeration. A $\Delta T_{ad}$ on the order of 3-6 K for a magnetic

$^1$Coefficient of performance (COP): is the ratio of the heat $Q_C$ removed from a cold reservoir $T_{Cold}$ under expending of work $W$; $\text{COP} = \frac{|Q_C|}{W} = \frac{T_{Cold}}{(T_{Hot} - T_{Cold})}$
field change up to 2 T (compare figure 3.6) is not sufficient for domestic refrigerators. To solve this issue, the active magnetic regenerative (AMR) refrigerator was proposed [62]. In such a device a temperature gradient in the magnetocaloric material is used to increase the temperature span between the hot and the cold end. Hence, each section of the magnetocaloric material performs a different thermodynamic cycle. To optimize the performance of such a device, the magnetocaloric working material can be fabricated as a sequence of magnetocaloric elements (Fig. 3.7), each of them having an adjusted working point. For near-room temperature applications the AMR cycle (based on the Brayton cycle) as shown in figure 3.8 is applicable. In the AMR cycle the magnetic material serves not only as a refrigerant but also as a regenerator. The AMR cycle is composed of two iso-field transformations (B-C, D-A) and two quasi-adiabatic transformations (A-B, C-D), for more details see BASSO ET AL. [63].

The magnetocaloric effect increases monotonically with the applied magnetic field. To achieve a large MCE, one needs to provide sufficiently high magnetic fields. However, the use of superconducting magnets is usually confined to laboratories rather than ordinary houses. The use of permanent magnets seems to be the only realistic solution to the problem, but such magnets in the right dimensions can be heavy and expensive. In particular, the need for rare earth metals such as neodymium and gadolinium can become a problem. Neodymium is mainly used for strong permanent magnets (Nd-Fe-B) and, since 0.5-10 kg of Nd will be used in one magnetic refrigerator, the availability and cost of Nd may become prohibitive for magnetic refrigeration applications [64]. Gadolinium is the element with the best magnetocaloric properties and almost all prototypes are based on gadolinium or related alloys. Another challenge is how to make optimal use of the temperature change of the magnetocaloric materials. In a magnetic refrigeration cycle, a heat-transfer medium is needed to transport heat from the cooled heat source to the warm heat sink. A common approach is to use water or a similar liquid as a heat-transfer medium, but this sets limitations on the operational frequency of the refrigeration system which is in the order of 1-5 Hz.

At present, over one hundred different magnetocaloric materials have been studied and there are more than 30 working magnetic refrigerator prototypes in the room-temperature range [64]. Nevertheless, besides some efforts in large scale material synthesis a full commercialization of the MCE has not yet been established.
3.2.4 Direct and indirect methods for determining the magnetocaloric effect

Indirect methods

Indirect methods for determining the MCE are based on magnetization and heat capacity measurements. By using thermodynamic equations the MC properties of a given material can be calculated.

Most of all the investigations published on magnetocaloric materials are based on magnetization measurements and the calculation of magnetic entropy changes. In such isothermal magnetization measurements the magnetization at constant temperature is measured as a function of the magnetic field $M(H)|T$. By use of equation 3.3, $\Delta S_M$ can be calculated. For practical reasons a numerical integration

$$\Delta S_M = \mu_0 \sum_i \left( \frac{M_{i+1} - M_i}{T_{i+1} - T_i} \right) \Delta H \quad (3.8)$$

is used. Equation 3.8 can be used for calculations of the magnetic entropy change for systems with second-order magnetic phase transitions. For first-order magnetic phase transitions the derivative $(\partial M/\partial T)$ can be infinite and $\Delta S_M$ has to be determined differently.

Nevertheless, in experimental first-order systems, the phase transition is broadened, and therefore the derivative of the magnetization with respect to temperature is finite; equation 3.8 may be used to estimate $\Delta S_M$. Problems in real first-order systems in terms of determining the magnetic entropy change arise from the thermal hysteresis (figure 3.3), which can result in too high values for the magnetic entropy change. The calculated magnetic entropy change corresponds to the area enclosed between two isothermal measurements (see figure 3.9).

A solution to the problem was proposed by L. CARON ET AL. [65], introducing a so-called loop method to determine the correct magnetic entropy change. In the regions with thermal hysteresis, history-dependent magnetic states can be observed. It is therefore essential to always cross the phase transition in the same sense as in isofield measurements. This is done by reinitializing the system by bringing it into the paramagnetic state by reheating above $T_C$ prior to each isothermal measurement.

To be able to calculate the adiabatic temperature change, $\Delta T_{ad}$, using equation 3.2, knowledge about the heat capacity of the sample is essential. It is important to mention that $T$ is changed during a change of the magnetic field and $C_{H,P}$ de-
Magnetocaloric materials

depends on the magnetic field. Therefore both quantities need to be taken into account when integrating equation 3.2.

Direct methods

In direct magnetocaloric measurements, the magnetic material is subjected to a magnetic field change and its temperature change, $\Delta T$, is recorded directly using a temperature sensor. The adiabatic temperature change is then given by $\Delta T(T_0, \Delta H) = T_F(H_F) - T_I(H_I)$; ($\Delta H = H_F - H_I$). A sufficiently fast magnetic field change is needed to ensure adiabatic conditions. Two common ways to accomplish this are: (1) measurements using a pulsed or ramped magnetic field with a rate higher than 10 kOe/s, and (2) measurements using a displacement of the magnetic material relative to the magnetic field. A direct $\Delta T$ measurement set-up based on the design published by GOPAL ET AL. [66] was built. A test measurement for a Gd 99.9 wt% sample is shown in figure 3.10. The accuracy of direct measurement techniques is usually in the 5 – 10 % range and depends on the errors in thermometry, setting of the magnetic field, and the quality of the thermal insulation of the sample [67]. Further details concerning direct measurements are given in the appendix A.1.

![Figure 3.10: Adiabatic temperature change during a magnetic field change of 1.1 T for a test sample of Gd 99.9 %. Measured using the equipment described in the appendix A.1.](39)
3.3 Fe\textsubscript{2}P-based magnetocaloric materials

3.3.1 Di-iron phosphide - Fe\textsubscript{2}P

[Image: Crystal structure of Fe\textsubscript{2}P. i) View of the ab-plane along the c axis. ii) View of the pyramidal 3g- and the tetrahedral 3f site. iii) View in the ab-plane.]

Di-iron phosphide, Fe\textsubscript{2}P, crystallizes in a hexagonal structure with space group D\textsubscript{3}\textsuperscript{h} (P\textsuperscript{6}2m) \cite{14} and the unit cell dimensions \( a = 5.8675(2) \) Å and \( c = 3.4581(2) \) Å. The iron atoms occupy two different crystal sites, the 3f-site with four phosphorus atoms surrounding one iron atom (referred to as type-I or tetrahedral site) and the 3g-site with 5 phosphorus atoms surrounding one iron atom (referred to as type-II or pyramidal site). The phosphorus atoms occupy the two dissimilar sites: 2c (type-I) and 1b (type-II). Each Fe(1) site is surrounded by two P(1) and two P(2) atoms, whereas Fe(2) is surrounded by four P(1) and one P(2) atom. The crystal structure is shown in figure 3.11.

Fe\textsubscript{2}P undergoes a first-order para- to ferromagnetic phase transition with a Curie temperature of \( T_C \approx 216 \) K (see e.g. W\textsuperscript{Ä}PPLING ET AL. \cite{68}, FUJI ET AL. \cite{69}, and LUNDGREN ET AL. \cite{70}). The isostructural compounds Ni\textsubscript{2}P and Mn\textsubscript{2}P are paramagnetic and antiferromagnetic (\( T_N = 103 \) K) \cite{12}, respectively. The magnetic properties of Fe\textsubscript{2}P vary significantly with small changes in the composition, external pressure, and alloying elements. Even minor changes in the composition can result in significant changes of the transition temperature. Furthermore, the phase transition for pure Fe\textsubscript{2}P is accompanied by a discontinuous change in the dimensions of the hexagonal unit cell \cite{70}. Specific heat data for Fe\textsubscript{2}P have been reported by BECKMAN ET AL. \cite{71}, compare figure 3.12, and low field magnetization data were published by LUNDGREN AND NORDBLAD \cite{72}.
Figure 3.12: Molar specific heat of Fe$_2$P as a function of temperature. The magnetic transition occurs close to 216 K and resembles a strong first order character. The inset shows a detailed view of the magnetic phase transition region. Adapted from Beckman et al. [71]

The specific heat is dominated by the lattice- and electron contributions and the magnetic part of the heat capacity appears as a sharp phase transition around 216 K. As previously mentioned, Fe$_2$P undergoes a para- to ferromagnetic transition at 216 K. Single crystals of Fe$_2$P can be synthesized in a liquid tin melt, as reported by Andersson et al. [73]. The low magnetic field (1 Oe) magnetization as a function of temperature for a single crystalline sample of Fe$_2$P is shown in figure 3.13 and reveals a phase transition with typical first-order character. The sharp transition contains a hysteresis region of about 0.5 K measured as the difference when recording the magnetization on heating or cooling. These properties agree with the criteria described for FOMT materials in chapter 3.2.3.

The microscopical reason for the metamagnetic transition with strong temperature dependence of an apparent phase transition under applied magnetic field (or on substitution on the pnictide site) has not been clearly understood for a long time. Recently, it has been argued that the exchange field created by the Fe(2) sublattice stabilizes the Fe(1) moments. The disappearance of the Fe(2) moment order at $T_C$ triggers a collapse of the Fe(1) moments and hence gives rise to the metamagnetic behavior [74]. A detailed theoretical description on Fe$_2$P based materials can be found in the PhD thesis by Erna-Krisztina Delczeg-Czirják [75].
3.3.2 The magnetic and magnetocaloric properties of polycrystalline Fe$_2$P

The magnetic and magnetocaloric properties of polycrystalline Fe$_2$P synthesized using the drop synthesis method (cf. chapter 2) are shown in figure 3.14. For increasing applied magnetic fields the phase transition, when defined as the inflection point of the magnetization curve, in Fe$_2$P shifts towards higher temperatures$^2$, as can be seen in figure 3.14a. The magnetic entropy change $\Delta S$ for polycrystalline Fe$_2$P is found to be in the order 4 J/kgK (2 J/kgK) in 5 T (1 T) field change, compare figure 3.14b. The $\Delta S$ vs. $T$ curve shows a sharp rise accompanied by a minor peak around 216 K due to the first-order character of the magnetic phase transition. Both characteristics appear to be rather independent of the applied magnetic field change. From the magnetic field dependence of the $M$ vs. $T$ data shown in figure 3.14a an increase of the transition temperature with the magnetic field was found. This increase deviates from a linear behavior for magnetic fields below 3 T. The field dependence is also reflected in a strong broadening of the magnetic entropy change curves to higher temperatures for increasing magnetic field changes.

$^2$The transition temperature $T_C$ is only defined in the limit $H \to 0$. For $H \gg 0$ an “apparent” transition is observed and it is common experimental practice to characterize that transition by the inflection point of the magnetization vs. temperature curve.
3.3.3 The anisotropic magnetocaloric properties of Fe$_2$P single crystals

The anisotropic properties of a Fe$_2$P single crystals are shown in figure 3.16. The measurements shown in figure 3.16 were performed along the needle-shaped Fe$_2$P single crystal (long side $\approx$ c-axis; aspect ratio $\sim$ 1/15).

The magnetic moments are oriented along the c-axis direction. The magnetization data for the c-axis direction mimics to the results found for the polycrystalline sample shown in
3.3.3 The anisotropic magnetocaloric properties of Fe$_2$P single crystals

Figure 3.15: Magnetic properties of Fe$_2$P single crystal for different applied magnetic fields (cf. ◊ = 0.01 T, ◦ = 0.1 T, and □ = 1 T). Black symbols indicate measurements with the magnetic field applied along the c-axis and red open symbols with the magnetic field applied perpendicular to the c-axis. The insets show: a) $M$ vs. $H$ and b) $dM/dT \cdot H$ vs. $T$.

When applying the magnetic field perpendicular to the c-axis, a competition between the temperature-driven spin alignment along the c-axis direction and the applied magnetic field perpendicular to the c-axis can be observed. For temperatures above the transition temperature ($T > T_C$) the magnetic behavior is controlled by the demagnetization factor of the sample. For a needle with c-axis orientation the demagnetization factors are $N_{\parallel c} \sim 0$ and $N_{\perp c} \sim 1/2$. Below the transition temperature ($T < T_C$) both the magnetocrystalline and shape (demagnetization) anisotropy govern the magnetic behavior.
The magnetocaloric properties obtained from $M$ vs. $H$ measurements are presented in figure 3.16. The magnetic entropy change along the $c$-axis closely mimics the polycrystalline case. When applying the magnetic field perpendicular to the $c$-axis the magnetic entropy change is significantly altered. First, both a negative and a positive magnetic entropy change are observed. The expected negative $\Delta S_M$ occurs in the same temperature region as for $H \parallel c$. The positive magnetic entropy change on the other hand occurs at lower temperatures. The maximal $\Delta S_M$ value in the 5 T field change decreases by a factor of $3/4$ to approximately 3 J/kgK. For a magnetic field change of 1 T, $\Delta S$ decreases by a factor of $1/4$ if compared to the $H \parallel c$ value.
3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

Even though the observed entropy changes are not very large it can be speculated that the anisotropic behavior of the magnetocaloric effect could be utilized. In the next section the focus will be put on improving the magnetocaloric properties of Fe$_2$P by element substitution.

### 3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

In terms of tuning the magnetocaloric properties, most studies focus on Mn substitution on the Fe site to enhance the saturation moment per f.u., and use different substitutes on the P site such as As, Ge, Si [39, 76, 77] for tuning the Curie temperature to room temperature. Prior studies on the structural and magnetic properties of (Fe$_{1-y}$Mn$_{y}$)$_2$P and Fe$_2$P$_{1-x}$Si$_x$ were published by Srivastava et al. [78] and Jernberg et al. [79].

Substituting Si on P sites, the para- to ferromagnetic transition temperature increases and a structural transformation from hexagonal to orthorhombic phase is observed. The distribution of Si on the two P sites in the hexagonal phase is found to be close to random [79]. Replacing Mn on the Fe sites, the crystal structure changes from hexagonal Fe$_2$P type to orthorhombic Co$_2$P type (at approx. 24 % Mn). For Mn-rich compositions (> 70 % Mn) of (Fe,Mn)P the hexagonal crystal structure is regained [78]. Concerning the magnetic order for increasing Mn content on the Fe sites, a transition from ferro- to antiferromagnetism is observed. The transition temperature of FeMnP was found to be $T_N = 265$ K.

A preliminary phase diagram for FeMnP$_{1-x}$Si$_x$ was given by Cam Thanh et al. [77] and indicates a structural phase transition from an orthorhombic (space group Pmna, No. 62) to a hexagonal structure (space group P62m, No. 189) for a silicon content of $x \approx 0.25$. For higher contents of silicon above $x \approx 0.70$, the structure is expected to be of orthorhombic type. Nevertheless, it is interesting to note that substitution of Si for P in FeMnP (Si/P ratio around one) favors a hexagonal phase and ferromagnetic ordering, in contrast to FeMnP which is orthorhombic and antiferromagnetic.

In the following sections, the magnetic and magnetocaloric properties for different compositions of (Fe,Mn)$_2$(P,Si) are discussed in more detail.
The nominal symmetric composition - FeMnP$_{0.5}$Si$_{0.5}$

An interesting starting point is the nominal symmetric composition FeMnP$_{0.5}$Si$_{0.5}$, where half the Fe has been replaced by Mn and half the P by Si. In the earlier work by CAM THANH ET AL. [77] that composition was shown to exhibit good magnetocaloric properties around room temperature. A more thorough study based on samples fabricated using the drop synthesis method (cf. chapter 2.1.1) is presented in this section and reveals different physical properties compared to those reported in Ref. [77]. FeMnP$_{0.5}$Si$_{0.5}$ is the nominal composition determined from the weighted ingots before the synthesis and the weight of the synthesized sample. The real composition was obtained on the refined occupancies extracted from the neutron powder diffraction data and was found to be Fe$_{1.018(3)}$Mn$_{0.982(3)}$P$_{0.5}$Si$_{0.5}$. In the following discussion the nominal composition FeMnP$_{0.5}$Si$_{0.5}$ is used. The results presented in this section were partly published in Paper II and Paper III.

Magnetic properties: The magnetic properties of FeMnP$_{0.5}$Si$_{0.5}$ are presented in figure 3.17. FeMnP$_{0.5}$Si$_{0.5}$ undergoes a first-order para- to ferromagnetic phase transition at 382 K (from low magnetic field magnetization data measured on cooling). A thermal hysteresis in the order 12 K for the first temperature cycle and about 7 K for the second was

![Figure 3.17: Magnetization as a function of temperature measured in a 5 T field for FeMnP$_{0.5}$Si$_{0.5}$. One can observe a difference between the first and second heating and cooling cycle.](image-url)
3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

measured. This so-called virgin effect is observed on first time cooling or heating and has not yet been explained. The saturation magnetization for FeMnP$_{0.5}$Si$_{0.5}$ at room temperature was measured to 3.9 $\mu_B$/f.u. (156 emu/g) and at 5 K to 4.4 $\mu_B$/f.u. (178 emu/g), which is significantly higher than the 3.8 $\mu_B$/f.u. reported in Ref. [77]. From density functional calculations (DFT) 4.2 $\mu_B$/f.u. is predicted [80].

Figure 3.18: XRD-patterns ($\lambda = 1.540598$ Å) of FeMnP$_{0.5}$Si$_{0.5}$ showing the structural transition occurring at approximately 385 K. Adapted from Paper II.

X-ray - and neutron powder diffraction: The XRD analysis for FeMnP$_{0.5}$Si$_{0.5}$ at 296 K confirmed the single-phase quality of the sample. FeMnP$_{0.5}$Si$_{0.5}$ crystallizes in the hexagonal Fe$_2$P-type structure, space group P6$_2$m with lattice parameters $a=6.2090(3)$ Å, $c=3.2880(3)$ Å. In figure 3.18, XRD-patterns for FeMnP$_{0.5}$Si$_{0.5}$ in the temperature range from 363 to 403 K are shown. It was found that FeMnP$_{0.5}$Si$_{0.5}$ undergoes an isostruc-
Table 3.2: Lattice parameters of FeMnP_{0.5}Si_{0.5} measured at 296 K and 450 K refined from XRD data, $\lambda = 1.540598$ Å. Adapted from Paper II.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å³)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>6.2090(3)</td>
<td>3.2880(2)</td>
<td>109.78(2)</td>
<td>0.5296(1)</td>
</tr>
<tr>
<td>450</td>
<td>6.0830(8)</td>
<td>3.4507(9)</td>
<td>110.58(4)</td>
<td>0.5672(1)</td>
</tr>
</tbody>
</table>

Structural transition between $\sim 373$ K and 393 K. The structural transition occurs in the vicinity of the magnetic phase transition. At the highest measured temperature, 450 K, the $a$-axis has decreased by $\sim 2\%$ and the $c$-axis has increased by $\sim 5\%$ when compared to 296 K values, cf. table 3.2. The changes in the $c/a$ ratio and the volume correspond to an increase of $\sim 7\%$ and 1%, respectively.

The magnetic structure of FeMnP_{0.5}Si_{0.5} is derived from neutron powder diffraction data at 296 K and 450 K, shown in figure 3.20. Structure refinements of the NPD data indicate that the Mn atoms prefer to be situated in the pyramidal 3g site. An almost perfect ordering of Mn and Fe on their respective sites (3g and 3f site, respectively) with the moments pointing in the $a$-axis direction was observed, compare figure 3.19. In FeMnP_{0.5}As_{0.5} [81] a similar alignment of the magnetic moments was reported, whereas in FeMnP_{0.7}As_{0.3} the moments deviate from the $c$-axis by 50°.

Figure 3.19: The crystal structure of one unit cell of FeMnP_{0.5}Si_{0.5}. The tetragonal (3f) and pyramidal (3g) metal sites have been highlighted with dashed blue lines. The magnetic moments of both the Fe (3f) and Mn (3g) magnetic ions are found to be oriented in the $a$-axis direction. The length of the arrows correspond to the magnitude of the magnetic moments.
3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

**Figure 3.20:** Neutron powder diffraction data and refinements for FeMnP$_{0.5}$Si$_{0.5}$ at 296 K and 450 K. The differences in intensity and position of the Bragg peaks are due to the combined magnetic and structural transition at $\sim$385 K. The peaks with the highest magnetic intensity are marked with an arrow. Adapted from Paper II.

The magnetic moments are found to be 1.9(1) $\mu_B$ and 2.5(1) $\mu_B$ on the Fe (3f) and Mn (3g) sites, respectively. The substitution of Fe by Mn hence increases the magnetic moment on both sites. The magnetic moment of the Fe atoms (3f) increases by $\sim$0.6 $\mu_B$ and the Mn moments (3g) with $\sim$0.8 $\mu_B$, compared to the site-specific moments in Fe$_2$P. The total magnetic moment of FeMnP$_{0.5}$Si$_{0.5}$ amounts to 4.4(2) $\mu_B$ and the magnetic symmetry group was found to be Cm2m. The occupancy of P and Si atoms on the two Fe$_2$P phosphorus sites (cf. figures 3.11 and 3.19) was found to be random.
Table 3.3: Magnetic state, Fe saturation magnetic moment and interatomic average distances for tetrahedral Feₜ in FeMX with Fe₂P structure, M_p = pyramidal Fe or Mn and X = P, Si and As. Adapted from Paper II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magn. state (T_C)</th>
<th>Fe_t sat. mom. (μ_B)</th>
<th>V (Å³)</th>
<th>Fe_t-X (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂P</td>
<td>PM (295 K)</td>
<td>-</td>
<td>103.1</td>
<td>2.255</td>
</tr>
<tr>
<td></td>
<td>FM (77 K)</td>
<td>1.03</td>
<td>102.9</td>
<td>2.253</td>
</tr>
<tr>
<td>FeMnP₀.₇As₀.₃</td>
<td>PM (250 K)</td>
<td>-</td>
<td>110.7</td>
<td>2.311</td>
</tr>
<tr>
<td></td>
<td>FM (100 K)</td>
<td>1.25</td>
<td>110.2</td>
<td>2.312</td>
</tr>
<tr>
<td>FeMnP₀.₅Si₀.₅</td>
<td>PM (450 K)</td>
<td>-</td>
<td>109.8</td>
<td>2.312</td>
</tr>
<tr>
<td></td>
<td>FM (296 K)</td>
<td>1.65</td>
<td>110.6</td>
<td>2.317</td>
</tr>
</tbody>
</table>

The interatomic distances for paramagnetic and ferromagnetic Fe₂P, FeMnP₀.₇As₀.₃ and FeMnP₀.₅Si₀.₅ are shown in table 3.3. It is found that the cell volume, the average near Feₜ–X distances (where Feₜ is the tetrahedral Fe(1) site and X represents the pnictite site) and Feₜ–M_p do not change significantly. Nevertheless, a large change in the interatomic Feₜ–Feₜ distances is observed for the high moment cases of FeMnP₀.₇As₀.₃ and FeMnP₀.₅Si₀.₅.

An x-ray magnetic circular dichroism (XMCD) study by TAKEDA ET AL. [83] on Fe₁.₁Mn₀.₉P₀.₅₅As₀.₄₅ found the Fe and Mn magnetic ions oriented in the same direction, with Mn moments being larger than the Fe moments. Mn was found to be in a Mn²⁺ state and Fe ions were found to be a mixture of Fe²⁺ and Fe³⁺. Preliminary measurements for the (Fe,Mn)₂(P,Si) were performed and the results are similar to those by TAKEDA ET AL.

Mössbauer spectroscopy: In figure 3.21, the Mössbauer spectra for the FeMnP₀.₅Si₀.₅ in the paramagnetic (upper graph) and ferromagnetic (lower graph) regimes are shown. The Mössbauer spectra in the paramagnetic regime (upper panel)
3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

Figure 3.21: Mössbauer spectra for FeMnP$_{0.5}$Si$_{0.5}$ measured at 295 and 440 K. Inset: Magnetic hyperfine field distribution at 295 K. Adapted from Paper III

shows a broad single line centered at around 0.17 mm/s with an average electric quadrupole splitting of 0.32 mm/s. This indicates that Fe populates the tetrahedral 3f site since any Fe located at the pyramidal 3g site would result in a marked shoulder on the high velocity resonance line [84, 85]. From the ferromagnetic spectra at 295 K (Fig.3.21 lower panel) a well resolved six-line pattern together with a central broad line is evident. The magnetic hyperfine field for Fe 3f atoms at 295 K is found to be $B_{hf} = -20.6(3)$ T and the isomer shift is $\delta = 0.30(1)$ mm/s. At 5 K, $B_{hf}$ was found to be -22.8(3) T. Fe$_2$P in comparison has a magnetic hyperfine field of $B_{hf}(\text{Fe(3f),Fe(3g)}) = (-11.4, -18.0)$ T [86] and a saturation moment of 2.94 $\mu_B$/f.u. with the site-specific magnetic moments of $m_{spec}(\text{Fe(3f),Fe(3g)}) = (1.03, 1.91)\mu_B$. Hence a strongly enhanced magnetic hyperfine field for Fe on the tetrahedral 3f site in FeMnP$_{0.5}$Si$_{0.5}$, accompanied by a correspondingly high saturation moment of 4.4 $\mu_B$/f.u. at 5 K, obtained from magnetic measurements, is found. A comparison of the magnetic hyperfine fields for different Fe$_{2-x}$Mn$_x$P$_{1-y}$Si$_y$ compounds is shown in figure 3.22.

The relation between the magnetic hyperfine field and the
Magnetocaloric materials

Figure 3.22: Magnetic hyperfine fields $B_{hf}$ for Fe at the tetrahedral 3f site for different $\text{Fe}_{2-x}\text{Mn}_x\text{P}_{1-y}\text{Si}_y$ compounds. All compounds show hexagonal crystal structure except along the green lines around FeMnP (green filled data markers) which have the closely related orthorhombic Co$_2$P structure. Data taken from Paper I and references [78, 79, 87]. Adapted from Paper III.

magnetic moment is non-trivial. Nevertheless, it can be estimated using the relation $B_{hf} = -12.6\mu + B_v$ given by ERIKSSON ET AL.[86] for Fe$_2$P (omitting small dipolar and orbital contributions). The s-valence term for FeMnP$_{0.5}$Si$_{0.5}$ is $B_v$(Me(1), Me(2)) = (-1.96, 17.1) T. Using the experimental $B_{hf}$ one arrives at a saturation Fe(3f) moment of 1.65 $\mu_B$, which corresponds to an increase of 60% compared with 1.03 $\mu_B$ in Fe$_2$P. This increase in the magnetic hyperfine field (and magnetic moment) can be linked to the increased Fe$_t$-Fe$_t$ interatomic distances when compared to corresponding distances in Fe$_2$P, see table 3.3.

Magnetocaloric properties: In figure 3.23, the magnetic entropy change $\Delta S_M$ for a field change of 1 T, 2 T and 5 T are shown. The data were obtained from only $M$ vs. $T$ measurements and the uncertainty for the data is higher (±20 %) compared to estimates based on $M$ vs. $H$ measurements. FeMnP$_{0.5}$Si$_{0.5}$ shows comparably good magnetocaloric properties, with a maximum value of $\Delta S_M$ of -31 J/kgK for a 5 T field change and -7.0 J/kgK for a 1 T field change. That is about 8 times the $\Delta S_M$ value obtain for pure Fe$_2$P in a 5 T field change (4 times for 1 T field change). The full width at half maximum (FWHM) of the $\Delta S(T)$ curve of FeMnP$_{0.5}$Si$_{0.5}$ is the same for both field changes and amounts to ~14 K. For practical matters
3.3.4 The effect of Mn and Si substitutions in Fe$_2$P

![Graph showing magnetic entropy change $\Delta S_M$ in FeMnP$_{0.5}$Si$_{0.5}$ for different fields.](image)

**Figure 3.23:** Magnetic entropy change $\Delta S_M$ in FeMnP$_{0.5}$Si$_{0.5}$ for a field change of 1 T, 2 T, and 5 T estimated from magnetization vs. temperature measurements.

The transition temperature is too high for room-temperature refrigeration and the thermal hysteresis might diminish the accessible temperature change.

The phosphorus-rich composition - FeMnP$_{0.75}$Si$_{0.25}$

A sample with composition FeMnP$_{0.75}$Si$_{0.25}$ is in a critical region between an orthorhombic and a hexagonal phase in the phase diagram by Cam Thanh et al. [77]. The sample of FeMnP$_{0.75}$Si$_{0.25}$ has been synthesized using the drop synthesis method. The chemical composition of FeMnP$_{0.75}$Si$_{0.25}$ was investigated by Electron Probe Micro-Analysis (WDS-EPMA) as well as energy dispersive spectroscopy (EDS). The results indicate an excess of iron to manganese with a Fe/Mn ratio of $\sim$ 1.24 and a composition Fe$_{1.13(5)}$Mn$_{0.91(9)}$P$_{0.71(11)}$Si$_{0.25(10)}$ with the relative error bars estimated by averaging over numerous measurements. Furthermore, an impurity phase of $\sim$5% (see figure 3.24), also evident on XRD patterns consisting of Fe and Si, was observed.

For FeMnP$_{0.75}$Si$_{0.25}$, it was shown that depending on the applied heat treatment and quenching, the magnetic properties of the samples are strongly altered. This behavior is illustrated in figure 3.25. After heat treatment and quenching, the samples show ferromagnetic-like behavior, whereas heat treatment and slow cooling yields antiferromagnetic-like behavior. A Möss-
Figure 3.24: EPMA measurements for FeMnP$_{0.75}$Si$_{0.25}$ showing approximately 5\% inclusions (Fe, Si).

The experimentally obtained magnetic moments per formula unit were compared to theoretically calculated values using DFT. The calculated moment for Fe on the tetrahedral site and Mn on the pyramidal site are 1.45 $\mu_B$ and 2.84 $\mu_B$, respectively. We find no agreement between the measured moment of 1.26 $\mu_B$/f.u. compared to the theoretical data, assuming ferromagnetic coupling which yields 4.3 $\mu_B$/f.u., but rather a ferrimagnetic-like type of coupling yielding 1.4 $\mu_B$/f.u. Further results concerning FeMnP$_{0.75}$Si$_{0.25}$ are discussed in detail in Paper I.

Figure 3.25: Magnetization as a function of magnetic field for an quenched (black circles) and a slowly cooled (red triangles) sample of FeMnP$_{0.75}$Si$_{0.25}$ at 30 K. Adapted from Paper I.
The manganese-rich composition - $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.5}\text{Si}_{0.5}$

With regard to the magnetocaloric properties, the composition $\text{FeMnP}_{0.5}\text{Si}_{0.5}$ was found to be promising. Nevertheless, the Curie temperature is too high and the thermal hysteresis is too large. Thus an improvement of these two properties: lowering the transition temperature and reducing the thermal hysteresis is desirable. This can be achieved by changing the Fe/Mn ratio since increasing the Mn content reduces the transition temperature [78]. The magnetization vs. temperature for $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.5}\text{Si}_{0.5}$ in a 1 T field is shown in figure 3.26. The transition temperature was lowered ($\sim$311 K measured on cooling) compared with $\text{FeMnP}_{0.5}\text{Si}_{0.5}$ and the thermal hysteresis reduced to $\sim$ 3 K. Data for magnetization vs. magnetic field for $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.5}\text{Si}_{0.5}$ in the temperature range from 250 K to 350 K (4 K steps) are shown in figure 3.27a and a para- to ferromagnetic phase transition is observed. An Arrott plot of the data is shown in figure 3.27a, refer to chapter 3.2.2. In this plot, the first-order character of the phase transition is evident, due to the negative slope in the data in the temperature range from 330 to 350 K.

In figure 3.28, the magnetic entropy change $\Delta S_M$ estimated from the $M - H$ data depicted in figure 3.27 for $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.5}\text{Si}_{0.5}$ is presented. The maximal $\Delta S_M$ for a
field change of 5 T and 1 T was measured to $\sim 21$ J/kgK and $\sim 5.5$ J/kgK, which is smaller than the values observed for FeMnP$_{0.5}$Si$_{0.5}$. The FWHM of the $\Delta S(T)$ curve for a 5 T field change is 20 K and for 1 T field change it is 12 K. In comparison to FeMnP$_{0.5}$Si$_{0.5}$, where FWHM was rather constant at a value of 11 K in the range of 1 to 5 T, the FWHM for Fe$_{0.75}$Mn$_{1.25}$P$_{0.5}$Si$_{0.5}$ is larger and increases with increasing field.

The temperature dependence of the maximum magnetic entropy change as a function of magnetic field change is shown to be linear, as can be seen in figure 3.29 (left graph). A better quantity for comparison and material characterization is the refrigerant capacity, $q$, (refer to equation 3.7). The refrig-

---

**Figure 3.27:** a) Magnetization as a function of magnetic field for different temperatures from 250 K in steps of 4 K to 350 K for Fe$_{0.75}$Mn$_{1.25}$P$_{0.5}$Si$_{0.5}$. b) Arrott plot $M^2$ vs. $H/M$ for Fe$_{0.75}$Mn$_{1.25}$P$_{0.5}$Si$_{0.5}$. 
3.3.4 The effect of Mn and Si substitutions in $\text{Fe}_2\text{P}$

Figure 3.28: Magnetic entropy change $\Delta S_M$ for $\text{Fe}_{0.75}\text{Mn}_{1.25}\text{P}_{0.5}\text{Si}_{0.5}$ as a function of temperature for $1, 2, \cdots, 5$ T field change.

erant capacity as a function of the magnetic field change was obtained by integrating the magnetic entropy change around $\pm 25$ K of the peak temperature and is presented in figure 3.29 (right graph). For a field change of 5 T the refrigerant capacity, $q$, corresponds to about 500 J/kg, which is in the order of $\sim 3.5$ J/cm$^3$. A linear dependency of the refrigerant capacity with the magnetic field change is evident.

Figure 3.29: Left graph: Temperature dependence of the maximum $\Delta S_M$ value as a function of magnetic field change, red line shows a linear fit. Right graph: Refrigerant capacity $q$ as a function of magnetic field change integrated over $\Delta T = \pm 25$ K, red line shows a linear fit.
3.4 Magnetocaloric properties of FeCrNi stainless steels

![Figure 3.30: Ternary phase diagram for Fe-Cr-Ni stainless steel alloys. The dotted-dashed black line indicates a structural phase transition ($m_S(T = 0 \text{ K})$) between a fcc $\gamma$- to a bcc $\alpha$-phase. Adapted from Reference [88].](image)

Since ancient times it has been known that an alloy of iron with minor amounts of carbon (between 0.01 % to 2.1 %) has preferable mechanical properties. Nowadays, such steels are among the most commonly used materials for the construction of buildings and infrastructure as well as the production of tools and all kind of machines. Stainless steel is a steel alloy with a minimum of $\sim 11$ mass% chromium content [89]. The major advantage of stainless steel as compared to ordinary steel, e.g. carbon steel, is its corrosion resistance. This property is obtained by the formation of an inert chromium oxide layer on the steel surface, which prevents oxidation and corrosion of the comprised iron. Stainless steel like other steels can be classified through its crystalline structure.

1. Austenitic stainless steel occurs in the iron $\gamma$-phase with a face-centered cubic (fcc) crystal structure and is usually metallic, paramagnetic alloy of iron with one or two other elements. Austenites have good properties for various applications (e.g. non-magnetic at room temperature) and are the most commonly used types of stainless steel.
2. Ferritic stainless steels appear in the $\alpha$-iron phase with a body-centered cubic (bcc) crystal structure. Ferrite is usually ferromagnetic at room-temperature.
3.4 Magnetocaloric properties of FeCrNi stainless steels

![Magnetocaloric properties of fcc FeNiCr](image)

**Figure 3.31:** Magnetocaloric properties of fcc FeNiCr. a) Magnetization as a function of temperature in different magnetic fields. b) Magnetic entropy change as a function of temperature of several magnetic field changes.

Martensitic stainless steels derive from different types of crystal structures and occur in a body-centered tetragonal (bct) crystal structure. Martensite refers to an extremely strong class of crystalline steel structures which are obtained through a martensitic transition, which can also be found in other materials, e.g. in certain minerals. A martensitic transition involves the rearrangement of atoms and occurs under a quenching process, which results in a non-equilibrium martensitic phase. A phase diagram for the iron-chromium-nickel system is shown in figure 3.30.

An interesting question is whether the magnetic phase transition in stainless steel shows a magnetocaloric effect that can be utilized. Samples of Fe-Cr-Ni stainless steel were synthesized using arc melting. In the fcc $\gamma$-phase the magnetic phase transition can be tuned around room temperature (100 K to 400 K) [88, 90]. The magnetic and magnetocaloric properties for fcc
Fe-Cr-Ni stainless steel are shown in figure 3.31. The transition temperature is at $T_C \approx 220$ K and is second order. The magnetic moment at low temperature and 5 T magnetic field is of the order of 60 Am$^2$/kg. The magnetic entropy change under a magnetic field change of 4 T is approximately 1 J/kgK, which is about 1 order of magnitude too small for making an application feasible.

In the bcc $\alpha$-phase the magnetic phase transition takes place at elevated temperatures of about 1000 K. Figure 3.32 presents the magnetic properties of bcc Fe$_{80}$Cr$_{10}$Ni$_{10}$. The tailoring of the structural transition temperature in Fe-Cr-Ni steels from a bcc $\alpha$-phase to a fcc $\gamma$-phase was suggested from DFT calculations [91]. When measuring the magnetization on heating, the system undergoes a magneto-structural phase transition (bcc $\rightarrow$ fcc). The bcc- phase is ferromagnetic whereas the fcc phase is non-magnetic. Under subsequent cooling the reversal transition occurs at much lower temperatures evident from a huge thermal hysteresis ($> 400$K) in the magnetization vs. temperature measurements. Similar behavior has been observed in other systems, for instance in Fe-rich FePt alloys [92].
3.5 The magnetic and magnetocaloric properties of Mn$_2$FeSbO$_6$ melanostibite

Figure 3.33: Octahedral representation of the melanostibite Mn$_2$FeSbO$_6$ crystal lattice with ilmenite structure; along c-axis (left panel) and in ab-plane direction (right panel). Adapted from Paper IV

The natural mineral melanostibite, Mn$_2$FeSbO$_6$, was discovered in Sjögruvan (Örebro, Sweden) at the end of the 19th century. It has been initially studied and described by LARS JOHAN IGELSTRÖM [93]. The name melanostibite is derived from the color (melanos = black in Greek) and composition (stibium = antimon in Latin) of the material. The mineral is a Mn-Sb-oxide with the chemical formula Mn$^{2+}$(Sb$^{5+}$,Fe$^{3+}$)O$_3$. Melanostibite forms in a hexagonal crystal structure with spacegroup $R\bar{3}$ (coordination number is 6) and the lattice parameters are $a = 5.226$ Å and $c = 14.325$ Å. It is hence an isostructural mineral of the ilmenite-pyrofanite group, described by P. B. MOORE [94]. An octahedral representation of ilmenite-type structure can be found in figure 3.33. The melanostibite mineral was formed under natural conditions inside the earth over a geological period of time. The conditions that formed melanostibite certainly involved both high temperature and high pressure conditions. It is therefore interesting to see whether the mineral sample can be reproduced in the laboratory. Materials with perovskite-type structure have been widely studied for their magnetocaloric properties [95–97]. Only a small number of materials with ilmenite-type structure and a magnetic transition close to room temperature [98] are known and little is reported on their magnetocaloric properties. The results discussed in this section are part of the publications Paper IV and Paper VI.
Fabrication of synthetic melanostibite  Synthetic samples of melanostibite have been fabricated by high-pressure synthesis by G. Bazuev [99] using conventional solid state reaction (including terminatory sintering at temperatures between 1300 and 1350 °C) and thermobaric treatment under a pressure of 3 GPa at 1000 °C for 30 min. The temperature and pressure parameters reflect the conditions under which the natural mineral might have been formed in the earth. An X-ray powder diffraction analysis of the synthetic melanostibite revealed that the main phase crystallizes in the hexagonal ilmenite-type structure (space group R3, $a = 5.237(1)$ Å and $c = 14.349(2)$ Å) similar to the single-crystal mineral of Mn$_2$FeSbO$_6$. Additionally, a minor amount ($\approx 2\%$) of a secondary phase of the MnFe$_2$O$_4$ spinel, which is ferrimagnetic below $T_N = 570$ K, was found after Rietveld refinement.

Figure 3.34: Magnetization as a function of temperature for a natural mineral (black) and synthetic sample (blue) melanostibite measured in a) 2 mT and b) 1 T. Adapted from Paper IV.
3.5 The magnetic and magnetocaloric properties of $\text{Mn}_2\text{FeSbO}_6$ melanostibite

![Figure 3.35: Magnetization as a function of magnetic field for the mineral $\text{Mn}_2\text{FeSbO}_6$ at 10 K and 300 K. The inset shows the behavior in high magnetic fields.](image)

**Magnetic properties of melanostibite** From the first study by IGELSTRÖM the mineral has been characterized as non-magnetic, although it showed some magnetic response after heat treatment [100]. Magnetic measurements of both the natural mineral and the synthetic sample are presented in figure 3.34. The synthetic sample and the mineral show a qualitatively similar behavior. In small probing fields of 2 mT (figure 3.34a) both mineral and synthetic $\text{Mn}_2\text{FeSbO}_6$ show a relatively sharp magnetic transition. This transition is also seen in the specific heat of the synthetic samples in 0 T field shown in the inset of figure 3.34a. The transition temperature for the mineral is found to be $\sim 268 \text{ K}$ and for the synthetic sample $\sim 264 \text{ K}$. When the probing magnetic field increased to 1 T, the magnetization increases linearly below $T_N$, cf. figure 3.34b.

The magnetization as a function of magnetic field at 10 K and 300 K for the natural sample is depicted in figure 3.35. At 300 K, the mineral sample shows pure paramagnetic behavior. For low temperatures (10 K), the sample reveals hysteresis behavior with a constriction for small magnetic fields. Similar behavior has been observed in exchange-bias systems [101]. The saturation magnetization for the mineral at 10 K is found to be $3.65 \mu_B$/f.u. (53.2 Am$^2$/kg ) and $4.35 \mu_B$/f.u. (63.1 Am$^2$/kg) for the synthetic melanostibite. This agrees with a ferrimagnetic arrangement of 2 Mn$^{2+}$ and 1 Fe$^{3+}$ cations (all carrying $S = 5/2$, $5 \mu_B$) per formula unit.
Magnetocaloric materials

Figure 3.36: Magnetization as a function of magnetic field for a) the mineral and c) the synthetic melanostibite sample around $T_C$. Corresponding Arrott plots for b) the natural mineral and d) synthetic melanostibite. A linear fit for the mineral sample near $T_C$ is shown in b), $R^2$ refers to the accuracy of the least-square fitting. Adapted from Paper IV.

Isothermal magnetization measurements are shown in figure 3.36 and the magnetic phase transition for the mineral sample and the synthetically fabricated sample of melanostibite are compared to each other. As can be seen in the Arrott plots figure 3.37b and 3.37d the data feature a positive slope in the entire temperature range.

The Arrott plots hence reveal a second order para- to ferrimagnetic phase transition, as one can conclude from Banerjee’s criterion [43]. The criterion states straight line with a positive slope in $M^2$ vs. $H/M$ data plot as an indication for a second-order magnetic phase transition. Furthermore, the presented data feature a set of parallel straight lines around the transition temperature, which indicates mean-field-like behavior of the phase transition. For the mineral melanostibite, the linear behavior of the data is highlighted by a red line (linear fit) shown in figure 3.36b.
3.5 The magnetic and magnetocaloric properties of Mn$_2$FeSbO$_6$ melanostibite

Magnetocaloric properties of melanostibite The magnetocaloric properties for the mineral and the synthetic sample of melanostibite are summarized in figure 3.37. As expected for a material with ferrimagnetic ordering, the magnitude of the magnetic entropy change is comparably small. $\Delta S_M$ for the mineral sample is estimated to be 1.7 J/kgK and 0.51 J/kgK for magnetic field changes of 5 T and 1 T, respectively. The magnetic entropy change for the synthetic sample under the same magnetic field change was found to be 1.8 J/kgK and 0.46 J/kgK, respectively.

Figure 3.37: Magnetocaloric properties for a mineral and synthetic sample of melanostibite. a) The magnetic entropy change $\Delta S_M$ of the synthetic sample under 1 T field change as derived from specific heat ($\varnothing$), $M$ vs. $H$ ($\bullet$) and the $-dM/dT \times H$ derived from $M$ vs. $T$ in 1 T ($\square$). b) $\Delta S_M(H)$ for the mineral ($\bullet$) and synthetic ($\bullet$) melanostibite at their respective transition temperature and the $H^n$ power law dependence with $n=1/3$ and 2/3 (dashed lines). Adapted from Paper IV.
Table 3.4: Magnetic and structural properties for mineral and synthetic Mn$_2$FeSbO$_6$ (MFSO). Adapted from Paper IV.

<table>
<thead>
<tr>
<th>Properties</th>
<th>min. Mn$_2$FeSbO$_6$</th>
<th>synth. Mn$_2$FeSbO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn:Fe:Sb</td>
<td>2.03:0.96:0.99</td>
<td>2.05:0.91:1.04</td>
</tr>
<tr>
<td>Space group</td>
<td>R$\bar{3}$</td>
<td>R$\bar{3}$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>5.226(1)</td>
<td>5.237(1)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>14.325(2)</td>
<td>14.349(2)</td>
</tr>
<tr>
<td>$T_N$ (K)</td>
<td>268(2)</td>
<td>264(2)</td>
</tr>
<tr>
<td>$\Delta S_{M</td>
<td>5T}^{PK}$ (J/kgK)</td>
<td>1.7</td>
</tr>
<tr>
<td>$\Delta S_{M</td>
<td>1T}^{PK}$ (J/kgK)</td>
<td>0.51</td>
</tr>
<tr>
<td>$\Delta T</td>
<td>_{1T}$ (K)</td>
<td>-</td>
</tr>
</tbody>
</table>

Interestingly, Mn$_2$FeSbO$_6$ crystallizes in a layered structure (cf. Fig. 3.33) in which the inter-layer coupling of the Mn and Fe/Sb layers is antiferromagnetic, whereas the intra-layer coupling is ferromagnetic. It is well know that the carrier doping and associated chemical pressure may change the inter-layer coupling towards ferromagnetic behavior, e.g. in perovskite manganites [102]. Therefore, it is reasonable to expect that cation substitution could be employed to enhance the ferromagnetic interaction in Mn$_2$FeSbO$_6$, yielding improved magnetocaloric properties.

Figure 3.37a depicts the magnetic entropy change $\Delta S_M$ for a 1 T field change derived from three different measurements - specific heat, isothermal $M$ vs. $H$ measurements and a single isofield $M$ vs. $T$ measurement. For the simple $M$ vs. $T$ measurement in 1 T applied field $\Delta S_M$ was derived from $-dM/dT \times H$. The $\Delta S_M$ curve from specific heat measurements was shifted with a constant offset to match the $\Delta S_M$ at 290 K obtained from $M$ vs. $H$ measurements and equation 3.8. One can conclude that all three measurements reproduce the qualitative behavior for the temperature dependence of the magnetic entropy change and only differ slightly in the absolute value for the $\Delta S_M$. It is interesting to note that a single $M$ vs. $T$ measurement at constant magnetic field gives an acceptable estimate of the magnetic entropy change for a second-order magnetocaloric material.

Using the magnetic entropy change and the specific heat as a function of temperature and magnetic field, one can derive an estimate for the adiabatic temperature change.
The magnetocaloric effect in terms of the change in temperature $\Delta T$ under a 1 T field change for the synthetic melanostibite sample can be estimated to

$$\Delta T = -\Delta S_M \frac{T}{C_P(264 \text{K}, 1 \text{T})} \approx 0.2 \text{ (K)},$$ \hspace{1cm} (3.9)

where $C_P(264 \text{K}, 1 \text{T}) = 231 \text{ J/molK}$ is the specific heat measured at 264 K in 1 T applied field.

In figure 3.37b the magnetic field dependence of the magnetic entropy change at the phase transition for the mineral (268 K) and synthetic (264 K) melanostibite as well as the $H^{2/3}$ and $H^{1/3}$ power law are shown. In agreement with the work of OESTERREICHER AND PARKER [103], a power law dependence for the magnetic entropy change $\Delta S \propto aH^n$ is observed. At the transition temperature the exponent $n$ for a system with well localized magnetic moments is expected to be $n = 2/3$, whereas for a system with more itinerant character $n = 1/3$. It is evident that the experimental data at the transition temperature for mineral and synthetic $\text{Mn}_2\text{FeSbO}_6$ follow a $H^{2/3}$ dependence and the magnetic moments of melanostibite are localized.

The magnetic and magnetocaloric properties of both mineral and synthetic $\text{Mn}_2\text{FeSbO}_6$ are summarized in table 3.4.
3.6 Concluding remarks

Fe₂P-based compounds - archetype first order magnetocaloric materials

Fe₂P is the initial compound for a whole series of well-studied magnetocaloric materials, which are potentially useful for heating and cooling applications. Fe₂P itself exhibits very interesting magnetic properties and the magnetocaloric effect in pure Fe₂P has been sparsely characterized. The two most striking magnetic properties of Fe₂P are first-order magnetic phase transition and large magnetocrystalline anisotropy both of which were studied in this thesis.

The chemistry of Fe₂P allows a tuning of the magnetic and magnetocaloric properties and the natural choice of abundant, non-toxic and cheap materials lead to an element substitution with Mn for Fe and Si for P. Several compositions of the (Fe,Mn)₂(P,Si) system were studied and the main conclusions are as follows:

The magnetic moment for FeMnP₀.₅Si₀.₅ was found to be in the order of 4.4 μₜ / f.u., which is higher than observed in previous experiments 3.8 μₜ / f.u. [77] and calculated from first principles 4.2 μₜ / f.u. [80]. Mössbauer spectroscopy measurements revealed an unexpected high magnetic moment of 2.1 μₜ for Fe atoms on the tetrahedral sites, Fe(1), in FeMnP₀.₅Si₀.₅. From neutron diffraction data it is evident that for FeMnP₀.₅Si₀.₅ the Fe and Mn atoms are strongly ordered to their respective site, Fe(1) and Fe(2). P and Si seem to be randomly distributed on the two possible lattice positions. FeMnP₀.₇₅Si₀.₂₅ shows a strong dependence on the applied heat treatment. Quenching results in ferrimagnetic-like behavior whereas slow cooling creates an antiferromagnetic state. Fe₀.₇₅Mn₁.₂₅P₀.₅Si₀.₅ shows good magnetocaloric properties with reduced thermal hysteresis. The magnetic entropy change was found to be -21 J/kgK (-5.5 J/kgK) for a 5 T (1 T) field change. These values can certainly be optimized in the future. Recently, improved magnetocaloric properties for non-stoichiometric (Fe,Mn)₁.₉₅(P,Si) was presented by N. H. DUNG ET AL. [52].

Stainless steels

Using stainless steels for magnetocaloric applications would be an interesting choice of material due to the fact that steel is cheap and available in large amounts. Fe-Cr-Ni steels in the fcc γ-phase exhibit a phase transition easily tunable around room-temperature and possess a magnetic entropy change in the order 1 J/kgK for a 4 T field change. For Fe-Cr-Ni steels in the
ferromagnetic bcc $\alpha$-phase a combined structural and magnetic transition to the fcc $\gamma$-phase is found. This reversible transition takes place at rather high temperatures and is accompanied by a huge thermal hysteresis not suitable for applications.

**Magnetic and magnetocaloric properties of natural and synthetic Mn$_2$FeSbO$_6$ with ilmenite structure**

The natural mineral Mn$_2$FeSbO$_6$ with ilmenite structure was characterized in terms of its magnetic and magnetocaloric properties. Magnetically, Mn$_2$FeSbO$_6$ undergoes a second-order para- to ferrimagnetic phase transition close to room temperature (268 K). Being a ferrimagnet, the saturation moment ($3.65 \mu_B$/f.u.) and the magnetic entropy change (order of -2 J/kgK for 5 T) are comparably small. Nevertheless, the Mn$_2$FeSbO$_6$ is interesting since the layered structure may open the possibility of tuning the magnetic ordering from ferrimagnetic to ferromagnetic. Furthermore, it has been shown by [99] that this rare natural mineral can easily be fabricated synthetically.

**What is next?**

The goal to commercialize magnetocaloric refrigeration has not been accomplished, yet. This ambitious goal is driven by the idea to save energy and is connected to the limited availability of the natural resource oil. In that context, it is interesting to notice that many emerging technologies, for example motor and generator devices in wind/water power generators and electrical cars, are based on another limited resource, namely rare earth elements. In the case of magnetocaloric materials, the bottleneck is likewise the rare earth elements which have been thoroughly replaced as magnetocaloric working materials but which are still crucial for the permanent magnet materials needed to create the high magnetizing fields. In a future perspective from a materials point of view, it seems to be equally important to find new permanent-magnet materials or alternative ways to magnetize the magnetocaloric material as to improve the material alone.
CHAPTER 4

MULTIFERROIC MATERIALS

This Chapter is dedicated to the investigation of strongly correlated electron systems. Such materials exhibit interesting phenomena such as magnetoelectric effects and even multiferroicity. After an introduction to the research topic, including theoretical and experimental fundamentals, experimental results for different magnetoelectric materials are presented in detail.

4.1 Introduction

Nowadays, materials exhibiting strong electron correlation are intensely studied in the field of condensed matter physics. Numerous interesting physical phenomena have been discovered within that framework, for example high-$T_C$ superconductivity [104] and the colossal magnetoresistance (CMR) effect [105]. In CMR materials, large changes of the electrical resistance are observed on the application of a magnetic field. The dielectric properties of strongly correlated oxides may also be affected by the magnetic field, as for example in magnetoelectric materials [33]. In these materials it is possible to control the magnetic state of the material with an applied electrical field (or current) and vice versa the electrical polarization with an applied magnetic field. This would enable a variety of new applications concerning data processing and data storage [106]. Materials exhibiting such cross-coupled properties can be explained by the magnetoelectric effect, first described by Pierre Curie in 1894 [107]. In short, the magneto-electric effect (ME) describes the coupling of the magnetic field $H$ with the electrical polarization $P$ or, vice versa, the coupling of the electrical field $E$.

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1This description has been inspired by the lectures of the 5th European School on Multiferroics (ESMF 2012) in Ascona, Switzerland.
4.2 Theoretical and experimental fundamentals

It has been a challenge to find materials exhibiting coupled electrical and magnetic properties, for example being both ferroelectric (FE) and ferromagnetic (FM). One problem is the difference in the microscopic nature of magnetic and electrical ordering. Magnetic ordering is based on the electron magnetic moment. Electrical ordering on the other hand is due to the polar displacement of electron or atomic electrical charge and can arise through several mechanisms.

Many classic ferroelectric materials can be found among the transition metal perovskites (with chemical formula ABO₃, see figure 4.2) including the reference ferroelectric material BaTiO₃ with a $T_{C}^{FE} = 120 \, ^{\circ}\text{C}$ and a electrical polarization of 0.27 C/m² [120]. However, BaTiO₃ does not order magnetically. It turns out that there is rather little overlap of FM and FE properties in the perovskite materials family. This situation can be understood from the fact that ferromagnetism requires partially filled inner shells (for example dⁿ), whereas ferroelectricity requires empty d-shells (d⁰). The d⁰ constrain needs to be fulfilled to enable strong covalent bonds, with the surrounding

with the magnetization $\mathbf{M}$,

$$
P_i = \sum \alpha_{ij} H_j + \sum \beta_{ijk} H_j H_k + \ldots
$$

$$
M_i = \sum \alpha_{ij} E_j + \sum \beta_{ijk} E_j E_k + \ldots
$$

(4.1)

The first attempts to combine electrical and magnetic behavior in one material were undertaken during the 1960s in the Soviet Union, for example by the group of G. Smolenskii in Leningrad (St. Petersburg) [108]. One archetype system for magneto-electric coupling is the antiferromagnetic Cr₂O₃. Following the theoretical prediction of a magnetoelectric effect in Cr₂O₃ by I. Dzyaloshinskii in 1959 [109], the effect was confirmed by D. Astrov in 1960 [110] and V. N. Folen et al. in 1961 [111]. In 1994, H. Schmid introduced the name multiferroics when referring to materials exhibiting several ferroic properties, such as ferroelectricity, ferromagnetism and ferroelasticity, simultaneously [112]. In such a material two or more order parameters are present. The most prominent case for such materials are so-called magnetoelectric multiferroics (Fig.: 4.1) which exhibit (ferro)electricity and (ferro)magnetism simultaneously. Several review articles on this subject have been published, for example [113–118].

4.2 Theoretical and experimental fundamentals

Figure 4.1: Ferroic ordering types (magnetization $\mathbf{M}$, polarization $\mathbf{P}$, strain $\epsilon$) and respective fields (magnetic $\mathbf{H}$, electrical $\mathbf{E}$, stress $\sigma$). Magnetoelectric multiferroics (green lines). Adapted from [119].

Currently also other types of magnetic and electrical ordering, for example antiferromagnetic and antiferroelectric materials are often referred to as multiferroics.
Multiferroic materials

oxygen giving rise to the ferroelectricity in these materials. Hence there is mutual exclusion of FM and FE in this material class [121].

One can identify two main classes of materials with coupled electrical and magnetic properties; one in which the electrical and magnetic properties have different origins and hence two separate order parameters (split-order-parameter multiferroics) and those in which the electrical properties stem from the magnetic ordering (joint-order-parameter multiferroics). Both types are described briefly in the next section (4.2.1).

4.2.1 Background

Split-order-parameter multiferroics (type-I)

Split-order parameter multiferroics are usually good ferroelectric materials with large electrical polarization in the order 0.1-1 C/m². The ferroelectric transition temperature is often far above room temperature and well separated from the magnetic transition, being lower in temperature. The coupling of magnetic and electrical properties is weak since they originate from different sources. Several main groups of type-I multiferroics are known and the four most prominent are:

1) Lone-pair multiferroics: A number of transition metal perovskites, such as for example BiMnO₃ [122] and BiFeO₃ [123], do indeed order magnetically. In these so-called lone-pair multiferroics the ferroelectricity occurs due to an electron lone-pair (6s) on the A site, whereas the magnetic ordering stems from the B site magnetic moments of Mn and Fe, respectively. Hence, the origin of the electrical and magnetic ordering is different and the coupling between them is very weak.

2) Charge-ordered multiferroics: Another mechanism that gives rise to combined electric and magnetic properties can be found in charge-ordered multiferroics, e.g. LuFe₂O₄ [124]. Here the ferroelectricity comes from the charge ordering of magnetic ions with different valence states giving rise to inequivalent bonds and hence ferroelectricity without ionic displacement.

3) Geometrically frustrated multiferroics: In geometrically frustrated multiferroics competition of magnetic interaction between different ion sites can give rise to lattice distortions, for example off-centering of ions, cf. YMnO₃ [125]. At low temperatures the frustrated systems can order into a non-collinear structure to compensate for the geometrical frustration, cf. triangular and Kagomé lattice shown in figure 4.3. An anomaly
4.2.1 Background

in the dielectric function at magnetic phase transition is evidence for the strong coupling between ferroelectric and magnetic ordering.

4) Strain-induced multiferroics: In thin film heterostructures (for example BiFeO₃ on SrTiO₃ [126]) the electrical and magnetic properties can be mechanically coupled. Such strain-induced multiferroics are based on magnetoelastic and magnetostrictive effects in which an applied magnetic field will change the lateral dimension in one of the layers. Coupling through the mechanical interface induces strain in the second layer (or the substrate), which may give rise to an electrical polarization. A high quality of the interface is crucial to ensure optimal coupling in these systems. Pulsed laser deposition (PLD) is a capable technique for the fabrication of such heterostructures with both piezoelectric and magnetostrictive layers.

Joint-order-parameter multiferroics (type-II)

In type-II multiferroics, the ferroelectric properties derive directly from the magnetic long range ordering and the coupling between electrical and magnetic properties is inherently strong. Such magnetically driven multiferroics are found among insulating transition metal oxides with competing interaction and frustration, in which the magnetic ordering favors complex magnetic structures, for example in a cycloidal spin spiral. Since the electrical polarization occurs at the magnetic phase transition temperature, such materials can be described by one joint order parameter. Unfortunately, the magnetically induced polarization is usually weak and several orders of magnitude smaller than in type-I materials. A condition for a spontaneous electrical polarization in these materials is the breaking of inversion symmetry, which is accomplished via the magnetic ordering. Three main mechanisms for the formation of magnetically-induced ferroelectricity are described in the literature and are addressed by the cluster model (see figure 4.4) [127, 128],

\[
P = P^{ES} e \cdot (s_i \cdot s_j) + P^{SC} (s_i \times s_j) \times e + P^{p-d} ((e \cdot s_i) \cdot s_i - (e \cdot s_j) \cdot s_j).
\]
All three mechanisms: (1) exchange-striction ($P^{ES}$), (2) spin-current ($P^{SC}$) and (3) $p-d$ hybridization ($P^{p-d}$) involving M-O-M bonds with M being a magnetic ion and O being oxygen. These mechanisms are described in some detail below:

1) Exchange-striction mechanism: In collinear spin-chains, multiferroicity can be understood in terms of the exchange-striction mechanism [129, 130]. Two types of exchange-striction interaction can be described, the symmetric exchange based on the Heisenberg exchange interaction and the antisymmetric exchange through the inverse Dzyaloshinskii-Moriya (DM) interaction (incl. spin-orbit coupling). The corresponding Hamiltonian is given by

$$H = \frac{1}{2} \sum_{i,j} J_{ij} s_i s_j + \frac{1}{2} \sum_{i,j} D_{ij} \cdot (s_i \times s_j),$$

(4.3)

with the first term being the Heisenberg exchange interaction and the second term being the Dzyaloshinskii-Moriya (DM) interaction. The Dzyaloshinskii-Moriya vector is given by $D_{ij} \propto x \times e_{ij}$, with $x$ being the displacement of the ligand ion vertical to $e$. For symmetric exchange the first term in equation 4.3 dominates and the occurrence of an electrical polarization can be explained by ionic displacements (non-centrosymmetric) due to the Goodenough-Kanamori-Anderson (GKA) rules [131–133]. If one considers simple configurations the GKA rules predict antiferromagnetic (AFM) coupling for bond angles close to $180^\circ$ and ferromagnetic (FM) coupling for a bond angle of approximately $90^\circ$. A schematic illustration for the electrical polarization based on symmetric exchange is shown in figure 4.5. The second term in equation 4.3 describes antisymmetric exchange interaction. In a noncollinear structure, such as helicoidal, cycloidal or conical spin arrangement, spin canting occurs and induces a polar displacement (inverse Dzyaloshinskii-Moriya interaction). Besides the magnetically-induced ferroelectricity due to ionic displacements, electronic charge displacements can also take place.

2) Spin-current mechanism: Spiral magnetic ordering is usually a consequence of magnetic frustration. The occurrence of ferroelectricity in these systems can also be understood in terms of the spin-current mechanism proposed by Katsura, Nagaosa, and Balatsky [134] and separately by M.

3KNB model
4.2.2 Symmetry considerations

Mostovoy [135]. In the spin-current mechanism, ions may be fixed in a centrosymmetric structure and the electrical polarization is due to electronic charge displacements. The spontaneous polarization can be explained via a spin current defined as $j_s \sim J_{ij}(s_i \times s_j)$, where $s_i$ and $s_j$ are noncollinear neighboring spins and $J_{ij}$ is the Heisenberg exchange constant. The spin-current can be understood as virtual electron hopping. For a cycloidal spin spiral the electrical polarization can be described as

$$P \sim e_{ij} \times j_s \sim e_{ij} \times (s_i \times s_j) \sim k \times r, \quad (4.4)$$

with $e_{ij}$ connecting two neighboring ions, $k$ being the propagation vector of the spiral and $r$ being the spin rotation axis. The electrical polarization is hence orthogonal to the spiral propagation vector and lies in the spiral plane. For applied magnetic fields the magnetic moments try to arrange in a plane perpendicular to the external field, which can result in spin-flop transition[116].

3) p-d hybridization mechanism: A second mechanism in non-collinear spin-spiral materials is due to variation of p-d hybridization. Here non-zero polarization develops along the direction of the M-O-M cluster, hence parallel to $e_{ij}$, connecting two neighboring ions.

Magnetically-induced ferroelectricity is comparably small, which makes it difficult to decide whether the ionic - or electronic displacements are the source of the electrical polarization. Magnetically-induced ionic displacements are close to the resolution limit of neutron and X-ray experiments.

4.2.2 Symmetry considerations

The magnetic and electrical properties of materials are strongly coupled to the symmetry characteristics. This can be seen when considering space inversion ($r \rightarrow -r$) and time reversal ($t \rightarrow -t$) on magnetic and electrical entities, as shown in figure 4.6. The electrical polarization and pyroelectricity\(^4\) are vectorial properties described by a first rank polar tensor. It follows that these properties disappear in all point groups with inversion symmetry and hence in all centrosymmetric materials. Spacial inversion reverses the direction of an electrical polarization $P$ and leaves the magnetization $M$ invariant, see fig-

\(^4\)Pyroelectricity refers to the formation of a voltage in a crystalline material when changing the temperature.
Table 4.1: Symmetry properties for different types of ferroic order.

<table>
<thead>
<tr>
<th></th>
<th>Time Invariant</th>
<th>Time Variant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space Invariant</td>
<td>Ferroelastic</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>Space Variant</td>
<td>Ferroelectric</td>
<td>Ferrotoroidic</td>
</tr>
</tbody>
</table>

In other words the electrical polarization breaks inversion symmetry. Magnetic moment and magnetic field, on the other hand are first rank axial tensors and do not break inversion symmetry, but break time reversal symmetry. Time reversal reverses $\mathbf{M}$ and leaves $\mathbf{P}$ invariant. In the case of magneto-electric multiferroics one can conclude that both space inversion and time reversal need to be broken. The symmetry properties for different types of ferroic ordering are summarized in Table 4.1. Ferroelastic ordering is invariant under both spatial inversion and time reversal whereas ferrotoroidic ordering is variant under both these symmetry operations. Ferrotoroidic ordering refers to a spontaneous magnetic vortex with a resulting toroidal moment $\mathbf{T} \propto \sum_i \mathbf{r}_i \times \mathbf{S}_i$.

4.2.3 Spin-phonon coupling

The coupling of spin and lattice degrees of freedom can be studied using Raman spectroscopy. Such phenomena are particularly interesting in multiferroic materials where the antiferromagnetic-ferroelectric (spin-lattice) coupling is relevant. In recent years, many rare earth manganites such as HoMnO$_3$ [136], YMnO$_3$ [137] and Eu$_{1-x}$Y$_x$MnO$_3$ [138] have been studied by Raman spectroscopy.

The interplay between spin and lattice degrees of freedom is reflected in a deviation of the phonon modes from the normal temperature-driven behavior. The renormalization of the phonon frequencies due to magnetic ordering for ferromagnetic insulators with superexchange was described by Balternspurger and Helman [139]. A similar model has been applied by D. J. Lockwood and M. G. Cottam [140] to treat the spin-phonon interaction in antiferromagnetic FeF$_2$ and MnF$_2$. The frequency shift of optical phonons can be estimated to

$$\omega_p(T) = \omega_p^0(T) + \lambda \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle,$$

where $\omega_p^0$ is the phonon frequency in the absence of spin-phonon coupling, $\lambda$ is the coupling constant and $\langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ the
statistical average of the spin-spin correlation function.

Strong spin-phonon coupling can result in significant softening of the phonon modes. In a mean-field approximation, the spin-spin correlation function $\langle s_i \cdot s_j \rangle$ can be estimated and the change in the phonon frequency as a function of temperature is given as

$$
\Delta \omega(T) = \omega_p(T) - \omega_p^0(T) = \lambda \langle s_i \cdot s_j \rangle \propto \frac{M^2(T)}{M_{\text{Max}}^2}, \quad (4.6)
$$

with nearest-neighbor spins $s_i$ localized at sides $i$ and $j$. $M(T)$ is the average magnetization per magnetic ion at temperature $T$.

However, such quantitative studies are difficult, since volume and magnetic (or electrical) polarization effects contribute to the observed shifts of the Raman modes.
4.3 Magnetic-field-induced polarization in cryolite-like $\text{Co}_3\text{TeO}_6$

[Image: Polyhedral representation of the crystal structure of $\text{Co}_3\text{TeO}_6$.]

New magnetoelectric multiferroics with magnetically-induced ferroelectricity are to be found among materials with complex magnetic structures. The cryolite-like $\text{Co}_3\text{TeO}_6$ compound is a member of an interesting family of metal oxides with the general chemical formula $\text{M}_3\text{TeO}_6$, where $\text{M}$ is a first-row transition metal. Another member of this family, $\text{Ni}_3\text{TeO}_6$, orders antiferromagnetically below 52 K, with a relatively simple magnetic structure [142]. $\text{Mn}_3\text{TeO}_6$ was recently reported to exhibit a complex incommensurate spin structure, consisting of two different magnetic orbits [143]. It is interesting to investigate the physical properties of the sparsely characterized $\text{Co}_3\text{TeO}_6$ compound. The work presented in this chapter is based on Paper VII and Paper VIII.

The crystal and magnetic structure of $\text{Co}_3\text{TeO}_6$ from X-ray and neutron powder diffraction

The crystal structure of $\text{Co}_3\text{TeO}_6$ was reported by R. Becker et al. [145] and the magnetic structure was solved recently by S. Ivanov et al. [144]. A polyhedral representation of the crystal structure of $\text{Co}_3\text{TeO}_6$ is shown in figure 4.7. The X-ray diffraction pattern and the associated Rietveld refinement at room temperature are shown in Fig. 4.8. $\text{Co}_3\text{TeO}_6$ adopts a monoclinic structure (space group $C2/c$), with lattice parameters $a = 14.8014(3)\,\text{Å}$, $b = 8.8379(2)\,\text{Å}$, $c = 10.3421(3)\,\text{Å}$, and a monoclinic angle $\beta = 94.83^\circ$. From temperature-dependent neutron powder diffraction data [144], it follows that $\text{Co}_3\text{TeO}_6$...
remains in the monoclinic C2/c cryolite-type structure in the whole temperature range from 296 K down to 1.6 K. The crystal structure of Co₃TeO₆ is complex and involves five different Co²⁺ (four octahedral and one tetrahedral) and two different Te⁶⁺ sites. Interestingly there is a large variation in the bond length \( <\text{Co-O} > \) in the Co₃TeO₆ compound, giving rise to competing magnetic interaction. The variation of the \( <\text{Co-O} > \) bond length is in the range (1.97 - 2.93 Å). This is much larger than the \( <\text{Ni-O} > \) in the case of Ni₃TeO₆ (2.10 - 2.15 Å) and the \( <\text{Mn-O} > \) in Mn₃TeO₆ (2.10 - 2.38 Å) [142, 143].

The neutron diffraction measurements [144] revealed a succession of magnetic phases at low temperatures. A picture of the neutron data from Reference [144] is shown in figure 4.9. Starting from room temperature, Co₃TeO₆ is paramagnetic and enters long range magnetic order below \( T_N = 26 \) K with the incommensurate propagation vector \( k_1 = (0, 0.485, 0.055) \) and the commensurate propagation vector \( k_2 = (0, 0, 0) \). Approaching \( T = 21 \) K, the incommensurate wave vector \( k_1 \) fades away and only \( k_2 \) is present. On further lowering the temperature below 17.4 K, a new commensurate magnetic structure (lock-in phase) with wave vector \( k_3 = (0, 0.5, 0.25) \) appears, while \( k_2 \) is still present down to the lowest temperatures studied. The structural model from reference [144] of the commensurate an-
Multiferroic materials

Figure 4.9: Neutron powder diffraction patterns showing changes of the magnetic intensities at separated temperatures, indicating different magnetic phases. Taken from Ref. [144].

tiferromagnetic structure $k_3$ in $\text{Co}_3\text{TeO}_6$ is shown in figure 4.10. To summarize, the study by S. Ivanov et al. revealed a complex magnetic structure with both commensurate and incommensurate phases below 26 K, which can be connected to competing ferro- and antiferromagnetic interaction in the system. Furthermore, a lattice contraction around 18 K was observed from the evolution of the lattice parameter as a function of temperature.

Figure 4.10: Schematic illustration of the commensurate magnetic structure $k_3$ for $\text{Co}_3\text{TeO}_6$ in the $bc$-plane, $2 \times 4$ unit cells are shown. Taken from Ref. [144].
Magnetization- and specific heat properties of Co$_3$TeO$_6$

![Graph](image)

Figure 4.11: a) Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetization measured in 20 Oe magnetic field. b) Heat capacity, plotted as $C/T$, as a function of temperature with an inset showing the temperature dependence of $d\chi T/dT$ ($\chi = M/H$) calculated from the magnetization data with $H \parallel c$. Adapted from Paper VII.

Magnetization measurements of Co$_3$TeO$_6$ with the magnetic field applied along the $a$-axis and the $c$-axis suggest antiferromagnetic ordering below $\sim 30$ K. Low-magnetic field (20 Oe) ZFC and FC magnetization data are shown in figure 4.11a. For sample orientation $H \parallel c$ the magnetization curve shows a kink at $T^* \sim 18$ K. Interestingly, a sharp peak is evident in the heat capacity measurement at 18 K, i.e. in the vicinity of $T^*$, shown in figure 4.11b. The heat capacity data confirm the existence of a phase transition near 26 K. The two characteristics, long-range ordering at 26 K and a sharp peak at 18 K, are evident in the temperature derivative of the magnetic susceptibility ($\chi = M/H$) times temperature ($T$): $d(\chi \cdot T)/dT$ shown in the inset of figure 4.11b. The proportionality of this quantity to the magnetic specific heat is known for antiferromagnetic systems [146]. A Curie-Weiss analysis yields a Weiss constant of $\theta = -54$ K and an effective Bohr magneton number of $p = 4.69$, indicating magnetic frustration ($|\theta| \sim 2T_N$). The data recently published by HER ET AL. [147] confirm our specific heat and magnetization results.
The coupling of magnetic and electrical properties in Co$_3$TeO$_6$ under an applied magnetic field

The magnetization in c-axis orientation in high-magnetic fields up to 14 T is shown in figure 4.12a. For increasing magnetic fields the drop in magnetization (at 18 K) is shifted towards lower temperatures and is altered for magnetic fields greater than 11 T, where an upward step is seen. This magnetization reorientation is also evident from magnetization vs. magnetic field measurements shown in the inset of figure 4.12a. The magnetization curves for the 7 T and 14 T field, which are measured both on cooling and heating, as well as the magnetization vs. magnetic field measurements (inset), show

Figure 4.12: a) Field-cooled magnetization and b) electric polarization as a function of temperature in several magnetic fields up to 14 T applied along the c-axis. Inset in a) shows magnetization as a function of magnetic field at 5 K and 35 K. c) Presents the temperature dependence of the polarization for applied magnetic fields of 7 T and 14 T for different orientations of the applied magnetic field and measured polarization. Adapted from Paper VII.
4.3 Magnetic-field-induced polarization in cryolite-like Co$_3$TeO$_6$

Figure 4.13: Electrical polarization as a function of magnetic field at $\sim 5$K for the different orientations. The inset shows the variation of the temperature onset of polarization $T^*_P$ for \([\mathbf{P} \parallel \mathbf{c}; \mathbf{H} \parallel a](\nabla)\) and \([\mathbf{P} \parallel a; \mathbf{H} \parallel c](\triangle)\), as well as the temperature $T^*_M(\bullet)$ below which a drop/step is observed in the magnetization recorded with $\mathbf{H} \parallel c$. Adapted from Paper VII.

hysteresis behavior, indicating that the 18 K transition is of first-order character.

The electrical polarization $\mathbf{P}$ shown in figure 4.12b was measured along the $a$ direction$^5$ with the magnetic field applied in the $c$ direction. It is evident that the applied magnetic field induces an electrical polarization in that orientation and reaches values of about 25 $\mu$C/m$^2$ at 5 K and 9 T. The electrical polarization and the magnetization are strongly interconnected. The onset temperature of the induced polarization at $T^*_M$ corresponds with the temperature of the step in the magnetization $T^*_M$. The small hump on the top of the polarization curves (for example in 5 T) is most likely due to movement of the domain walls. On increasing the magnetic field to above 9.3 T, the onset polarization is shifted outside of the measurement window. The temperature dependency of the electrical polarization with $\mathbf{H} \parallel a$ (7 T and 14 T) is shown in figure 4.12c. From the plot of the polarization as a function of magnetic field at 5 K, shown in figure 4.13, it follows that the $\mathbf{H} \parallel a$ induced polarization is persistent up to 14 T and reaches about 160 $\mu$C/m$^2$ in orientation $[\mathbf{P} \parallel c / \mathbf{H} \parallel a]$. It can be concluded that the field-induced polarization depends approximately linearly on the

$^5$The measurements in $a$ direction also comprise a $b$-axis component such as [310].
applied magnetic field. The onset temperature of the induced polarization $T^*_P$ has an orientation dependence on the magnetic field, as seen in the inset of figure 4.13. For $H \parallel a$ orientation $T^*_P$ increases with increasing magnetic field whereas for $H \parallel c$ orientation $T^*_P$ decreases.

A remaining question is whether Co$_3$TeO$_6$ exhibit a spontaneous electrical polarization. Experimentally, a possible low-temperature spontaneous polarization of the order of 5 $\mu$C/m$^2$ was detected, see Fig. 4.10b. Nevertheless, that value is close to the resolution limit of our experimental set-up and needs to be verified.

**Physical properties of the low-temperature phase sequence from the Landau theory.**

The neutron data by S. Ivanov et al. revealed a sequence of three different AFM phases (I, II and III) as sketched in figure 4.14. The physical properties of these three phases were analyzed in collaboration with Pierre Toleå in using the Landau theory. Further details of this calculation can be found in Paper VIII. In phase I two propagation vectors ($k_1$ and $k_2$) and hence two order parameters are present. The Landau free-energy $\mathcal{F}$ can be derived from the irreducible representation and minimizing this leaves two possible equilibrium states. From the point symmetry of phase I, which is $2/m$ it follows that phase I is centrosymmetric and hence non-polar. For phase II only one propagation vector remains and the C$2'$/c space group has 4 irreducible representations. In this magnetic symmetry no spontaneous polarization is allowed. Nevertheless, under applied magnetic fields, the linear magnetoelectric effect and the reverse linear magnetoelectric effect are possible:

$$
\begin{align*}
P_{x,z} &= \delta H_y \\
M_{x,z} &= \delta E_y \\
M_{y,z} &= \delta E_{x,z}.
\end{align*}
$$

(4.7)

Phase III is governed by the coupling of two commensurate order parameters. This phase gives interesting results in pyroelectric current measurements. The wave vector $k_3$ in phase III corresponds to the locked-in wave vector of $k_1$ (Phase I). From minimizing the associate Landau free-energy of phase III and considering the observed symmetry of the neutron experiments, the possible magnetic symmetry is found to be C$2'$.

For this symmetry a spontaneous polarization and spontaneous magnetization such as $P_y = \delta^2 \rho^4 \cos(4\theta)$ and $M_{x,z} = \delta^4 \cos(4\theta)$ are feasible.
In the case of an applied magnetic field the linear magneto-electric effect and reverse magneto-electric effect are predicted in phase III:

\[
\begin{align*}
    P_{x,z} &= \delta \rho^2 H_y & \Delta P_y &= \delta \rho^2 H_{x,z}, \\
    M_y &= \delta \rho^2 E_{x,z} & \Delta M_{x,y} &= \delta \rho^2 E_y.
\end{align*}
\] (4.8)

From the magnetic field dependence of the electrical polarization, shown in figure 4.13, the coupling term \(\delta \rho^2\) can be estimated. Considering that the \(a\) direction was in fact [310] one has to correct the applied magnetic field by \(H_y \sim 0.3 \cdot H_a\) and \(\delta \rho^2 = P_z / H_y \sim 4 \cdot 10^{-5} \text{ C/m}^2\text{T}\). This suggest a magnetization of the order 1 A/m for an applied electrical field of 25 kV/m.

Second harmonic generation (SHG).

Second-harmonic generation (SHG) depends on the symmetry properties of a material where the SHG signal can be coupled to both the magnetic and the electrical properties. In the non-linear optical SHG the coupling of incident light \(E(\omega)\) with frequency \(\omega\) to the induced polarization \(P(2\omega)\) in the material at frequency \(2\omega\) can be described by \(P_i(2\omega) = \varepsilon_0 \chi_{ijk} E_j(\omega) E_k(\omega)\) [26]. The symmetry of the materials defines a set of non-zero

\[
\begin{align*}
\chi_{aaa} \quad \chi_{ccc} \quad \chi_{bbb}
\end{align*}
\]

**Figure 4.15:** Second harmonic (SH) intensity at \(T = 5\) K for \(k || a\) (upper panel) and \(k || b\) (lower panel). \(k\) represents the wave vector of the incident light and \(\chi_{aaa}\) and \(\chi_{ccc}\) are SHG susceptibility tensor components; the red line depicts \(\chi_{bbb}\) which does not contribute to the SHG signal. The inset shows the temperature dependence of the \(\chi_{ccc}\). Adapted from Paper VII.
tensor components $\chi_{ijk}$. In the case of inversion symmetry all tensor components $\chi_{ijk}$ are equal to zero. Therefore one would not expect a SHG signal for Co$_3$TeO$_6$ in the non-ferroic high-temperature phase with space group $C2/c$ (point group 2/m). A broken inversion symmetry in the low temperature ferroic phase would reduce the point symmetry to $m$, 2 or 1 [11].

The neutron data from S. Ivanov et al. [144] revealed a magnetic symmetry $C2$ in the low temperature phase. The monoclinic $C2$ symmetry and magnetic ordering suggest the observation of the $\chi_{aaa}$ and $\chi_{ccc}$ components of the SHG susceptibility tensor and no signal for the $\chi_{bbb}$ component. [11]. As can be seen in figure 4.15 there are $\chi_{aaa}$ and $\chi_{ccc}$ tensor component contribute to the SHG in both the $a$ and $b$-cut samples. The inset of figure 4.15 highlights the coupling of the ferroic transition at 18 K and the $\chi_{ccc}$ tensor component. In the case of ferroelectric ordering observed by SHG, the situation is different and the exclusive observation of $\chi_{aaa}$ and $\chi_{ccc}$ would point towards point group $m$. The observation of the $\chi_{bbb}$ component would indicate group 2.

In the case of SHG coupled to the ferromagnetic order the situation is different and the observation of $\chi_{aaa}$ and $\chi_{ccc}$ suggest a monoclinic symmetry $2'$ for phase phase III [11]. The SHG technique allows us to get spatial resolved data and hence pictures of the domain structure of the material. A coupling to the ferromagnetic order is confirmed by the experimental observation of a magnetic domain pattern using SHG measurements. The domain structure for Co$_3$TeO$_6$ at 5 K is shown in figure 4.16. It is interesting to note that from SHG imaging a domain pattern with a rigid orientation in the "$ab$"-plane is visible, cf. figure 4.16. A detailed study of the domain structure

Figure 4.16: Picture of the magnetic domain structure of Co$_3$TeO$_6$ at 5 K measured from SHG (In collaboration with Vera Carolus; University of Bonn, Germany).
4.3 Magnetic-field-induced polarization in cryolite-like $\text{Co}_3\text{TeO}_6$

**Figure 4.17:** $H - T$ phase diagram of $\text{Co}_3\text{TeO}_6$ for $H \parallel c$-axis. SF1 - SF3 denote different spin-flop phase which occur at the critical magnetic fields $H_{C1}$ and $H_{C2}$. SRMO denotes short range magnetic ordering. Taken from HER ET AL. [147].

in $\text{Co}_3\text{TeO}_6$ will be presented in the Ph.D. thesis of VERA CAR-OLUS [148].

**Other studies concerning $\text{Co}_3\text{TeO}_6$**

Recently, HER ET AL. [147] investigated the magnetic field dependence of the specific heat and ac susceptibility of $\text{Co}_3\text{TeO}_6$ [147]. Their results indicate a strong field dependence of the $T^* = 18$ K ($H = 0$) transition. In their specific heat measurements $T^*$ is linearly shifted towards higher temperatures (20 K in 14 T). The antiferromagnetic transition at 26 K, on the other hand shows a very minor shift and decreases to 25 K in 14 T. Their results on the magnetic field dependence agree with our findings from pyroelectric current measurements. Furthermore, they observe a second spin-flop transition in magnetic fields above 25 T and propose a $H - T$ phase diagram featuring several magnetic states at low temperature. The $H - T$ phase diagram of $\text{Co}_3\text{TeO}_6$ for $H \parallel c$-axis is reprinted in figure 4.17. In low magnetic field the phase diagram shows a sequence of transition from a paramagnetic state with short range magnetic ordering to a first AFM phase below 26 K and a second AFM phase below 18 K. For increasing the magnetic field at temperatures below 26 K a transition to a spin-flop state is observed. Their results agree with our finding from polarization and magnetic measurements and the neutron study by S. IVANOV ET AL. [144]
4.4 Spin-phonon coupling in the single-chiral Ba$_3$NbFe$_3$Si$_2$O$_{14}$ langasite

Langasite materials, for example La$_3$Ga$_5$SiO$_{14}$ [149], are isostructural to the Ca$_3$Ga$_2$Ge$_4$O$_{14}$ compound [150]. They have been known and studied for their piezoelectric and nonlinear optical properties [151, 152]. Recently, an interest in their magnetic properties and electrical behavior arose when it was found that some langasites, such as Ba$_3$NbFe$_3$Si$_2$O$_{14}$, could crystalize in a Kagomé-like lattice structure (cf. Fig. 4.3) consisting of rare-earth and transition metal cations [153–156]. A common feature of magnetic ions on a triangular or Kagomé-like lattices is frustration of the magnetic interactions, since not all competing interactions can be satisfied simultaneously. Typically, helical or other non-collinear spin structures form due to competition between exchange interaction and the destabilization of magnetic order via the antisymmetric DM exchange.

In the case of Ba$_3$NbFe$_3$Si$_2$O$_{14}$, the A-site is occupied by Ba, which are topologically Kagomé-like, and the C-site is occupied by Fe and has a triangular configuration. The long range magnetic ordering stems from the Fe on the C-site and the resulting magnetic structure consists of magnetic moments oriented with an angle of 120° to each other within each triangle of the triangular lattice.

A detailed study of the Ba$_3$NbFe$_3$Si$_2$O$_{14}$ (BNFSO) compound based on XRD, NPD, magnetic and electrical measurements was presented by KAROL MARTY [157]. A fascinating feature found in BNFSO is a single magnetic chirality state due to geometrical frustration in the triangular lattice. It is furthermore reported that dominating exchange paths between the planes are chirally modulated along the high symmetry c-axis. There is hence a strong interest in the magnetic and electrical properties of BNFSO, due to the possibility of multiferroic coupling. The single chiral state has also become the focus of several investigations [158, 159].

In this study we focused on the electrical properties and the coupling of the spin and lattice degrees of freedom. For that purpose single crystalline samples of Ba$_3$NbFe$_3$Si$_2$O$_{14}$ were synthesized (in collaboration with the CERG group at RIKEN, Japan) using the floating zone technique. Details on the fabrication technique and the synthesis conditions are described in chapter 2. The results presented in this chapter are summarized in Paper IX.
The structural properties of Ba$_3$NbFe$_3$Si$_2$O$_{14}$

Ba$_3$NbFe$_3$Si$_2$O$_{14}$ crystallizes in the non-centrosymmetric trigonal space group P321 (No. 150, Schönflies notation $D_3^2$), which is a subgroup of the hexagonal crystal system. Space group P321 is a symmorphic group and all symmetry operations can be performed within the first Brillouin zone. BNFSO possesses a 3-fold rotational symmetry with respect to the $c$-axis. The corresponding point group of the non-centrosymmetric lattice is 32 and the crystal symmetry allows the piezoelectric effect. The structure is non-polar and hence no spontaneous polarization can be expected for point group 32 [11].

The unit cell contains 23 atoms, which are distributed on six non-equivalent atomic positions specified in table 4.2. Within this structure, iron atoms are the only magnetic ions. They are arranged in triangle units on a triangular lattice [153], see figure 4.18. As mentioned earlier (cf. chapter 5), a triangular

Table 4.2: Atomic positions and symmetry of Ba$_3$NbFe$_3$Si$_2$O$_{14}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>PG sym.</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 Ba</td>
<td>3e</td>
<td>2</td>
<td>(x,0,0); (0,x,0); (-x,-x,0)</td>
</tr>
<tr>
<td>1 Nb</td>
<td>1a</td>
<td>32</td>
<td>(0,0,0)</td>
</tr>
<tr>
<td>3 Fe</td>
<td>3f</td>
<td>2</td>
<td>(x,0,1/2); (0,x,1/2); (-x,-x,1/2); (1/3,2/3,z); (2/3,1/3,-z)</td>
</tr>
<tr>
<td>2 Si</td>
<td>2d</td>
<td>3</td>
<td>(1/3,2/3,z); (2/3,1/3,-z)</td>
</tr>
<tr>
<td>2 O</td>
<td>2d</td>
<td>3</td>
<td>(x,y,z); (-y,x,y,z); (-x+y,-x,z); (y,x,-z); (x-y,-y,-z); (-x,-x+y,-z)</td>
</tr>
<tr>
<td>12 O</td>
<td>6g</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>
The lattice is favorable for showing frustration of interactions. The Fe$^{3+}$ triangles are arranged within the $ab$-plane and are incommensurably modulated along the $c$-axis. The propagation vector is reported to be $k = (0,0,\sim 1/7)$ [153]. The coordination of the different atom sites with respect to the oxygen atoms is as follows. The Ba$^{2+}$ site is decahedrally coordinated and the Nb$^{5+}$ site is octahedrally coordinated. Both Fe$^{3+}$ and Si$^{4+}$ sites are tetrahedrally coordinated with respect to the oxygen anions [153].

The Ba$^{2+}$ and Fe$^{3+}$ sites determine the magnetic and electrical properties. The magnetic structure was refined by Marty et al. [153, 155]. As mentioned previously, the Ba$^{3+}$ atoms are arranged in a Kagomé-like lattice. The Fe$^{3+}$ sub-lattice consists of a triangular lattice in which inter-triangular magnetic interactions are mediated through the super-exchange mechanism ($\text{Fe}^{3+} - \text{O} - \text{Fe}^{3+}$). Intra-triangular interactions in the $ab$-plane and along the $c$-axis on the other hand are much weaker and take place via super-super exchange with two oxygen atoms ($\text{Fe}^{3+} - \text{O} - \text{O} - \text{Fe}^{3+}$).

X-ray powder diffraction analysis of the synthesized powder and single crystalline samples confirmed the langasite structural type. The XRD patterns of several BNFSO samples are shown in chapter 2. From Rietveld refinement of the pure powder samples, the lattice parameters were found to be $a = 8.5292(1)$ Å and $c = 5.2379(1)$ Å ($c/a = 0.614$) and the cell vol-
4.4 Spin-phonon coupling in the single-chiral $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ langasite

Volume 330.0 Å$^3$ (Rietveld residuals: $R_p = 10.9\%$, $R_{wp} = 15.0\%$, $R_b = 7.82\%$). The corresponding powder pattern and refinement is shown in figure 4.19. For crushed single crystal samples synthesized using the FZ technique, the lattice parameters of BNFSO were found to be $a = 8.5301(1)$ Å and $c = 5.2384(1)$ Å. The reported values from literature are summarized in table 4.3.

Table 4.3: Lattice parameters and cell volume for $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ from references S. Ivanov et al. [160], Zhou et al. [154] and Marty et al. [156].

<table>
<thead>
<tr>
<th>Reference</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Vol. (Å$^3$)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivanov et al.</td>
<td>8.5219(2)</td>
<td>5.2399(2)</td>
<td>329.6</td>
<td>-</td>
</tr>
<tr>
<td>Zhou et al.</td>
<td>8.6049(2)</td>
<td>5.2523(3)</td>
<td>336.8</td>
<td>$R_b = 7.0%$</td>
</tr>
<tr>
<td>Marty et al.</td>
<td>8.5227(2)</td>
<td>5.2353(1)</td>
<td>329.3</td>
<td>$R_b = 3.2%$</td>
</tr>
<tr>
<td>This work</td>
<td>8.5292(1)</td>
<td>5.2379(1)</td>
<td>330.0</td>
<td>$R_b = 7.8%$</td>
</tr>
</tbody>
</table>

Figure 4.20: Specific heat for $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ measured on both heating and cooling showing a phase transition at 28 K.

The magnetic properties of $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$

It has been reported that BNFSO undergoes an antiferromagnetic phase transition at approximately 27 K [153]. Specific heat data for a single crystalline sample of BNFSO were measured both on heating and cooling and are shown in figure 4.22. The data confirm the appearance of a phase transition at 27 K and no other transition is evident in the low temperature region.
The magnetic properties of BNFSO are presented in figure 4.21. BNFSO is an antiferromagnet with a Néel temperature of approximately $T_N = 27$ K. Figure 4.21a presents the magnetization as a function of temperature for ZFC, FC and TRM protocols and additionally the in-phase component of the ac susceptibility $\chi'$ measured in a small field of 0.4 mT (1.7 Hz – 510 Hz). From the irreversibility between ZFC and FC magnetization
and the finite value of the TRM, the existence of an additional phase which contributes to the magnetization is evident. That additional phase could not be observed in the XRD patterns, cf. figure 2.4, suggesting that it amounts to less than 1%. The high temperature magnetization is shown in the inset i) of figure 4.21a and reveals an onset of irreversibility between ZFC and FC magnetization at about 850 K and an additional transition at 700 K. These high temperature features are likely due to the presence of a minor Fe$_3$O$_4$ phase which possesses a ferrimagnetic transition at $T_C \sim 850$ K.

For a magnetic system of Fe$^{3+}$ the angular orbital moments are quenched and the magnetic properties are mainly due to the spin moments [8]. The magnetic properties reported by MARTY ET AL. [156] state an effective magnetic moment of 5.95 $\mu_B$ and a negative Curie-Weiss temperature of $\theta \approx -175$ K. This value of the Curie-Weiss temperature indicates antiferromagnetic ordering at a temperature much higher than the observed $T_N = 27$ K. This is an indication of a strongly frustrated system [161].

Recently, ac susceptibility data for BNFSO were reported by CHOI ET AL.[162]. In their study it was argued that spin-glass-like behavior is observed. Measurements of the ac susceptibility depicted in the inset ii) of figure 4.21a show no indication of a frequency dependency in the low temperature phase. The observed frequency dependency in Reference [162] may be

![Figure 4.22: Electrical polarization as a function of temperature and magnetic field for Ba$_3$NbFe$_3$Si$_2$O$_{14}$. The dashed line represents $T_N$.](image-url)
caused by impurities, for example Ba$_2$FeNbO$_6$.

The magnetic field dependence of the magnetization at $T = 15$ K and 150 K for magnetic fields up to 5 T is depicted in figure 4.21b. The inset i) of figure 4.21b shows the moment per iron atom as a function of magnetic field up to 14 T measured at 2 K and 35 K. The minor bending of the $M$ vs. $H$ at low fields is due to the presence of a minor magnetic impurity phase. Below $T_N$ the magnetization as a function of magnetic field exhibits an anisotropic behavior. Depending on the orientation of the applied magnetic field $\parallel c$ or $\perp c$, higher or lower magnetization is measured. This behavior is also evident in the $M$ vs. $T$ data (not shown).

The electrical properties of Ba$_3$NbFe$_3$Si$_2$O$_{14}$

Dielectric properties of BNFSO were reported by MARTY ET AL. [156] and ZHOU ET AL. [154]. For point group 32 no spontaneous polarizations can be expected from symmetry considerations. Point group 32 allows the piezoelectric effect but not the pyroelectric effect. Nevertheless, ZHOU ET AL. reported an electrical polarization along the $c$-axis direction after breaking the inversion symmetry by an applied electrical field. In the langasite family the most probable transitions with decreasing symmetry are P321 $\rightarrow$ P3 and P321 $\rightarrow$ C2 [163]. In the first case, the twofold axes are lost and in the second case, the threefold axis disappears. High-resolution x-ray diffraction data, reported in reference [156], suggest a structural distortion at $T_N$ and lowering of symmetry to P3.

Pyroelectric current measurements under applied magnetic field were performed to study symmetry breaking via a magnetic field. The results for polarization vs temperature measurements in different magnetic fields are shown in figure 4.22. The magnetic field was applied along the $a$-axis direction and the polarization was measured $\perp a$ within the $ab$-plane. For magnetic fields higher than $\sim 5$ T a field-induced electrical polarization can be observed. The magnetic field dependence on the induced polarization for different directions of the applied magnetic field at 5 K is shown in figure 4.24. The experimental findings resemble the onset of the field-induced polarization for fields higher than $\sim 5$ T and a symmetric coupling of the polarization with the magnetic field. The appearance of an electrical polarization perpendicular to the threefold axis of space group P321 ($c$-axis) suggests a magnetic-field-induced transition to space group C2. This result agrees with the results from

---

\[6\] The piezoelectric and pyroelectric effects refers to the formation of a voltage in a crystalline material when applying pressure or changing the temperature.

---

Figure 4.23: Orientation scheme for a hexagonal lattice.
4.4 Spin-phonon coupling in the single-chiral $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ langasite

Mössbauer spectroscopy, reported by Lyubutin et al., suggesting a possible symmetry lowering to space group C2 [163].

A measurement of the capacitance (or dielectric constant) with $E \parallel c$ reveals a low temperature transition around 30-40 K and a high temperature transition between 100-150 K (not shown). For the $E \parallel a$ the capacitance as a function of temperature does not show the two features observed in $E \parallel c$ instead there is a kink at $T_N = 27$ K.

**Raman spectroscopy**

A room temperature Raman spectroscopy study on the isostructural compound $\text{Sr}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ was reported by Y. Li et al. [164]. In a group theoretical analysis they arrived at 66 principle vibrational modes (neglecting the three acoustical modes $A_2 + E$) at the center of the Brillouin zone (Γ-point):

$$\Gamma_{Vib} = 10A_1(R) + 12A_2(IR) + 22E(R, IR).$$  \hspace{1cm} (4.9)

In this notation $A_1$ and $A_2$ represent 10 Raman (R) and 12 Infrared (IR) active one-dimensional non-polar symmetry modes. $E$ corresponds to 44 two-dimensional polar symmetry modes, which are both Raman and IR active. The total number of Raman active modes is hence 54. The Raman scattering

![Graph](image-url)
Multiferroic materials
tensors for point group 32 can be found by using the program SAM [165], which is part the Bilbao Crystallographic Server\(^7\).
The corresponding Raman tensors for BNFSO are:

\[
A_1 = \begin{bmatrix}
a & 0 & 0 \\
0 & a & 0 \\
0 & 0 & b
\end{bmatrix}
\] (4.10)

\[
E_x = \begin{bmatrix}
c & 0 & 0 \\
0 & -c & d \\
0 & d & 0
\end{bmatrix} ;
E_y = \begin{bmatrix}
0 & -c & -d \\
-c & 0 & 0 \\
-d & 0 & 0
\end{bmatrix}
\] (4.11)

The scattering geometry for a Raman experiment can be described using the Porto notation. For example \(k_i(e_i,e_s)k_s\) corresponds to an experiment were the incident beam propagates along \(k_i\) and is polarized in orientation \(e_i\), and the scattered beam propagates along \(k_s\) with analyzer orientation \(e_s\). All orientations are measured with respect to the sample geometry. Using the Raman tensor 4.10 one can conclude that \(A_1\) modes are only observable in \((XX), (YY)\) or \((ZZ)\) polarized light. From factor group theory the number of \(A_1\) Raman active modes can be calculated and it follows that 10 \(A_1\) modes are predicted for scattering geometry \(Y(ZZ)\). For scattering geometry \(Y(ZX)\) the 22 \(E^e\) modes and for \(Z(YX)\) the 22 \(E^o\) modes are allowed [164].

The polarized Raman spectra were recorded with an imaging spectrometer (HoloSpec/1.8i, Kaiser Optical Systems) equipped with a holographic transmission grating and thermoelectrically cooled two-dimensional multichannel CCD detector (Newton, Andor Technology, 1600×400 pixels, -60 °C). A linearly polarized argon ion laser (514.5 nm line) was used for the excitation. The spectrometer was calibrated by fluorescence lines of the neon lamp. Raman spectra were collected in the back-scattering geometry, in the range 150 - 2340 cm\(^{-1}\), at a resolution of about 2 - 3 cm\(^{-1}\). Accuracy of spectral measurements, resulting from the wavelength calibration procedure and experimental conditions, is estimated to be about 1 cm\(^{-1}\). The acquisition time was typically 20 sec. The polarization direction of laser was controlled by using quartz l/2-plate. The polarizing efficiency of the analyzer was 99 %.

A room temperature Raman spectra for the three scattering geometries is shown in figure 4.25. \(A_1\) modes can be observed in parallel polarization. For scattering geometry \(Y(ZZ)\) 8 out of the 10 possible \(A_1\) modes could be identified and are highlighted with vertical dashed lines in figure 4.25. The 8 Raman

\(^7\)http://www.cryst.ehu.es/
active modes are 183, 199, 333, 510, 573, 777, 885, and 982 cm\(^{-1}\). For the second scattering geometry \(Y(ZX)\bar{Y}\) 12 out of the 22 \(E\) modes could be observed: 147, 189, 201, 251, 303, 416, 503, 567, 615, 675, 869, and 942 cm\(^{-1}\). In the following discussion the room temperature values of the phonon frequencies will be used as nomenclature.

An assignment of the observed modes to the corresponding lattice vibrations is difficult without the support of first principle calculations. Nevertheless, using the work by Y. Li et al. on \(Sr_3TaGa_3Si_2O_{14}\) some conclusions can be drawn. The “high” frequency \(A_1\) modes 885 and 982 cm\(^{-1}\) are likely to correspond to Si—O stretching vibrations. The modes in the intermediate frequency range are probably due to Fe—O—Nb, O—Fe—O, and O—Nb—O stretching vibrations, whereas lower frequency modes may correspond to Ba-Ba translations.

Unpolarized Raman spectra of \(Ba_3NbFe_3Si_2O_{14}\) as a function of temperature and magnetic field was measured using the Raman set-up described in appendix 6. All \(T\) and \(H\) dependent measurements were done with an the incident beam along the [1-10] direction.

![Figure 4.25: Room temperature polarized Raman spectrum of \(Ba_3NbFe_3Si_2O_{14}\) with three scattering geometries \(Y(ZZ)\bar{Y}\), \(Y(ZX)\bar{Y}\), and \(Z(YX)\bar{Z}\). The dashed lines correspond to the position of \(A_1\) modes. The spectra for \(Y(ZZ)\bar{Y}\) and \(Y(ZX)\bar{Y}\) have been shifted with a linear offset.](image)
Temperature dependence The temperature dependence of the unpolarized Raman spectra of Ba$_3$NbFe$_3$Si$_2$O$_{14}$ in 0 T is shown in figure 4.26. For better visualization spectra (50 - 300 K) have been shifted vertically with a linear offset. A detailed view of the temperature dependence of the Raman-active phonon modes 416, 510, 573, 615, 675 and 982 cm$^{-1}$ is shown in figure 4.27. The red line in (4.27) depicts a linear regression of the data in the 100 - 300 K temperature range. The shown phonon modes exhibit a frequency hardening and narrowing of the line-width on reducing temperature.

The temperature dependence of the lattice parameters for the isostructural langasite La$_3$Ga$_5$SiO$_{14}$ was reported by KRÄUSSLICH ET AL. [166]. The following relations were obtained ($T$ in °C):

\[
a(T) = a_{RT}(1 + \alpha_{11}(T - 20) + \beta_{11}(T - 20)^2),
\]

\[
c(T) = c_{RT}(1 + \alpha_{33}(T - 20) + \beta_{33}(T - 20)^2),
\]

(4.12)

where $\alpha$ and $\beta$ are the linear and quadratic thermal expansion coefficients, and $a_{RT}$ and $c_{RT}$ are the room temperature lattice parameters, quantified in table 4.4.
4.4 Spin-phonon coupling in the single-chiral $\text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14}$ langasite

Table 4.4: Lattice parameters for BNFSO. Thermal expansion coefficients for a $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ single crystal. Adapted from KRÄUSSLICH ET AL. [166].

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BNFSO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameter at RT (20°C)</td>
<td>8.5292(1) Å</td>
<td>5.2379(1) Å</td>
</tr>
<tr>
<td><strong>LGSO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$a_{11}, a_{33}$</td>
<td>5.20(8)·$10^{-6}$ K$^{-1}$</td>
<td>3.72(8)·$10^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td><strong>LGSO</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{11}, \beta_{33}$</td>
<td>6.7(1)·$10^{-9}$ K$^{-1}$</td>
<td>1.1(1)·$10^{-9}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

Figure 4.27: Temperature dependence of the Raman shift for the 416, 510, 574, 624, 675 and 982 cm$^{-1}$ modes. The red line corresponds to a linear regression in the 100 - 300 K temperature range. The vertical dashed line depicts $T_N$. 


Table 4.5: Estimation of the Grüneisen parameter $\gamma$ for the 416, 510, 573, 615, 675 and 982 cm$^{-1}$ modes.

<table>
<thead>
<tr>
<th>Mode cm$^{-1}$</th>
<th>416</th>
<th>510</th>
<th>573</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grüneisen parameter $\gamma$</td>
<td>3.03(2)</td>
<td>1.32(1)</td>
<td>0.41(1)</td>
</tr>
<tr>
<td>Mode cm$^{-1}$</td>
<td>615</td>
<td>675</td>
<td>982</td>
</tr>
<tr>
<td>Grüneisen parameter $\gamma$</td>
<td>2.47(2)</td>
<td>1.14(1)</td>
<td>0.44(1)</td>
</tr>
</tbody>
</table>

In a quasi-harmonic approximation, the frequency shift can be attributed to the volume change only. Anharmonic effects due to phonon-phonon and spin-phonon interaction are ignored. The Grüneisen parameter $\gamma$ is defined as

$$\frac{d\omega}{\omega} = -\gamma \frac{dV}{V}. \quad (4.13)$$

Using the the results for the thermal expansion from Kräusslich et al. the mode Grüneisen parameter ($\gamma = -d(\ln \omega)/d(\ln V)$) for all modes shown in figure 4.27 was estimated from the high temperature linear part of the Raman data, cf. table 4.5.

From the insets in figure 4.27 additional changes in the phonon frequencies when approaching $T_N$ are evident. For instance, the 416 and 510 cm$^{-1}$ phonon modes reveal softening behavior with an onset above $T_N$ and a subsequent hardening below 25 K. Similar behavior is observed for the other modes in figure 4.27, suggesting spin-phonon coupling. The observed changes in the $T$-dependent Raman spectra can be linked to a structural deformation (or transition) with a minor deviation from the P321 symmetry, as reported in Reference [156].

Raman scattering probes excitation at the center of the BZ and is sensitive to changes in short length scales. From magnetic measurements a strongly frustrated magnetic state was revealed in BNSFO with a negative Curie-Weiss temperature of $\theta \approx -175$ K ($T_N = 28$ K). Strong magnetic correlations hence exist also above $T_N$. 

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4.4 Spin-phonon coupling in the single-chiral Ba₃NbFe₃Si₂O₁₄ langasite

Figure 4.28: Magnetic field dependence of the unpolarized Raman spectrum of Ba₃NbFe₃Si₂O₁₄ at T = 5 K. The spectra for 0 T applied field is highlighted in red and the spectra for ±9 T in black. The dashed lines correspond to the position of $A_1$ modes. The spectra for $\mu_0H > -9$ T have been shifted with a linear offset.

**Magnetic field dependence**  The magnetic field dependence of the unpolarized Raman spectra of Ba₃NbFe₃Si₂O₁₄ at 5 K is shown in figure 4.28. In this measurement the magnetic field was set to the highest field (9 T) and the first Raman spectrum was collected. Subsequently, the magnetic field was swept from 9 T $\rightarrow$ -9 T. In the polarization measurements shown in figure 4.24, a magnetic field-induced polarization and hence breaking of inversion symmetry was observed for magnetic fields higher than 5 T. That change in the symmetry of the crystal structure should be reflected in the Raman spectra, for example through the appearance or disappearance of certain Raman modes. At a first glance, a strong change in the intensity of the 310, 416 and 510 cm$^{-1}$ modes and in the position of the 615 cm$^{-1}$ mode are found. Furthermore, several new modes appear at 250, 322, 760 and 840 cm$^{-1}$ when the field is changed from 9 T $\rightarrow$ -9 T.

A more detailed view of the magnetic field dependence at 5, 50 and 300 K for some modes is shown in figure 4.29. All modes in figure 4.29, independent of the temperature, show some magnetic field dependence. Figure 4.29b depicts the field dependence in the magnetically ordered state at 5 K. The influence of the magnetic field on phonon modes 510, 573, 675 and
982 cm\(^{-1}\) is weak and only the 416 and 615 cm\(^{-1}\) modes exhibit major changes in the frequency.

The interpretation of the field-dependent Raman data at the current stage is difficult. Intuitively one would expect a symmetric dependency of the phonon frequency with the magnetic field, as seen in the behavior of the electrical polarization. P. ROVILLAIN ET AL. [167] studied spin waves in BiFeO\(_3\) under applied electrical fields using Raman spectroscopy. They observed a quadratic dependency of \(\omega\) vs. \(E\) shifted by the coercivity field \(E_c\) due to hysteresis of the \(P\) vs. \(E\) curve. The presented results, for example the 416 cm\(^{-1}\) mode, may reflect a similar behavior. Nevertheless, for a profound understanding more experiments with different field cycling protocols are needed.
4.5 Concluding remarks

Magnetic field induced polarization in cryolite-like Co$_3$TeO$_6$

Co$_3$TeO$_6$ is a new magneto-electric material with a complex magnetic structure at low temperatures. The presented experimental data and the reported neutron data [144] reveal two characteristic ordering temperatures, $T_N$ ($\sim$26 K) and $T^*$ ($\sim$18 K). The transition at $T^*$ has a first-order character as evidenced, for example, from the sharp peak in the specific heat. At $T_N$, the spins form a sinusoidal antiferromagnetic arrangement directed along the $c$-axis, which turns into a spin spiral arrangement below $T^*$. From magnetization vs. magnetic field measurements a spin-flop transition at 5 K and 12 T is found. The symmetry of the low temperature phase is C2'. The SHG signal is coupled to the magnetic order and reveals a domain structure in the low temperature region. The monoclinic symmetry C2' of the multiferroic phase permits spontaneous polarization and magnetization along the $b$-axis direction, as well as direct and reversed linear magnetoelectric effects.

Spin-phonon coupling in the single-chiral Ba$_3$NbFe$_3$Si$_2$O$_{14}$ langasite

The langasite Ba$_3$NbFe$_3$Si$_2$O$_{14}$ exhibits an interesting crystalline and magnetic structure, with single handed chirality and magnetic Fe$^{3+}$ moments oriented 120° from each other within triangular units. The point group 32 is non-centrosymmetric and non-polar. Therefore, the piezoelectric, but not the pyroelectric, effect can be observed. Under applied magnetic fields a small field-induced electrical polarization is observed in Ba$_3$NbFe$_3$Si$_2$O$_{14}$, suggesting a lowering of symmetry from P321 $\rightarrow$ C2. Raman spectroscopy is used to study the coupling between electrical and magnetic degrees of freedom. The temperature dependence of the Raman-active phonon modes in Ba$_3$NbFe$_3$Si$_2$O$_{14}$ deviates from only thermally driven behavior and indicates spin-phonon coupling. The effect of a magnetic field on the Raman-active phonon modes shows interesting properties but demands further detailed measurements, including field cycling protocols to be fully utilized.
What is next?

Two novel materials were studied and several questions are still open. Co$_3$TeO$_6$ should exhibit spontaneous electrical polarization a fact, which still needs to be verified. Furthermore, little is known about the dynamic properties of the observed domains in Co$_3$TeO$_6$. Domain switching on fast timescales is a crucial property for possible applications. The Raman spectroscopy study of Ba$_3$NbFe$_3$Si$_2$O$_{14}$ is ongoing and more measurements are needed to fully understand both the temperature and magnetic field dependent behavior.

Pressure is another variable that can be use to probe the spin-electron-lattice coupling in our materials. As mentioned in appendix A.2, we also have the ability to apply large hydrostatic pressure (up to 50 GPa) while collecting Raman spectra. Figure 4.30 illustrates the results of such an experiment on the LiCu$_2$O$_2$ system synthesized as single-crystals by R. Berger [168]. The complex spiral magnetic structure of LiCu$_2$O$_2$ brings forth an electrical polarization and magnetoelectric effects [169, 170]. The network of magnetic Cu ions is essentially two-dimensional, yet the electrical polarization seems to be associated with the three-dimensional character of the magnetic interaction below 22 K [170]. It is thus interesting to investigate the pressure effects on the Raman spectra of these materials at low temperatures. As seen in figure 4.30,
the effect of increasing pressure is evident, yielding the shift of all major Raman peaks observed at low temperatures. In the future, we will perform a detailed study and analysis of such pressure-dependent Raman spectra, and combine them to our magnetic and electrical field studies.

Another interesting subject within the field of multiferroic materials is the study of ferrotoroidic moments. Recently, it was shown that a possible realization of such a ferrotoroidic material may be found in certain spin-glass materials, namely the XY-like spin-glass system Ni$_x$Mn$_{1-x}$TiO$_3$ [171]. Interestingly, Ni$_x$Mn$_{1-x}$TiO$_3$ is closely related to the Ising model system Fe$_x$Mn$_{1-x}$TiO$_3$ which is studied in the next chapter.
CHAPTER 5

SPIN GLASSES

In this chapter some of the remarkable magnetic properties of spin-glass materials are discussed. First, a short introduction to the complex field of spin glasses and the underlying theoretical models is given. Subsequently, dynamic properties of some spin glass systems are studied using IRM recooling experiments. After that, the effect of magnetic field perturbations on the SG state is discussed and results on spin glasses of different spin dimensionality are compared.

5.1 Introduction

The concept of perfect order and symmetry, often used in theoretical descriptions and models, is rarely realized in natural materials. In reality, all solid materials contain some randomness, e.g. impurities and dislocations. It is interesting to notice that even small amounts of such impurities may change the macroscopic properties significantly and in some cases even dominate the physical properties. Prominent examples of such materials are spin glasses. A magnetic material which incorporates both disorder and frustration in its spin system can form a spin glass [172]. The disorder can be due to randomness in the distribution of magnetic ions in the crystal structure as well as in the distribution of magnetic interactions. As a consequence of disorder, competition among the different types of interaction may arise and hence not all interactions can be fulfilled simultaneously. The system therefore remains in a state of frustration. Some examples of disorder and frustration are shown in figure 5.1. As a consequence of disorder and frustration spin glass materials exhibit interesting physical phenomena such as aging, memory and rejuvenation (concepts which will be introduced in the next section).

Figure 5.1: Schematic spin structure showing examples of disorder and frustration. a) FM state without disorder and frustration. b) AFM state with geometrical frustration and c) frustration due to the bond disorder (“+” indicates FM and “-” AFM coupling).
5.2 Spin-glass materials: short overview

Depending on the spin dimensionality $n$ one can classify spin glasses and other materials: *Ising* $(n = 1)$, *XY* $(n = 2)$ and *Heisenberg* $(n = 3)$, see figure 5.2. In an *Ising* spin glass the spins have only two possible states, $\pm S$, see figure 5.2a. In an *XY* spin glass (5.2b) the spins are arranged in a plane and in a *Heisenberg* spin glass (5.2c) the spins can be arbitrary arranged in a three-dimensional space.

**5.2 Spin-glass materials: short overview**

The spin-glass systems investigated in this thesis were chosen to model different spin dimensionality in systems of three-dimensional spatial character.

**Heisenberg-like spin glasses:** Cu(Mn), Ag(Mn), and Au(Fe) are non-magnetic noble metals diluted with transition metal impurities. Cu(Mn), for instance, is a conductor and the magnetic interactions are of RKKY type (described in chapter 1). The interaction strength in this case depends on the distance between the magnetic ions and can be both anti- or ferromagnetic. Cu(Mn) is a classical Heisenberg SG for compositions containing less than 15 at.% Mn. A polycrystalline sample of Cu(Mn) with 13.5 at.% Mn and a spin glass transition temperature at $T_g = 57$ K has been synthesized using the drop synthesis method and characterized. Within this thesis the related Ag(11at.%Mn)(Ag(Mn)), $T_g = 31$ K and the anisotropic Au(6at.%Fe) (Au(Fe)), $T_g = 24$ K [173] have been used in the investigations.

**XY-like spin glass:** Eu$_{0.5}$Sr$_{1.5}$MnO$_4$ (ESMO) is a layered manganite and the magnetic properties resemble those of a XY spin-glass system. The ESMO system has been characterized by R. Mathieu et al. [174] and the SG transition temperature was found to be $T_g = 18$ K. The origin of the anisotropic spin-glass state has been attributed to the two-dimensional Mn network in the layered manganites and the associated orbital ordering. The high-quality single crystals of the A-site disordered Eu$_{0.5}$Sr$_{1.5}$MnO$_4$ studied in this thesis were grown by Y. Tokunaga using the floating-zone method.

**Ising-like spin glass:** Fe$_x$Mn$_{1-x}$TiO$_3$ (FMTO) is a derivate of the two ilmenites FeTiO$_3$ and MnTiO$_3$ in which the magnetic ions are arranged in a honeycomb-type lattice in a plane perpendicular to the $c$-axis. FeTiO$_3$ and MnTiO$_3$ are both anti-ferromagnetic and insulating. The Fe$^{2+}$ ions possess a strong single ion anisotropy compared to Mn$^{2+}$. Fe$_x$Mn$_{1-x}$TiO$_3$ has

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**Figure 5.2:** Schematic view of spin dimensionality for a) Ising, b) XY and c) Heisenberg spins.
a wide stability range with a spin glass phase existing in the low temperature range ($< 30$ K) for concentrations ($x \approx 0.5 \pm 0.1$). The magnetic properties in FMTO are dominated by nearest neighbour (nn) interactions. FMTO is considered to be a model Ising system. Single crystalline samples with composition Fe$_{0.5}$Mn$_{0.5}$TiO$_3$ and a spin glass transition temperature at $T_g = 21$ K fabricated by A. ITO and H. ARUGA-KATORI were studied within this thesis [175].

5.3 Theoretical and experimental fundamentals

The theory of spin glasses is rich and complex and to give a full theoretical description is beyond the scope of this thesis. However, it is helpful to introduce the main concepts and models to have a topical discussion of the field.

5.3.1 The Edwards and Anderson (EA) model

The question whether there is a true magnetic phase transition in a spin glass and what the order parameter is has been a long standing problem. A simple model to describe the spin glass phase transition was developed in the Edwards-Anderson model (1975) [176] which proposes an order parameter $q$ of the type

$$q = \lim_{\Delta t \to \infty} \langle S_i(t) \cdot S_i(t + \Delta t) \rangle. \quad (5.1)$$

where $\langle ... \rangle$ is the thermodynamic average of a spin $S$ at site $i$ and time $t$. In the EA model the interaction is short-range and the Hamiltonian in case of an Ising system is given by

$$\mathcal{H} = -\frac{1}{2} \sum_{i,j} J_{ij} S_i S_j, \quad (5.2)$$

with the random interaction $J_{ij}$. The distribution of bonds $P(J_{ij})$ is assumed to be Gaussian with $\bar{J} = 0$. Using equation 5.2 the order parameter can be calculated and is found to be non-zero for $0 \leq T \leq T_C$ with $q(T = 0) = 1$ and $q(T \geq T_C) = 0$. The EA model is hence able to describe spin glasses in a simple framework.
5.3.2 Mean field models of spin-glass systems

The Sherrington and Kirkpatrick (SK) model

The Sherrington-Kirkpatrick model (1975) [177] is a mean-field model based on the EA model in which the magnetic interactions are acting on an infinite-range. The interactions are distributed according to the probability function $P(J)$ which can be described by a Gaussian distribution with zero or finite mean ($J_0 = 0$ or $J_0 \neq 0$). The SK model introduces a second order parameter $m$ and provides a phase diagram, see figure 5.5. The first order parameter $q$ describes magnetic ordering in general, whereas the second order parameter $m$ describes the onset of ferromagnetic ordering in particular. In the SK phase diagram one can identify three distinct regimes: (1) a paramagnetic state, (2) a spin glass state and (3) a ferromagnetic state.

In a certain part of the phase diagram the system undergoes first a transition from the paramagnetic to ferromagnetic state and second a so-called reentrant transition from the ferromagnetic to spin glass state. Nevertheless, the SK model has some shortcomings and gives, for example negative entropy values at low temperatures.

The Parisi solution by replica symmetry breaking (RSB)

The main shortcomings of the SK model could be resolved by the Parisi solution [178]. In the low temperature phase $T < T_g$ an infinite number of possible thermodynamic states, minima in the energy landscape, are present separated by an infinite energy barrier. A crucial step in the RSB model is the definition of the order parameter in terms of an integral over the order parameter density $q(x)$ representing the possible thermodynamic states. The continuous parameter $x$ ranges from 0 to 1 and the order parameter $q$ becomes continuous in the local magnetic field. Therefore, the RSB model resolves the shortcomings of the SK model, namely a negative susceptibility $\chi_{SG}$ below $T_g$, and allows an SG phase transition under applied magnetic field (see AT-line in chapter 5.3.5). The experimentally measured ac susceptibility can be qualitatively reproduced from the second derivative of the free energy. The spin interaction in the RSB model, as in all mean field models, is assumed to be infinite and $J_{ij}$ connects all spin pairs and not only nearest neighbors.
5.3.3 The droplet model

In 1986 Fisher and Huse [179, 180] suggested a theoretical approach based on the renormalization group picture to describe SG with short-range interaction. Within this model the definition of the order parameter is similar to the EA order parameter. The equilibrium ground state is two-fold degenerated (e.g. \( \Gamma \) and \( \bar{\Gamma} \)) with respect to global spin reversal. Low energy excitations from the ground state can be described as coherent spin flips, called droplets. The surface area of a droplet of size \( L \) is given to \( A_L = L^d \), with \( d \) being the spacial dimension. Droplets of size \( L \) hence include \( L^d \) spins. The droplet excitations in the zero temperature limit occur with a characteristic energy \( E \sim L^\theta \), due to the presence of droplet domain walls with fractal dimension \( d_s \) ((\( d - 1 \)) < \( d_s \) < \( d \)). A small perturbation \( \Delta J \) of the bond strength will change that energy by \( E_{\Delta J} \sim L^{d_s/2} \). Likewise, a small perturbation \( \Delta E \), such as a change in the bond strength \( \Delta J \) or temperature \( \Delta T \), will rearrange the ground state on overlap length scales (cf. Fig. 5.6) longer than

\[
L_{\Delta E} = \Delta E^{-1/(d_s/2-\theta)}.
\]

The relaxation of the system from a non-equilibrium state is described by the movement of droplet domain walls.

5.3.4 Experimental properties of spin-glass systems

In a spin glass there is no conventional long-range order and it is therefore difficult to describe the spin glass phase transition. Experimentally, only a cusp in the vicinity of the phase transition is evident in the ac-susceptibility and ZFC magnetization as a function of temperature [181].

Critical slowing down

Spin-glass materials exhibit interesting dynamic properties over a broad range of time scales. Critical slowing down, for instance, is a common property of second order phase transitions. The correlation length \( l(\epsilon) = l_0 \epsilon^{-\nu} \) diverges at the phase transition \( T_g \) and the time to reach an equilibrium state becomes longer with a likewise divergence of the relaxation time \( \tau(\epsilon) = \tau_0 \epsilon^{-z} \). For a spin glass \( z\nu = 6 - 10 \) whereas for a ferromagnet \( z\nu = 2 - 3 \). In experiments the probed time scales correspond to the observation time of the measurement technique used (compare chapter 2) and only a small time frame can be observed. Yet, scaling analyses of the critical slowing
5.3.5 The effect of a magnetic field on spin glasses

down can be performed in order to prove evidence of an SG phase transition [174].

**Aging, memory and rejuvenation**

As discussed previously the ground state of a spin glass may be disturbed by a perturbation such as a change in temperature $\Delta T$ or magnetic field $H$. The system is therefore in an non-equilibrium state and evolves towards its equilibrium via a relaxation process called aging. Aging reflects the growth of correlation with time and was reported for the first time by L. LUNDGREN ET AL. [182] The age of the system $t_a = t_w + t_m$ (at a constant temperature) corresponds to the wait time, $t_w$, before the measurement plus the time, $t_m$, which has evolved since the measurement was started. For a measurement of the magnetization as a function of time (plotted on a logarithmic time axis) an inflection point at the waiting time $t_w$ is evident, cf. figure 5.7. This inflection point describes a crossover from a time regime $\log t << \log t_w$ where the equilibrium fluctuations of the systems on short length scales are probed (Note: the system is still in a global non-equilibrium state). Towards a time regime $\log t >> \log t_w$ probing the global non-equilibrium dynamics. An illustrative picture can be obtained from the logarithmic relaxation rate $S(t)$,

$$S(t) = \frac{1}{h} \frac{dM(t)}{d\log(t)} \approx -\frac{2}{\pi} \chi''(\omega),$$

with $t = 1/\omega$ and $h$ being a very small magnetic field. In the relaxation rate $S$, this crossover is evident as a maximum at the waiting time $t_w$, see figure 5.7.

Another important property of spin glasses is the memory effect. In a memory experiment the spin glass is aged by applying a wait time at a constant temperature $T_h$ below $T_g$. The memory effect is evident as a dip at $T_h$ in the ZFC (or a hump in the TRM) magnetization curve if compared with a measurement with no applied wait time at $T_h$ (reference curve), c. f. figure 5.10. At temperatures away from $T_h$ the magnetization curves with and without wait time merge - this behavior is called rejuvenation. The width of the memory dip is governed by the magnitude of the overlap length scale. Indeed, spin glass order may coexist at different temperatures and different length scales due to the chaotic nature of the SG phase. [183]

**5.3.5 The effect of a magnetic field on spin glasses**

The spin glass behavior under an applied magnetic field is different from the zero-field case. From time- and temperature...
dependent measurements it is known that the FC spin state has a local minimum and is hence in quasi-equilibrium. The question is now what happens to the spin glass state. In a mean-field model a spin glass transition under an applied magnetic field would be possible. For the Ising spin glass the change of the transition temperature when applying a magnetic field is described by the de-Almeida-Thouless (AT) line. The AT line is a thermodynamical line that separates a paramagnetic phase from an equilibrium SG phase. In vector spin glasses the AT-line is not present anymore and the Gabay-Toulouse (GT) line occurs.

In the droplet model the spin glass state is destroyed by the application of a magnetic field and the system will not exhibit a phase transition in a magnetic field. For an applied external magnetic field \( \Delta H \) the change in energy is proportional to \( \sim L^d/2 - \theta \). Hence the instability introduced by the magnetic field breaks the two-fold degeneracy of the ground state on a length scale \( \sim \Delta H^{-1/(d/2 - \theta)} \), and destroys the spin glass phase. This result could be verified experimentally for the Ising spin glass Fe\(_{0.5}\)Mn\(_{0.5}\)TiO\(_3\) [184] and via simulations [185].

### 5.3.6 Hysteresis and high magnetic-field properties of spin-glass systems

The magnetic-field dependence of spin glasses outside the linear response regime has been studied intensively. For the Ising-like Fe\(_{0.5}\)Mn\(_{0.5}\)TiO\(_3\) spin glass, for instance, field-induced collective spin reversal has been reported by A. ITO [186]. Results on the hysteresis behavior of XY-like SG systems are rare. Some results of the hysteresis behavior of ESMO are reported within this thesis. For metallic Heisenberg-like spin glasses (e.g. Cu(Mn)), a shift of the hysteresis loops similar to the exchange-bias effect is known. For bulk spin glasses this was first observed by SCHMITT AND JACOBS in 1957 [187]. The phenomenon has been studied in greater detail by KOUVEL in the early 60s for Cu(Mn) and Ag(Mn) [188–190]. Through the years numerous studies on the hysteresis behavior of Cu(Mn) have been performed [191–194]. IWATA ET AL. [195] performed torque measurements on a single crystal of Cu(Mn). P. BECK [196] studied the mictomagnetic behavior of Cu(Mn) with medium concentrations of Mn in Cu. Systematic studies on samples with low concentration of Mn in Cu were performed by KNITTER ET AL. [197, 198] and MONOD ET AL. [199, 200]. Caloric measurements on Cu(Mn) were done by BERTON ET AL. [38] and the magnetic and atomic short-range order in Cu-rich Cu(Mn) was studied by SCHÖNFELD ET AL.
The shift of the magnetic hysteresis has been theoretically interpreted by A. Fert and P. M. Levy [202] as an effect of a Dzyaloshinskii-Moriya type interaction brought forth by spin-orbit scattering of the conduction electrons. An applied magnetic field introduces a unidirectional anisotropy which becomes evident experimentally in the shift of the hysteresis loop similar to the exchange bias effect.

The conventional exchange-bias effect has been known for more than 50 years [203] and has been a subject of great interest from both a fundamental as well as a technological point of view, due to its use in magnetic recording and sensor devices [5]. The phenomenon is commonly described for a ferromagnet (FM) in contact with an antiferromagnet (AFM) and may be explained in terms of an electronically mediated interface exchange interaction [204]. These interface exchange interactions give rise to an additional unidirectional anisotropy (exchange anisotropy) which affects the magnetization reversal process of the whole system. In experiments this is manifested as a horizontal shift of the hysteresis-loop from the symmetrical position around zero when cooled in a magnetic field, see figure 5.8. Recent theoretical and experimental investigations have reported the exchange-bias phenomenon for a ferromagnet in contact with a spin glass [205, 206].
The conventional exchange-bias is often observed in magnetic nanoparticle systems, in which the magnetism may be locked by field cooling in a similar way as in the heterostructures mentioned above. Figure 5.9 shows hysteresis measurements performed on a system of interacting MnFe$_2$O$_4$ nanoparticles (average size: 2 nm) at low temperatures after ZFC and FC conditions.

As we will discuss further, due to dipolar interactions between the particles, the system behaves like a superspin glass$^1$ below 40 K. Interestingly, as seen in figure 5.9, the hysteresis curves obtained after cooling in 1 Tesla from high temperatures (150 K) is horizontally shifted as in "conventional" exchange bias systems. It is interesting to note that the coercivity increases in FC conditions, as well as the remanent magnetization (vertical shift).

$^1$i.e. A spin glass in which the fluctuating entities are superspins, not atomic ones; a superspin refers to a cluster or domain of coherently arranged magnetic moments.
5.4 Memory and rejuvenation in the canonical Cu(Mn) spin glass

The non-equilibrium behavior of spin glasses is an ongoing interesting topic of investigation. Non-equilibrium properties are usually studied in the linear response regime using different temperature protocols, as described in chapter 2.3. In a ZFC measurement with a halt for instance, the sample is zero field cooled to a temperature \( T_h \) \((T_h < T_g)\) and the system is aged while the temperature is kept constant at \( T_h \).

The aged spin structure is kept in the memory of the system when the sample cooling is resumed. By the time measuring the magnetization on reheating, the system recalls the spin configuration and a deviation from the reference measurement with no hold is found. Further away from the memory dip the system is recovered to the reference value of the magnetization. An example for the temperature- and time-dependent relaxation behavior of a Cu(Mn) spin glass showing aging, memory and rejuvenation phenomena is presented in figure 5.10. The finite width of the memory dip is a consequence of the overlap length, cf. inset of figure 5.10. The top panel shows the temperature dependence of a dc-magnetization experiment using ZFC, FC and TRM cooling protocols for an applied field of 0.5 Oe. The measurements were done without (open symbols) and with (filled symbols) an intermediate stop at \( T = 40 \) K for \( t_w = 3000 \) s when cooling from the reference temperature \( T_{Ref} = 70 \) K. The principle of superposition: \( M_{ZFC}(t) = M_{FC}(t) - M_{TRM}(t) \) is valid [207], confirming a linear response to the field changes. In the bottom panel of figure 5.10 the corresponding time dependence of the magnetization at \( T = 40 \) K after cooling from \( T = 70 \) K and waiting for 3 or 3000 s is shown. The difference in the magnetization evolution with waiting time (3 s) and waiting time (3000 s) reflects the aging and the associated rearrangement of its spin configuration that occurred while the spin glass was kept at a constant temperature. The dynamic behavior in figure 5.10 is governed by the temperature- and age-dependent response function of the spin glass. In the slightly different IRM experiment, the sample is zero-field cooled to a temperature \( T_h \) \((T_h < T_g)\) and a spin configuration is imprinted by applying a magnetic field \( h \) \((h \) is within linear response) while holding the temperature constant at \( T_h \).

By combining in-field temperature cycling procedures in the linear response regime with dc-memory experiments it is possible to distinguish between a magnetization part governed by the dynamic response of the spin glass and a part that is frozen in after a perturbation of the system with a magnetic
**Figure 5.10:** a) temperature dependence of the ZFC, FC, and TRM magnetization for $H = 0.5$ Oe recorded on reheating. In the inset, a difference plot of a ZFC curve with and without stop is shown. b) Time dependence of the ZFC, FC and TRM magnetization at $40$ K (after cooling from $70$ K) is shown. The vertical dotted line indicates the experimental time scale of temperature-dependent measurements. In both plots the open symbols (□, ◊, ▽) indicate a reference measurement without stop, and filled symbols (♦, ▼) indicate a measurement with a stop at $40$ K for a time $t_s = 3000$ s. Adapted from Paper XIII.
field. The results for a Cu(Mn) SG presented in this chapter were published in Paper XIII.

Experimental procedures

Figure 5.11: Schematic representation of the different experimental procedures employed. The arrows indicate the time at which the magnetization starts to be recorded. a) Variation of the temperature $T$ and magnetic field $H$ as a function of time during the procedures A1, A2 (continuous line) and B1, B2 (dotted line) in the ZFC case. In the case of A1, B1, $t_w = 0$, while $t_w = 3000$ s for A2, B2. b) Shows the procedures A1, A2 in the IRM (continuous line) and TRM (dotted line) cases. Adapted from Paper XIII.
As already mentioned, the chosen approach to study the effect of a magnetic field perturbation was to combine in-field temperature cycling with dc-memory experiments. The experiments were performed on a home-built SQUID magnetometer described in chapter 2.X. The following procedures were utilized:

R1 Conventional ZFC experiment without halt during the initial cooling.

R2 Conventional ZFC experiment with halt (3000 s at 40 K) during the initial cooling.

A1 The system is ZFC to \( T = 40 \) K, a magnetic field \( H = 0.5 \) Oe is switched on and the magnetization is recorded on cooling from 40 K \( \rightarrow \) 20 K, and on reheating from 20 K \( \rightarrow \) 70 K.

A2 The system is ZFC to \( T = 40 \) K where a halt for 3000 s is performed, subsequently a magnetic field \( H = 0.5 \) Oe is switched on and the magnetization is recorded on cooling from 40 K \( \rightarrow \) 20 K, and on reheating from 20 K \( \rightarrow \) 70 K.

C The system is ZFC to \( T = 40 \) K, a magnetic field \( H = 0.5 \) Oe is switched on and a halt for 3000 s at 40 K is performed, subsequently the magnetization is recorded on cooling from 40 K \( \rightarrow \) 20 K, and on reheating from 20 K \( \rightarrow \) 70 K.

B1 The system is ZFC to \( T = 20 \) K, a magnetic field \( H = 0.5 \) Oe is switched on and the magnetization is recorded from 20 K \( \rightarrow \) 40 K \( \rightarrow \) 20 K \( \rightarrow \) 70 K.

B2 The system is ZFC to \( T = 20 \) K where a halt for 3000 s is performed, subsequently a magnetic field \( H = 0.5 \) Oe is switched on and the magnetization is recorded from 20 K \( \rightarrow \) 40 K \( \rightarrow \) 20 K \( \rightarrow \) 70 K.

A schematic sketch of the measurement procedures for the ZFC, TRM and IRM can be found in figure 5.11.

**Magnetic field-induced excess magnetization in Cu(Mn)**

The results of the combined in-field temperature cycling with dc-memory experiments are depicted in figure 5.12, where only the low temperature range for the ZFC magnetization is shown. Following figure 5.12a, the initial magnetization value \( M_{A1}(T = 40 \) K) is larger than \( M_{A2}(T = 40 \) K) which is in agreement with the time-dependent relaxation behavior shown in
5.4 Memory and rejuvenation in the canonical Cu(Mn) spin glass

**Figure 5.12:** a) Temperature dependence of the ZFC magnetization recorded using the A, C and R heating/cooling protocols. b) Temperature dependence of the ZFC magnetization recorded under the B and R heating/cooling protocols. The inset shows the difference plots of the B2-B1 (open symbols), A2-A1 (filled symbols), as well as R2-R1 (continuous line) curves. Adapted from Paper XIII.

Figure 5.10. On re-cooling the magnetization first increases and becomes flat with a constant magnetization value \( M_{A1}(T \rightarrow 0 \text{ K}) > M_{A2}(T \rightarrow 0 \text{ K}) \) at low temperatures. It is evident from figure 5.12a that the equilibration, which was reached during the \( T \) halt in the initial cooling (A2 and R2) is stored in the memory and recovered on the reheating measurement when
both curves merge with their respective reference curves. In figure 5.12b results of the B1 and B2 procedure, in which the magnetization was recorded from 20 K → 40 K → 20 K → 70 K, are shown. Similarly in procedures A1 and A2, shown in figure 5.12a, the final reheating curves merge with their respective references and the magnetization curves become flat at low temperatures. The difference plots (R2-R1, A2-A1, B2-B1) are depicted in the inset of figure 5.12b. The (R2-R1) curve is identical with a standard dc-memory experiment, compare figure 5.10. The (A2-A1) curve corresponds to dc-memory experiments with in-field temperature cycling. The frozen-in magnetization implies that $\Delta M/H$ remains nearly constant as the temperature decreases below 40 K, outside the width of the memory dip exhibited by the reference (R2-R1) curve.

In figure 5.13a the corresponding ZFC, FC and TRM curves for all thermal protocols (R, A, B and C) are depicted. It is evident that ZFC and TRM behavior corresponds nicely with each other in accordance with the principle of superposition. The effect of wait times and temperature cycling on the FC magnetization is weak. As seen from the inset of figure 5.13a, the difference curves obey a linear response, with $\Delta M_{\text{ZFC}} \sim |\Delta M_{\text{TRM}}|$. Figures 5.13b and 5.13c present results of the isothermal remnant magnetization (IRM) after thermal protocols R, A, and B. IRM experiments are particularly interesting, since the magnetic field is applied only to imprint magnetization during the $T$ halt and turned off elsewhere.

At a first glance, the IRM curves look, as expected, similar to the ZFC(A2-A1) and ZFC(B2-B1) curves shown in the inset of figure 5.12 b). Nevertheless, the thermal history of the IRM curves is different, because there is always a 3000 s stay at 40 K during which the magnetic field is applied. The magnetization that is attained during $T$ halt and magnetic field application is frozen in when the cooling process is continued. Hence, the nature of this magnetization is fundamentally different from the dynamically controlled magnetization that occurs with time at a constant temperature after a magnetic field perturbation in the thermal protocols A and B. In protocol A and B the frozen-in magnetization state is also attained when the sample is cooled under applied magnetic field from 40 to 20 K. The weak temperature dependence of the magnetization curves in the low temperature region corresponds to the frozen-in magnetization states. Increasing the temperature above the temperature where the frozen-in magnetization was attained results in a drop in the magnetization to zero; the frozen-in state fades away.
5.4 Memory and rejuvenation in the canonical Cu(Mn) spin glass

Figure 5.13: a) Temperature dependence of the ZFC, FC, and TRM magnetization recorded under the same heating/cooling protocols. Procedures A2 (open symbols), C (pluses), and B1 (filled symbols), and reference curves (continuous lines) are shown. The inset shows the corresponding difference plots (A2-R2, C-R1, and B1-R1) for the ZFC and TRM (plotted as $-M_{\text{TRM}}$) data. b) Temperature dependence of the IRM magnetization recorded under the A1 and A2 procedures. c) Temperature dependence of the IRM magnetization recorded under the B1 and B2 procedures. In the reference IRM measurements, a magnetic field of $H = 0.5$ Oe is applied for 3000 s at 40 K and removed, and $M$ is recorded (in $H = 0$) from 40 K $\rightarrow$ 20 K $\rightarrow$ 70 K. The inset shows the difference plot A2-A1 obtained for ZFC experiments for comparison. Adapted from Paper XIII.

Conclusion

Interestingly, all reheating IRM curves exhibit an upturn when they reach 40 K, suggesting that an excess magnetization was imprinted in the direction of the field (i.e. unidirectional anisotropy). This excess magnetization is washed out by random spin fluctuations without preferred direction as the temperature is shifted away from 40 K.
5.5 Isothermal remanent magnetization (IRM) of several spin glasses with different spin dimensionality.

The approach developed in the previous chapter 5.4, using IRM experiments, is now used to compare spin glasses with spatial dimensionality three and different spin dimensionality. The studied systems are: (1) Fe\textsubscript{0.5}Mn\textsubscript{0.5}TiO\textsubscript{3} a single crystal Ising SG ($T_g \sim 21$ K), (2) Eu\textsubscript{0.5}Sr\textsubscript{1.5}MnO\textsubscript{4} a single crystal XY SG ($T_g \sim 18$ K) and (3) a Cu(Mn) a polycrystalline Heisenberg SG ($T_g \sim 57$ K) and Au(Fe) polycrystalline Heisenberg SG ($T_g \sim 24$ K).

Experimental procedure

The experiments were performed using a commercial SQUID magnetometer (Quantum design, Inc. MPMS-XL) with low magnetic field option, residual field $< 0.05$ mT. The temperature-dependent magnetization was recorded using a probe field of 1mT, well within the linear response regime, following ZFC and FC protocols as described in chapter 2.3 and the A IRM protocols as described in the previous chapter 5.4. Furthermore, a reference IRM, called R\textsubscript{IRM} after immediate cooling, was recorded on heating from the lowest temperature. In all cases a temperature halt was performed at $T_h$, ($T_h/T_g \approx 0.7$). In the measurements on Cu(Mn), the reference temperature $T_{ref}$ is 70 K, the halt temperature $T_h$ is 40 K, and the lowest measurement temperature $T_{min}$ is 10K. For Au(Fe), $T_{ref} = 40$ K, $T_h = 14$ K, and $T_{min} = 5$ K, while for the Ising and XY systems, $T_{ref} = 30$ K, $T_h = 12$ K, and $T_{min} = 5$ K. The sample was cooled at 10 K/min and measured on cooling and heating at 1K/min.

Results

Figure 5.14 shows the normalized ZFC and FC magnetization as functions of normalized temperature of all studied systems. For the Ising- (FMTO), figure 5.14 a, and XY (ESMO) spin glass sample, figure 5.14b, both anisotropy directions paralle and perpendicular to $c$- axis are shown. Henceforth, only results along the spin directions for the Ising and XY systems, i.e. along the $c$-axis for the Ising system, and perpendicular to it for the XY system, are considered. The Heisenberg SG samples, figure 5.14c and 5.14d, exhibit isotropic magnetic properties.

In figure 5.15 IRM results for the different spin glasses on a reduced temperature and magnetization scale are shown. The IRM protocols follow the definition A1 and A2 of the previous chapter. The IRM stop was performed at ($T_h/T_g \approx 0.7$). All
5.5 IRM of several spin glasses with different spin dimensionality

Figure 5.14: Temperature dependence of the zero-field cooled (ZFC) and field-cooled (FC) magnetization \( M \) recorded for all systems using a small magnetic field \( H = 1 \) mT. \( T \) is normalized by the freezing temperature \( T_f \sim T_g \) at which the cusp in \( M_{ZFC}(T) \) is observed, while \( M \) is normalized by the field-cooled magnetization value at \( T_f, M_{FC}(T_f) \). Adapted from Paper XIV.

Samples in figure 5.15 show common features such as a frozen-in magnetization with weak temperature dependence at low temperature. In all cases the frozen-in magnetization rapidly fades away above the temperatures of the IRM stop \( (T_h/T_g \approx 0.7) \).

Furthermore, the IRM is dependent on the waiting time applied during the stop at \( T_h \). The IRM for a 3 s wait (filled symbols) is larger than that with 3000 s (open symbols). This difference can be understood in terms of the time dependence of the response function of spin glasses (aging) [182]. The increase in magnetization becomes slower with evolving time at constant temperature.

Nevertheless, there are also remarkable differences in the behavior of the IRM curves of the different samples. These differ-

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Figure 5.15: Temperature dependence of the Isothermal remanent magnetization (IRM). $T$ is normalized by the freezing temperature $T_f$, while $M$ is normalized by the value of the field-cooled magnetization in 1 mT at the halt temperature $T_h$, $M_{FC}(T_h)$. Reference magnetization data $R_{IRM}$ are plotted using cross symbols ($t_w = 3$ s) or without symbols ($t_w = 3000$ s), while A1 and A2 IRM data are plotted using filled ($t_w = 3$ s) and open ($t_w = 3000$ s) circles, respectively. The employed IRM condition were $\Delta H = 1$ mT and $t_{\Delta H} = 3000$ s in all experiments. Arrows in panel (b) illustrating the direction of the temperature sweeps. Adapted from Paper XIV.

References may derive from the different spin dimensionality of the samples, which is known to influence the dynamical properties of spin glasses [208, 209]. The changes in the magnitude of the IRM introduced by the stop at $T_h$ are strongest for the Heisenberg system, followed by the XY and Ising system. This is in accordance with the aging behavior of the response functions for the three different spin systems [174, 208]. The Heisenberg systems, Cu(Mn) and Au(Fe), show an additional feature on the reheating curves where the initial magnetization peak is recovered. This behavior can be interpreted as excess magnetization imprinted by the magnetic field, as discussed in the previous chapter.
Discussion and conclusions

The aging phenomenon is a common feature of spin glasses and reflects a re-organization process of the spin structure towards an energetically favorable state. The reference IRM curves (shown by the thin red and blue lines in figure 5.15) mirror the excess magnetization that is acquired from a field application at constant temperature. This magnetization is frozen in when cooling to lower temperatures. It is evident that the behavior of the Au(Fe) and Cu(Mn) Heisenberg system differs significantly from that of the XY and Ising system. The frozen-in magnetization of both the Ising and XY system is approximately constant below $T_h$. In case of the Heisenberg system the magnetization first drops strongly before stabilizing at low temperatures at about 2/3 of the initial magnetization value. On re-heating the magnetization curves of the Heisenberg system are recovered. This pronounced increase of the IRM is surprising since it is not observed in the XY and Ising samples.

The Heisenberg systems hence show an additional directional memory of the equilibrated spin structure imprinted at $T_h$. This property is observed for both the Cu(Mn) and the Au(Fe) spin glass and may reflect the unidirectional character of the Dzyaloshinskii-Moriya interaction inherent to the metallic Heisenberg systems [202]. It is interesting to note that the critical exponents associated with the XY spin-glass phase transition had values between those of the Heisenberg and Ising systems [174], and that ac or dc memory experiments

\[ \text{Figure 5.16: IRM measurement for MnFe}_2\text{O}_4 \text{ nanoparticles with halt at } T_h/T_f = 0.8 (\Delta H = 10 \text{ Oe, } t_w = 3 \text{ s}). \]
Spin glasses showed dynamical properties closer to those of Ising systems. By this study it is shown that the dynamical behavior of the XY system probed by the IRM experiments is similar to that of the Ising system.

For comparison, the different IRM protocols were employed on an MnFe$_2$O$_4$ nanoparticle system [210]. This system behaves like a (super)spin glass at low temperatures. For a review on the dynamical properties of magnetic nanoparticle systems see P. JÖNSSON [211]. Possibly due to the relative larger size of the superspins fluctuating at low temperature, the aging in nanoparticle systems is usually found to be more accumulative, in contrast to for example canonical Heisenberg spin glasses, in which the spin glass phase seems very chaotic. Interestingly, it seems that an anisotropy may be imprinted in the nanoparticle system as for Heisenberg systems, suggesting that the DM interaction may also be relevant in those systems.
5.6 The in-field magnetic properties of the canonical Cu(Mn) Heisenberg spin glass

In the previous chapters the dynamic properties of different spin glass materials in the linear response regime were discussed. The dynamics are governed by the response function of the material. For Cu(Mn) Heisenberg SG the IRM perturbation with a small magnetic field gave rise to excess magnetization in the direction of the magnetic field, likewise an additional unidirectional anisotropy. The next interesting point is what happens under the application of even higher magnetic fields, eventually exceeding the linear response regime. This issue is discussed in the following chapter.

To recapitulate the low-field behavior, the temperature dependence of the magnetization for the Cu(Mn) Heisenberg SG in a very small probing field is shown in figure 5.17. The ZFC curve shows a characteristic spin glass cusp slightly above the spin glass temperature and the magnitude of FC $M/H$ remains closely constant at temperatures below the ZFC cusp temperature. Figure 5.18 depicts the influence of an increasing applied magnetic field on the temperature dependence of the ZFC/FC magnetization. It is evident that the cusp in the ZFC magnet-

**Figure 5.17:** Magnetic susceptibility as a function of temperature for a Cu(Mn) spin glass sample in the low magnetic field linear response regime after employing different cooling protocols (ZFC, FC and TRM).
Figure 5.18: Magnetic susceptibility \((M/H)\) as a function of temperature for the Heisenberg-like Cu(Mn) SG sample measured with increasing applied magnetic fields 0.001 T, 0.01 T, 0.1 and 1 T after employing ZFC and FC cooling protocols. Adapted from Paper XV.

...ation is suppressed with increasing magnetic field. The ZFC and FC curves merge at a field-dependent temperature which marks the onset of irreversibility. The magnitude of \(M_{ZFC}/H\) increases with increasing field below the irreversibility temperature, whereas the magnitude of \(M_{FC}/H\) always decreases with increasing field. Corresponding behavior has been observed in FMTO \[186\] and is characteristic for all spin glasses.

Results and discussion

In figure 5.19, the magnetic hysteresis of a Cu(Mn) spin glass at 5 K after field-cooling in 1 T and measuring in magnetic fields up to 14 T (red circles) and 5 T (blue squares) is shown. The inset of figure 5.19 shows a detailed view of the observed spin reversal at low magnetic fields. Both hysteresis loops are displaced from their symmetrical position around zero field. The applied magnetic field hence introduces an additional unidirectional anisotropy to the system. From the low field IRM study it was concluded that this anisotropy has a similar character to anisotropy observed in the presence of the Dzyaloshinskii-Moriya (DM) interaction.
5.6 The in-field magnetic properties of the canonical Cu(Mn) Heisenberg spin glass

The effect of an applied magnetic field is illustrated in greater detail in figure 5.20, where the hysteresis loops for the ZFC and FC (in 1 T) with subsequent field sweep to ±$H_{\text{max}} = 1$ T and 5 T are shown. Both the FC in 1 T and the field sweep to ±$H_{\text{max}} = 5$ T introduces an enhanced remanent magnetization state with a sharp step in the spin reversal. Sharp magnetization reversals are observed for Cu(Mn) for hysteresis loops exceeding the inflection field $H_{w}$ of the S-shaped virgin curve [212]. Additionally, field cooling produces displaced hysteresis loops ($H_{\text{shift}} \neq 0$). For ZFC and ±$H_{\text{max}} = 1$ T the behavior differs and both features the enhanced remanent magnetization state and the displacement of the hysteresis loops are absent. Hence, striking effects appear when the hysteresis loops are confined to fields below the reversibility field, e. g. ≤ 1 T in figure 5.20. The measurements that are confined within the irreversible field range show a behavior where the height of the magnetization step is governed by the field-cooled magnetization and $H_{\text{shift}}$ is pushed to larger values. It follows that the observed unidirectional anisotropy $H_{\text{shift}}$ (at constant temperature $T < T_g$ and constant field sweep rate) is governed by two field parameters: (1) The maximal applied magnetic field $H_{\text{max}}$ and (2) the cooling field $H_{\text{cooling}}$. 

![Figure 5.19: Magnetization vs. magnetic field for Cu(Mn) SG at 5 K measured up to ±14 T (quasi-reversible, ○) and ±5 T (□) after FC cooling in 1 T. The insets show the i) high-field and ii) low-field part of the hysteresis loop. Adapted from Paper XV.](image-url)
Figure 5.20: $M$ vs. $H$ for a Cu(Mn) SG measured at 5 K after ZFC and FC (in 1T) and subsequent hysteresis measurement up to $\mu_0 H_{\text{Max}} = 1$ T, and 5 T. Adapted from Paper XV.

FC protocols with different $H_{\text{cooling}}$ and $\pm H_{\text{max}}$ were used to study the influence of the magnetic field on the magnetic state of the Cu(Mn) SG. In all cases the cooling rate and the field sweep rate were kept constant. The experimental procedure can be described as follows. First, the sample was kept at a reference temperature $T_{\text{ref}} = 70$ K far above the spin glass transition temperature. From that reference temperature the SG sample was FC to the measurement temperature $T_M = 5$ K using different cooling fields $H_{\text{cooling}}$. The observed hysteresis behavior for FC in 0.15 T is shown in figure 5.21. The high-field behavior is identical for a hysteresis loop (compare e.g. figure 5.19) and only a detailed view of the low field region is shown. The open symbols in figure 5.21 indicate a magnetic field sweep from $H_{\text{cooling}} \to -H_{\text{cooling}} \to H_{\text{cooling}}$. For this field protocol ($\pm H_{\text{cooling}}$) a hysteresis shift $H_{\text{shift1}}$ and a coercivity field $H_{c1}$ are observed.

The filled symbols correspond to a measurement up to the maximal accessible magnetic field $H_{\text{max}}$, such as $H_{\text{cooling}} \to -H_{\text{max}} \to H_{\text{max}} \to -H_{\text{max}}$. The second field protocol ($\pm H_{\text{max}}$) gives rise to a hysteresis shift $H_{\text{shift2}}$ and a corresponding coercivity field $H_{c2}$. 

Spin glasses
Displaced hysteresis loops for the Cu(Mn) SG resemble those observed due to the exchange bias effect in many other systems [203, 204, 206]. Exchange bias is usually observed in magnetic system with FM/AFM interfaces and investigated after field cooling the sample and subsequently measuring hysteresis loops, see section 5.3.6. The evolution of the Cu(Mn) magnetic hysteresis for different magnetic cooling fields $H_{\text{cooling}}$ is presented in figure 5.22. $\pm H_{\text{cooling}}$ and $\pm H_{\text{max}}$ loops are labeled as in figure 5.21 with open and filled symbols, respectively. It is evident that throughout the experiment $H_{\text{shift1}}$ (in absolute values) is larger than $H_{\text{shift2}}$ and decreases with increasing cooling fields to the value of $H_{\text{shift2}}$. The coercivity field $H_{c1}$ is smaller than $H_{c2}$ and both coincide for the highest measured cooling fields.

A summary of the measured temperature- and cooling-field dependences of $H_{c1}$, $H_{c2}$, $H_{\text{shift1}}$, $H_{\text{shift2}}$ and $M_{\text{rem}}$ are shown in figure 5.23. The temperature-dependent parameters were derived after cooling the sample in a field of 1 T and the cooling-field dependent parameter were measured at 5 K. The red circles correspond to $\pm H_{\text{cooling}}$ loops and the blue squares correspond to $\pm H_{\text{max}}$ loops. From the temperature dependence (plots figure 5.23 left column) a decrease of the hysteresis shift $H_{\text{shift}}$ with increasing temperature was found for both protocols. For the 1 T FC measurements the hysteresis shift...
Figure 5.22: Detailed view of the magnetization vs magnetic field at 5 K after FC in different magnetic fields $H_{\text{cooling}}$. The open symbols indicate a magnetic field sweep between $\pm H_{\text{cooling}}$. The filled symbols correspond to a measurement up to the maximal accessible magnetic field $\pm H_{\text{max}} (= 5 \text{ T})$, after FC in $H_{\text{cooling}}$. Adapted from Paper XV.

shift vanishes between 20 - 30 K, far below the spin glass transition temperature $T_g$. In a conventional exchange bias system the observed hysteresis displacement is strongly coupled to the Néel temperature of the AFM and displaced hysteresis loop are measured up to $T_N$ [213]. The $H_c$ vs $T$ curves of both protocols are rather similar and show a maximum value around 20 - 25 K.

The cooling-field dependence (figure 5.23 right column) highlights the difference between the two protocols, $\pm H_{\text{cooling}}$ and $\pm H_{\text{max}}$, respectively. For measurements of $\pm H_{\text{cooling}}$ loops after cooling in $+H_{\text{cooling}}$ the hysteresis shift decreases with increasing cooling field. In conventional exchange bias systems the displacement of hysteresis loops tends to increase towards a maximum value with increasing cooling field and
reaches a saturation value of the shift for higher cooling fields.

In the case of $\pm H_{\text{max}}$ loops the hysteresis shift behaves approximately in this manner. Nevertheless, for small cooling fields the hysteresis shift is inverted and a positive shift after FC in a positive field is observed, see inset top figure 5.23 right column. This is an indication that for small cooling fields the subsequent application of high magnetic fields $\mp H_{\text{max}}$ rearranges the spin system, where the positive shift is attributed to the application of $-H_{\text{max}}$. Nevertheless, with increasing cooling fields this effect is washed out and the system enters a regime in which the cooling fields dominate the applied maximal fields. From the presented results it is evident that the

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure523.png}
\caption{Temperature dependence for $H_{\text{cooling}} = 1$ T (left column) and magnetic field dependence $T = 5$ K (right column) of the $H_{c1}$, $H_{c2}$, $H_{\text{shift1}}$, $H_{\text{shift2}}$ and $M_{\text{rem}}$ values obtained from $\pm H_{\text{cooling}}$ (red circles, black circles, index 1) and $\pm H_{\text{max}}$ (blue squares, index 2) loop.}
\end{figure}
characteristics of the displaced hysteresis loops in Cu(Mn) spin glasses are of a somewhat different character as compared with conventional exchange bias systems.

The “conventional” exchange bias shift is affected by training effects - the loops become less shifted when the hysteresis loop is repeatedly measured. Figure 5.24 shows the effect of training on the hysteresis loop of Cu(Mn) at $T = 5$ K after cooling in 1 T and measuring the loops in $\pm 5$ T and $\pm 1$ T. For the $\pm 5$ T loops $H_{shift2}$ decreases with training, i.e. the loops become less asymmetrical on repeating the loops. The $\pm 1$ T loops on the other hand are not affected by the training effect and no significant change of the $H_{shift1}$ is observed on repeating the loops. The magnetic field for the $\pm 1$ T loops is hence below the reversibility field and not sufficient to rearrange the spin structure obtained during the FC in 1 T.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{hysteresis_loop.png}
\caption{Training effect for a Cu(Mn) SG measured after FC in 1 T up to $\mu_0 H_{Max} = 1$ T (red squares) and $\mu_0 H_{Max} = 5$ T (blue circles). Adapted from Paper XV.}
\end{figure}
5.6 The in-field magnetic properties of the canonical Cu(Mn) Heisenberg spin glass

Figure 5.25: Schematic drawing of $H - T$ diagram and measurement protocol; indicating a measurement to a reversible $H_{Rev}$ or irreversible $H_{Irr}$ magnetic field. Adapted from Paper XV.

Conclusion

The presented results for the hysteresis behavior in Cu(Mn) SG reveal numerous interesting properties. From an experimental point of view the hysteresis behavior in Cu(Mn) can be summarized as follows:

(i) An additional remanent magnetization can be introduced by field-cooling procedures (TRM), or by application of sufficiently high magnetic fields (IRM) at temperatures below $T_G$.

(ii) Displaced hysteresis loops are observed in the Heisenberg-like Cu(Mn) and Ag(Mn) SG system. The behavior resembles that of an additional anisotropy obtained via the Dzyaloshinskii-Moriya interaction [202].

Experimentally, two different regimes with respect to the magnetization reversibility under applied magnetic field were observed. One in which the magnetization as a function of field is reversible and the magnetic field $H_{Rev}$ is able to rearrange the spin system and a second $H_{Irr}$ in which the magnetization vs. magnetic field is irreversible. Irreversibility and thus magnetic hysteresis in spin glasses occurs below a constant relaxation time contour in the $H - T$ plane (the position and
shape of this contour is governed by the observation time of the experiment). This behavior is sketched in the schematic constant relaxation time contour in the $H - T$ plane shown in figure 5.25, where the experimental time scale of this line corresponds to order seconds, i.e. some 15 decades longer than the atomic time scale ($10^{-13}$ s). Such contours in the $H - T$ plane are often mistaken in the literature for experimental realization of the theoretical concept AT-line ([214]) that distinguishes a paramagnetic high temperature phase from a low temperature equilibrium spin glass phase. However, experimentally-derived contours are only lines that on the time scale of the experiment distinguish a region where the sample exhibits irreversible properties from a region of reversible behavior at higher temperatures and fields.

To be able to probe these two regimes FC protocols were used. The experimentally-observed displacement of the hysteresis loops after FC and/or application of high magnetic fields is qualitatively different to that observed in “conventional” exchange bias systems. It can be addressed by the Dzyaloshinskii-Moriya interaction which is brought forth by spin-scattering scattering of the conduction electrons [202]. The DM anisotropy energy appears to be large for small magnetic fields $H_{\text{max}}$ and decreases with increased maximal applied fields. In literature, it is reported that for sufficiently high magnetic fields no displacement of the magnetic hysteresis and hence no unidirectional anisotropy can be observed [215]. This behavior can be understood qualitatively from the $S_i \times S_j$ characteristic of the DM interaction, which for an alignment of the spin moments in high magnetic fields vanishes.
5.7 Comparison of the magnetic hysteresis for SG systems with different spin dimensionality

In the previous sections it was found that the magnetic field dependence of the magnetization in spin glasses is governed by relaxation effects which are driven by a combination of magnetic field and thermally related processes. Below the spin glass temperature $T_g$ there is a linear low field part of the magnetization vs. magnetic field curve whose slope is partly governed and tuned by aging phenomena [216]. Experiments in the linear response regime, such as the IRM studies in the previous section, are probing that regime.

Figure 5.26: $M$ vs. $H$ for FMTO, ESMO and Cu(Mn) measured at $T/T_g = 0.3$ K (▲) and 0.8 K (♦). Adapted from Paper XV.
Spin glasses

Figure 5.27: $M$ vs. $H$ for FMTO, ESMO, and Cu(Mn) measured at $T/T_g = 0.3$ K (red triangles), 0.5 K (green squares) and 0.8 K (blue diamonds). The upper row shows the first quadrant of the hysteresis loop. The lower row shows a zoomed picture of low magnetic field region. Adapted from Paper XV.

For higher magnetic fields the effect of aging on the magnetization is wiped out. In the section to follow the magnetic field dependence for SG with different spin dimensionalities (Ising, XY, and Heisenberg-like) is studied.

Results and discussion

In general, the governing parameters for the hysteresis behavior of spin glasses are: Temperature ($T$), field ($H$), field sweep rate ($t_H$) and cooling field ($H_{\text{cooling}}$). In figure 5.26 the full hysteresis loops measured at different temperatures ($T/T_g \sim 0.3$ and 0.8) for: (a) the Ising FMTO ($H$ along the $c$-axis), (b) the XY ESMO ($H$ in the $a-b$ plane) and (c) the Cu(Mn) Heisenberg-like spin glass are shown. Figure 5.26 illustrates common features of the measured hysteresis behavior of model spin glasses. This universal behavior of the magnetization of model spin glasses implies that the spin glass response can be subdivided into an irreversible part including correlated spin flips - (processes on time scales longer than the individual spin flip time) and a reversible part that responds atomically (at the spin flip time). On the time scales of magnetization exper-
iments, the size of the irreversible fraction appears strongly temperature-dependent due to increased relaxation (rate) with increasing temperature. A substantial irreversible fraction is observed for $T/T_g \sim 0.3$. For increasing temperature ($T/T_g \sim 0.8$) the temperature-dependent irreversible part is diminished and the hysteresis is governed by a reversible part at high enough fields.

A detailed view of the zero-field-cooled $M_{ZFC}$ vs. $H$ curves measured at different temperatures below $T_g$ ($\sim 0.3$, $\sim 0.5$, and $\sim 0.8$) for FMTO, ESMO, and Cu(Mn) is shown in figure 5.27. At all temperatures, the curves have an initial linear behavior at low enough fields with a slope that is temperature- and age-dependent ([216]). Above a temperature-dependent field $H_{\text{nonlin}}$ ($H_{\text{nonlin}} < H_{\text{w}} < H_{\text{irrev}} < H_{\text{rev}}$) the magnetization enters a nonlinear regime ($M_{\text{nonlin}}$) with increased slope of $M$ vs. $H$, followed by an inflection point at higher fields after which the slope again decreases.

Figure 5.28: Magnetization normalized to the magnetization values at 7 Tesla for a) FMTO (■), ESMO (◀), and Au(Fe) (♦) b) FMTO (■), ESMO (◀), and Cu(Mn) (•). Adapted from Paper XV.
The reversible high field part of the $M$ vs. $H$ curves is nearly temperature independent for all three spin glasses. Hysteresis experiments where the sample was zero-field-cooled and the magnetic field was swept (at a constant rate) to a field $\sim H_{rev}$ above the apparent irreversibility field in both positive and negative directions are presented in figure 5.28. Panel a) shows the Ising (FMTO), XY (ESMO) and Au(Fe) sample measured at $T/T_g \sim 0.1$. In Panel b) the Heisenberg-like Cu(Mn) sample at $T/T_g \sim 0.1$ and the Ising (FMTO), XY (ESMO) at $T/T_g \sim 0.2$ are plotted. The Ising sample shows a hysteresis loop with pronounced jumps in the spin reversal for $T/T_g \sim 0.1$ which is discussed further down in the text. The coercivity field of the Ising sample was measured to $H_c = (H_{c+} - H_{c-})/2 = 14600$ (6030) Oe for $T/T_g \sim 0.1$ ($\sim 0.25$) and there was no significant shift of the loop $H_{shift} = (H_{c+} + H_{c-})/2 \approx 0$ Oe. The XY system (ESMO) reveals continuous change of the magnetization and almost symmetrical behavior. The Cu(Mn) loop is quite different, showing a sharp spin reversal and significant asymmetry indicated by a finite value of $H_{shift} = -60$ Oe ($H_c = 220$ Oe). Compare section 5.6 for more details of the hysteresis.
behavior for the Cu(Mn) SG. Figure 5.29 presents $M$ vs. $H$ for the Ising-like FMTO SG at different temperatures, field sweep rates and cooling fields. At low temperatures ($T < 3$ K) jumps appear in the evolution of the magnetization as a function of the magnetic field. Initially, these jumps are only observed in the positive and negative branches of the hysteresis loop ($T = 3$ K), see figure 5.29a. At even lower temperature ($T = 2$ K) the jumps are also present in the virgin curve at fields higher than that of the subsequent jumps in the two branches of the hysteresis loop. The formation of magnetization jumps in the virgin curve at constant temperature and field sweep rate is tuned by the cooling field, see figure 5.29c.

Different cooling fields imply different initial states of magnetization. For increasing cooling fields the spin system is more destabilized and the point at which the jump occurs in the virgin curve is shifted to smaller values of the magnetic field. However, the subsequent hysteresis loops remain essentially symmetrical irrespective of cooling field (in contrast to the exchange shifted behavior of Cu(Mn)). In a similar manner, the field sweep rate does alter the formation of jump in the spin system. Figure 5.29 b shows $M$ vs. $H$ at 2 K using different field sweep rates, where an increased rate promotes the magnetization jumps and shifts them to lower fields. The development of magnetization jumps in FMTO was discussed earlier by A. ITO ET AL. [186] and was observed for the mixed-spin oxide FeTiO$_3$-Fe$_2$O$_3$ by M. CHARILAOU ET AL. [217].
5.8 Concluding remarks

The temperature- and magnetic-field-dependent behavior of spin glasses with different spin dimensionality was studied. A significant difference in the behavior of the three different SG systems in both the linear response and the high magnetic field regime was revealed. The FMTO Ising and the ESMO XY SG systems are both insulating oxide materials and show approximately similar properties in the IRM study using a very small magnetic field. For the Cu(Mn) Heisenberg SG the observed IRM behavior revealed an additional remanent magnetization in-printed during the IRM stop. This difference was addressed by the presence of the Dzyaloshinskii-Moriya (DM) interaction in the case of the metallic Heisenberg-like Cu(Mn) and Ag(Mn) spin glasses with RKKY interaction. The apparent DM interaction is mediated through the conduction electrons present in the metallic Cu matrix. The study of the hysteresis behavior for the three different SG systems using high magnetic fields endorses this picture. The evolution of magnetization of spin glasses in magnetic fields is governed by temperature, field, cooling field and field sweep rates. Displaced hysteresis loops are exclusively observed in Heisenberg-like Cu(Mn) and Ag(Mn) spin glasses. The physical origin of this apparent difference between metallic Heisenberg and isolating Ising (and XY) systems may again be assigned to the Dzyaloshinskii-Moriya interaction giving rise to an unidirectional anisotropy. The formation of a sharp step-like spin reversal in Cu(Mn) and Ag(Mn) and the magnetic field-induced jumps at low temperatures in the FMTO Ising spin are of a different physical character.

From the presented results it seems that the Dzyaloshinskii-Moriya interaction present in the metallic Heisenberg spin glasses plays a crucial role in the magnetic properties of these systems. It also sheds new light on the interpretation of certain experimental observations in these systems.
What is next?

For a final interpretation of our results it seems necessary to investigate the properties of a non-metallic 3d Heisenberg system. Likewise it would be interesting to study Ising (or XY) systems with a metallic matrix. From an experimental point of view our studies are limited to a rather small observation time window. The physics of $M$ vs. $H$ of spin glasses would hence be further elucidated by extensive Monte Carlo simulations, where the observation time can be ‘freely’ varied and $T = 0$ K can be readily measured. Such studies could possibly verify the concept reversible and irreversible fractions of the magnetization response and illustrate differences between three dimensional systems of different spin dimensionality.
This thesis is concerned with experimental studies of different functional magnetic materials: magnetocaloric, multiferroic and spin-glass materials. It is necessary to understand the origin of the functional properties to be able to find and develop new materials for a specific application.

In magnetocaloric materials the functionality is related to a change in the temperature of the material due to the magnetic ordering - called the magnetocaloric effect. These materials are hence particularly interesting for use in cooling and heating applications such as refrigerators or air-conditioners. Practically, all magnetic materials are indeed magnetocaloric and yield a change in temperature when magnetized. The aim of my research has been to understand and identify ways to enhance the magnetocaloric properties. Simplicity has been a requirement in the choice of materials, since applicable materials should consist of abundant, non-toxic (environmentally friendly) and cheap elements.

Following this path, the magnetocaloric materials mainly studied in this thesis are Fe₂P-based compounds. The chosen approach of my investigations was that of fundamental science: i.e. studying polycrystalline and single-crystalline materials of high sample quality. The material fabrication process is an important detail and for polycrystalline samples the drop synthesis method was used. The drop synthesis method is a very clean high temperature fabrication technique suitable for the synthesis of materials containing volatile elements, such as Fe₂P-based compounds. Fe₂P-based materials are interesting due to their high saturation magnetization and first-order magnetic phase transition. It is found that these magnetic properties can be tuned chemically by material substitutions of Mn.
on the Fe sites and Si on the P sites. The chemistry of quaternary materials is complicated and even small changes in the composition cause big changes in the magnetic properties.

The quest for applicable magnetocaloric materials needs to include new material classes. In this thesis the mineral Melanostibite and certain stainless steel compositions were studied with respect to magnetocaloric potential. Holding the material in hand it is finally important to measure its performance, for example, how much the actually temperature change amounts to. An experimental set-up serving this purpose was constructed and tested.

In magnetoelectric multiferroics the coupling between the magnetic and electrical properties holds the functionality, which in a practical case makes it possible to control the magnetic properties (magnetization) with an electrical field or the electrical properties (polarization) with a magnetic field. Knowledge of the crystal and magnetic symmetry of the material is important in this context since it can tell if these properties may exist or not. Materials exhibiting such (cross correlated) properties can, for example, be found among insulating transition-metal oxides with a strong correlation between the electrons. A non-trivial question is to identify the coupling mechanism between the magnetic and electrical properties present in these materials. This coupling is strong in materials where the polarization, for example, is directly induced by the magnetic state and hence inherently coupled to the magnetic field. It is therefore most desirable to find such types of multiferroic materials. Two new materials of this type Co$_3$TeO$_6$ and Ba$_3$NbFe$_3$Si$_2$O$_{14}$ were studied in this thesis.

In the case of Co$_3$TeO$_6$ the low temperature magnetic structure is formed by five different magnetic sites (Co$^{2+}$) and allows several antiferromagnetic phases. In such complex magnetic structures several exchange paths are possible and may compete with each other, causing magnetic frustration. As a consequence of magnetic frustration the formation of non-collinear spin structures is promoted. Such structures are known to be favorable for generating magnetically-induced ferroelectricity. Co$_3$TeO$_6$ is an example of such a material and it is found that Co$_3$TeO$_6$ exhibits the linear magnetoelectric effect and an electrical polarization at low temperatures.

Ba$_3$NbFe$_3$Si$_2$O$_{14}$ forms in a triangular crystal symmetry which, like-wise to Co$_3$TeO$_6$, yields frustration of the magnetic state at low temperature. Ba$_3$NbFe$_3$Si$_2$O$_{14}$ is non-polar and exhibits an electrical polarization only after symmetry breaking under applied fields, for example a magnetic field. The coupling between the lattice and spin degrees of freedom
was investigated using Raman spectroscopy. It is found that \( \text{Ba}_3\text{NbFe}_3\text{Si}_2\text{O}_{14} \) shows spin and lattice coupling effects in the vicinity of the phase transition and a magnetic field dependence of its Raman spectra. These experiments were done in a Raman set-up, allowing measurements at low temperatures and high fields that was developed during the course of my Ph.D. work.

Spin glasses may not be regarded as very functional materials but they can serve as model systems. Spin-glass-like behavior is found in many functional materials as a consequence of chemical or magnetic disorder, and such behavior profoundly influences the magnetic and electrical (functional) properties. From our study of spin-glass materials it was found that the dynamic properties of metallic Heisenberg spin glasses are influenced by the presence of an induced unidirectional anisotropy (Dzyaloshinskii-Moriya interaction) giving rise to excess magnetization. The Dzyaloshinskii-Moriya interaction is proportional to the relative orientation of two spin moments to each other and is zero for parallel spins. In Ising and XY spin glasses the spin moments are restricted to certain orientations, for example along one axis in the case of an Ising system. In a Heisenberg spin glass the spin moments can arrange in all directions in space. The Dzyaloshinskii-Moriya interaction is not relevant in collinear systems; however it seems to tip the scales in frustrated systems, for example non-collinear antiferromagnetic materials or Heisenberg systems.
Magnetiska material med anpassningsbara termiska, elektriska och dynamiska egenskaper

Min avhandling behandlar fundamentala experimentella studier av funktionella magnetiska material: magnetokaloriska, multiferroiska och spinn glas material. I mitt avhandlingsarbete har jag sökt förstå ursprunget till materialens funktionella egenskaper för att kunna förfinna prestanda hos redan etablerade material system och finna nya potentiellt användbara materialklasser. Funktionaliteten hos magnetokaloriska material baseras på att materialet ändrar temperatur då det magnetiseras - den magnetokaloriska effekten. Sådana material utgör den funktionella delen i nya energieffektiva kyl- värmemaskiner som förväntas ersätta nuvarande kompression/förångning baserade system för bruk i våra kyl/fryskåp och luftkonditioneringsanläggningar. Målet med min forskning på magnetokaloriska material har varit att finna vägar för att förstå och förbättra de funktionella egenskaperna hos redan etablerade materialsystem och att hitta nya materialklasser med lovande egenskaper. Kravet på material som skall kunna användas i framtida kommersiella produkter är att de består av rikligt förekommande (inte sällsynta jordartsmetaller), icke-giftiga (miljövänliga) och billiga grundämnen. Detta krav har styrt mitt val av materialsystem och jag har koncentrerat min forskning mot Fe₂P-baserade föreningar, både enkristallina och polykristallina material. Provmaterialen har framställts med metoder som ger högsta möjliga kristallina kvalitet. Droppsyntes metoden har använts för att nå bästa möjliga kontroll över sammansättning och renhet hos de polykristallina provmaterialen. Fe₂P-baserade material har goda magnetokaloriska egenskaper på grund av att övergången från para- till ferromagnetism är en första ordningens fasövergång och att mättnadsmomentet i ferromagnetiska fasen är användbart högt. Av största betydelse
för materialets användbarhet är att fasövergångstemperaturen (och mättndomsmomentet) kan styras till önskat temperatur-område med lämplig mängd substitutionselement: t.ex. viss del mangan för järn och kisel för fosfor. Kemin hos en förening med fyra olika element är komplicerad och i Fe₃P-systemet leder också små sammansättningsändringar till stora förändringar i övergångstemperatur och andra magnetiska egenskaper. Min forskning visar att med lämplig sammansättning och värmebehandling har (Fe(Mn))₂P(Si) potential att bli ett användbart legeringssystem i magnetokaloriska applikationer. Det behövs dock alternativa materialsystem för att magnetokaloriska kylskåp skall förverkligas. I min forskning har jag studerat mineralet melanostibite och vissa sammansättningar hos rostfritt stål med avseende på magnetokalorisk potential och funnit att egenskaperna vad gäller övergångstemperatur och magnetisering kan styras mot användbara områden. Jag har också konstruerat en apparat för att direkt mäta temperaturändringen hos ett material då det magnetiseras/avmagnetiseras - vilken är en avgörande parameter då användbarheten hos ett givet provmaterial skall utvärderas.

Co₃TeO₆ uppvisar linjär magnetelektrisk effekt och elektrisk polarisation vid låga temperaturer. Ba₃NbFe₃Si₂O₁⁴ har triangulär kristallsymmetri som leder till magnetisk frustration vid låga temperaturer. Materialet ordnas magnetiskt i en antifermagnetisk struktur utan elektrisk ordning vid 28 K. I ett pålagt magnetiskt fält induceras elektrisk polarisation i materialet. Raman spektroskopi avslöjar att det finns koppling mellan gitret och spinnsystemet i Ba₃NbFe₃Si₂O₁⁴ genom anomalier i temperaturberoendet hos vissa Raman moder vid fasövergången och fältberoende i samma Raman moder vid låga temperaturer. Raman mätningarna gjordes i en experiment uppställning för mätning vid låga temperaturer och höga magnetfält som jag utvecklat under mitt doktorandarbete.

Spinn glas är magnetiska material utan direkt användbara funktionella egenskaper, dock tjänar spinn glas som modell för utveckling av teorier för oordnade system i allmänhet och särskilt för deras dynamiska egenskaper. Spinn glas lika egenskaper finns i många funktionella material på grund av kemisk och magnetisk oordning och denna oordning styr på ett avgörande sätt materialens magnetiska och elektriska egenskaper. I min avhandling har studierna på spinn glas material fokuserats på spinn-dimensionalitetens inverkan på egenskaperna. Det visar sig att Heisenberg systems (spinn dimensionality, n=3) egenskaper i väsentliga delar skiljer sig från egenskaperna hos XY (n=2) och Ising (n=1) system. Orsaken till detta kan hänföras till att Dzyaloshinskii-Moriya växelverkan ger upphov till en fältinducerad anisotropi i Heisenberg system som starkt påverkar de fysikaliska egenskaperna, denna mekanism saknas i XY och Ising spinnsystem.

"Kan någon nu säga vad magnetism är, eller vad elektricitet är?"1

1August Strindberg (1849-1912), Svensk författare, målare och forskare.
Diese Doktorarbeit beschäftigt sich mit der experimentellen Untersuchung verschiedener funktionaler magnetischer Materialien. Dies sind magnetokalorische, multiferroische und Spin-glas Materialien.


Im Rahmen meiner Arbeit konnte gezeigt werden, dass die magnetischen und magnetokalorischen Eigenschaften durch

In magnetoelektrischen Materialien ermöglicht die Kopplung von magnetischen und elektrischen Eigenschaften eine interessante Funktionalität. Diese macht es in der praktischen Anwendung möglich, magnetische Eigenschaften (Magnetisierung) mittels eines elektrischen Feldes oder elektrische Eigenschaften (Polarisation) durch ein magnetisches Feld zu steuern. Materialien mit solchen wechselseitig kontrollierbaren Eigenschaften finden sich beispielsweise unter den isolierenden Übergangsmetalloxiden mit starker Elektronenwechselwirkung.

Eine nicht triviale Fragestellung ist es, die Kopplungsmechanismen zwischen dem magnetischen und elektrischen Verhalten in diesen Material, zu finden. Diese Kopplung ist stark, wenn zum Beispiel die Polarisation direkt durch die magnetische Ordnung hervorgerufen wird und daher inhärent an das magnetische Feld gekoppelt ist. Es ist daher besonders wünschenswert, magnetoelektrische Materialien dieses Typs zu finden.

Zwei neue Materialien dieser Art, Co₃TeO₆ und Ba₃NbFe₃Si₂O₁₄, wurden in dieser Doktorarbeit untersucht. Im Fall von Co₃TeO₆ wird die magnetische Ordnung bei tiefen Temperaturen durch fünf magnetische (Co²⁺) Ionen bestimmt und erlaubt verschiedene antiferromagnetische Phasen. In dieser komplexen magnetischen Struktur sind verschiedene miteinander konkurrierende Wechselwirkungen möglich und können magnetische Frustration hervorrufen. In Folge dieser magnetischen Frustration können nichtlinearen Spin-Strukturen entstehen. Diese Strukturen sind für das Auftreten von magnetisch-induzierter Ferroelektizität verantwortlich. Co₃TeO₆ ist ein Beispiel eines solchen Materials und zeigt nachweislich den linearen magnetoelektrischen Effekt sowie elektrische Polarisation bei niedrigen Temperaturen.
Ba$_3$NbFe$_3$Si$_2$O$_{14}$ besitzt eine Dreiecksgitter Symmetrie, die ähnlich wie Co$_3$TeO$_6$ bei niedrigen Temperaturen zur Frustration der magnetischen Ordnung führt. Ba$_3$NbFe$_3$Si$_2$O$_{14}$ ist nicht polar und zeigt elektrische Polarisation erst nachdem die Symmetrie mittels eines angelegten magnetischen oder elektrische Feld aufgehoben wurde. Die Kopplung zwischen den Freiheitsgraden der Elektronen und dem Kristallgitter wurde mit Hilfe der Raman-Spektroskopie untersucht. Es ist erwiesen, dass Ba$_3$NbFe$_3$Si$_2$O$_{14}$ Kopplungseffekte zwischen Gitter und magnetischen Freiheitsgraden beim Phasenübergang zeigt. Diese Experimente wurden mittels eines Raman-Versuchsaufbaus durchgeführt, der Messungen bei niedrigen Temperaturen und starken Feldern erlaubte und während meiner Promotionszeit entwickelt worden ist.

Spin-Gläser sind magnetische Materialien, in denen die magnetischen Momente ungeordnet sind und das Erreichen eines geordneten Zustandes aufgrund von Frustration, d.h. des gleichzeitigen Auftretens verschiedener mit einander konkurrierender Wechselwirkungen, nicht möglich ist. Spin-Gläser sind keine besonders funktionalen Materialien, dennoch können sie als Modellsysteme dienen. Spin-Glas-artiges Verhalten findet sich in vielen funktionalen Materialien und beeinflusst die magnetischen und elektrischen Eigenschaften in hohen Maße.


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Secondly, I would like to thank the people I had the pleasure to work with. All present and past members of the “magnetism group”, especially Prof. Peter Svedlindh, Doc. Klas Gunnarsson, Dr. Magnus Wikberg, Rebecca Stjernberg Bejhed, Puri Anil Kumar and Dr. Luana Caron.

I am glad to have been part of the Division of Solid State Physics (FTF) under the wise leadership of Prof. Claes-Göran Granqvist. I would like to thank all FTF coworkers for a wonderful time especially, Sara Green, Pia Lansåker, and Annica Nilsson.

I have been involved in a number of projects and I would like to express my gratitude to all collaborators for their support, teaching me and sharing their knowledge with me. In the project on magnetocaloric materials I am greatly thankful to Prof. Yvonne Brandt Andersson, Dr. Martin H. Sahlberg, Viktor Höglin, Prof. Olle Eriksson, Prof. Lennart Häggström, Erna-Krisztina Delczeg-Czirjak, Prof. Levente Vitos, Dr. Petros Souvatis, Dr. Torbjörn Björkmann, Dr. Petra Jönsson, Dr. Evangelos Papaioannou, and Atieh Zamani. I also wish to thank Dr. Kurt Engelbrecht for welcoming me at Risø.

To have the chance to work on multiferroic materials has been an true inspiration for me. I would like to thank Prof. Sergey Ivanov, Prof. Manfred Fiebig, Dr. Thomas Lottermoser, Vera Carolus, Prof. Pierre Tolédano, Prof. Rolf Berger, Prof. Peter Lazor, and Dr. Viktor Struzkhin. I am deeply grateful
to Prof. Yoshinori Tokura and his group at RIKEN, especially Prof. Yasujiro Taguchi and Dr. Yusuke Tokunaga for hosting me and for their excellent guidance and help. I would like to thank Prof. D.D. Sarma for delightful workshops and scientific discussions.

During my time at the Ångström Laboratory I had the chance to meet and work with many inspiring people I would like to thank Dr. Davide Peddis, Åsmund Monsen, Doc. Gabriella Andersson, Dr. Cristina Bran, Prof. Olof “Charlie” Karis, Ronny Knut, Emma Tysk and Dr. Martin Amft. For technical and administrative support Dr. Ping Huang, Bengt Götesson, Åke Jönsson., Åke Dahlberg, Joakim Andersson, Anders Lund, Inger Ekberg, Anja Hohmann, Sebastian Alonso, Ingrid Ringård, Maria Skoglund, Jonatan Bagge, Victoria Sternhagen, Marko Swoboda, Anja Schachtschabel, and Bobbie.

Life is not only work and a big thank-you goes to all the people who have made my time in Uppsala even more enjoyable. I would like to express my thanks to Edin, Magnus, Victoria and Sebastian; Panos, Christoph, Atieh; Roland, Petra, Linnéa and Alfred; Timo, Ralph, Zuzana, Micke, family Landberg Persson, and Uppsala Volleyboll. I am grateful for my dear friends back in Germany Mirko, Matthias, Christian, René, Rico, Mirko and especially Anja.

Zum Abschluss möchte ich meiner Familie für all Ihre Liebe und Unterstützung danken. Danke Schwester♥.

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Uppsala, February 2012

Matthias

"Now this is not the end. It is not even the beginning of the end ..."²

²Sir Winston Churchill
A.1 An experimental set-up for direct measurements of the magnetocaloric effect

During the time of my Ph.D. work an experimental set-up for direct measurements of the magnetocaloric effect (ΔT) in quasi-adiabatic conditions was constructed. The design is based on the measurement set-up described by GOPAL ET AL. [66].

The set-up is constructed to fit the cryostat of a 9 T Quantum Design PPMS. The temperature range for measurements is

![Figure 1](image-url)  
**Figure 1:** Estimate for the strength of the magnetic field $B$ inside the Quantum Design Inc. PPMS along the vertical z-axis. Inset shows the field gradient along the vertical z-axis.
Figure 2: Raw data for the measurement of the quasi-adiabatic temperature change $\Delta T$ for Gd metal in a magnetic field change of 1.1 T. The arrows indicate the time when the magnetic field was turned on and off. Field sweep rate 189 Oe/s.

20 - 400 K. Temperature measurements are performed using a Lake Shore CX-1080-SD-HT Cernox temperature sensor glued to the sample. The typical magnetic-field-dependent temperature error is $\leq 0.04 \%$ ($\Delta T/T$) in the accessible temperature and field range. For good thermal insulation the sample container was Cu shielded and measurements are performed at high vacuum conditions (order $10^{-5}$ mbar). The accuracy of the data is estimated to 5 - 10 % accounting for the accuracy of thermometry, setting of the magnetic field, and quality of the thermal insulation of the sample.

Two modes of operation have been tested: (1) the magnetic field is kept constant and the sample is extracted or inserted into the magnetic field and (2) the sample is kept in the center of the superconducting solenoid and the magnetic field is swept. The vertical displacement (extracting or inserting the sample from/into the magnetic field) of the magnetocaloric sample is done using an electrical motor which can be controlled using a computer. The accessible magnetic field change rate due to the sample displacement is up to 3 T/s. When sweeping the magnetic field (no sample displacement) the accessible magnetic field change rate is in the order 0.02 T/s.
Appendix

Operation mode (1) can be used for magnetic field changes up to 9 T. The strength of the magnetic field inside the PPMS can be estimated from the equation describing the magnetic field of a solenoid, see e.g. ref. [2]. The magnetic field along the vertical z-axis inside the PPMS is shown in figure 1. It is evident that a displacement of only 50 cm decreases the magnetic field strength by about 3 orders of magnitude, which yields a reasonable approximation for zero field.

Operation mode (2) is found useful for characterizations in magnetic field changes up to ~1 T. The sample temperature is recorded as a function of time. A plot of the raw data for a $\Delta T$ measurement of Gd metal under a magnetic field change of 1.1 T is depicted in figure 2. The measured temperature dependence of the adiabatic temperature change for the same 99.9% Gd sample is shown in figure 3.10.
A.2  Raman spectroscopy under applied magnetic and electrical fields at low temperatures and high pressure

Raman spectroscopy is a versatile technique for studying the coupling of spin and lattice degrees of freedom. A Raman set-up for in-situ measurements of such properties at low temperature, magnetic field, electrical field and applied pressure was constructed in collaboration with P. LAZOR. The technical platform to provide temperature and magnetic field control is a 9 T Quantum Design PPMS. Temperature and magnetic field control as well as spectra acquisition has been automated. A schematic drawing of the PPMS Raman set-up is shown in figure 3.

Figure 3: Schematic view of the PPMS Raman set-up. BS - beamsplitter, F - optical filter, L - lens, NF - notch filter, and OW optical window. Courtesy of P. LAZOR.
System performance:

1) Temperature: 3 - 350 K
2) Pressure: 0 - 100 GPa
3) Static magnetic field: 0 - ±9 Tesla
4) Static electric field: 0 - ±1 000 000 V/m

This system is suitable for long-term Raman experiments and typical operation parameter, e.g. temperature, magnetic field and helium consumption, for a 3.5 days Raman experiment are shown in figure 4.

![Figure 4: PPMS measurement protocol for a long time measurement starting at Time = 0 h. a) temperature profile, b) magnetic field profile, and c) helium consumption as function of time. Horizontal dashed line describes the limit for using high magnetic fields up to 9 T. Adapted from Paper X.](image-url)
In this set-up the Raman spectra are recorded with a SR-303I-A Shamrock 303i spectrometer (Andor Technology) coupled by a single mode optical fiber to the PPMS set-up. The spectrometer is equipped with 1200/mm grating and thermoelectrically cooled multichannel CCD detector (iDus, Andor Technology, 1024×256 pixels, -50 °C). A linearly polarized argon ion laser (488 nm line) is used for the excitation at powers up to 15 mW. The spectral axis can be calibrated by fluorescence lines of a neon lamp. Inside the PPMS, Raman spectra are collected in the back-scattering geometry, at a resolution of about 4 cm⁻¹. The accuracy of the spectral measurements, resulting from the wavelength calibration procedure and experimental conditions, is estimated to be about 2 cm⁻¹. Typical acquisition times vary between 20 - 120 sec.

Figure 5 shows data collected using the PPMS Raman set-up. Hydrogen exists in two different spin isomers, orthohydrogen with two parallel proton spins and parahydrogen with two antiparallel proton spins. At room temperature and ambient pressure the ortho- to parahydrogen ratio is approximately 1/3. This equilibrium ratio is temperature dependent and at low temperatures the equilibrium state is parahydrogen. H₂ conversion, from ortho- to parahydrogen can be traced measuring an H₂ rotation mode. The the evolution of the Raman spectrum (from 0 h (black line) to 8 h) for an H₂ conversion experiment at ∼20 K, 9 T magnetic field and 27 GPa hydrostatic pressure is depicted in figure 5.

![Figure 5: A measurement reflecting the ortho to para conversion of H₂ at ∼20 K at applied magnetic field (9 T) and high pressure (27 GPa). Adapted from Paper X.](image-url)
This thesis is based on the following publications and manuscripts. My main or partial contribution to each publication is indicated by (I) for idea and design of experiment, (S) for synthesis and sample fabrication, (M) for measurements and data acquisition, (A) for data analysis, (D) for discussion and interpretation of results, and (W) for writing of the manuscript.

A) Magnetocaloric materials

I Order-disorder induced magnetic structures of \( \text{FeMnP}_{0.75}\text{Si}_{0.25} \)
(M, A, D, W)

II The crystal magnetic structure of the magnetocaloric compound \( \text{FeMnP}_{0.5}\text{Si}_{0.5} \)
V. Höglin, M. Hudl, M. Sahlberg, P. Nordblad, P. Beran, and Y. Andersson
(D, W)

III Strongly enhanced magnetic moments in ferromagnetic \( \text{FeMnP}_{0.5}\text{Si}_{0.5} \)
(M, A, D, W)
IV Magnetic and magnetocaloric properties of natural mineral and synthetic melanostibite
M. Hudl, R. Mathieu, P. Nordblad, S. A. Ivanov, G. V. Bazuev, and P. Lazor
Submitted (2011)
(M, A, D, W)

V Magnetocrystalline anisotropy and the Magnetocaloric Effect in Fe$_2$P
L. Caron, M. Hudl, V. Höglin, Y. Andersson, and P. Nordblad
In manuscript (2012)
(I, M, A, D, W)

B) Multiferroic materials

VI Magnetic order near 270 K in mineral and synthetic Mn$_2$FeSbO$_6$ ilmenite
R. Mathieu, S. A. Ivanov, G. V. Bazuev, M. Hudl, P. Lazor, I. V. Solovyev, and P. Nordblad
(M, D)

VII Complex magnetism and magnetic field-driven electrical polarization on Co$_3$TeO$_6$
M. Hudl, R. Mathieu, S. A. Ivanov, M. Weil, V. Carolus, Th. Lottermoser, M. Fiebig, Y. Tokunaga, Y. Taguchi, Y. Tokura, and P. Nordblad
(M, A, D, W)

VIII First-order multi-k phase transition and magnetoelectric effects in multiferroic Co$_3$TeO$_6$
P. Tolédano, V. Carolus, M. Hudl, Th. Lottermoser, D. D. Khalyavin, S. A. Ivanov, and M. Fiebig
To be submitted (2012)
(D)

IX Coupling of magnetic and electrical properties in the chiral langasite Ba$_3$NbFe$_3$Si$_2$O$_{14}$
M. Hudl, Y. Tokunaga, Y. Taguchi, P. Lazor, R. Mathieu, and Y. Tokura
In manuscript (2012)
(I, S, M, A, D, W)
X An experimental set-up for measuring Raman spectroscopy under applied magnetic and electrical fields, high pressure and low temperatures  
P. Lazor, M. Hudl, R. Mathieu and V. V. Struzhkin  
In manuscript (2012)  
(M, A, D, W)

C) Spin glasses

XI Aging experiments in a superspin glass system of Co particles in Mn matrix  
D. Peddis, M. Hudl, C. Binns, D. Fiorani, and P. Nordblad  
(M, A, D, W)

XII Dynamical studies on model spin glasses  
R. Mathieu, M. Hudl, and P. Nordblad  
(S, M, D)

XIII Memory and rejuvenation in a spin glass  
R. Mathieu, M. Hudl, and P. Nordblad  
(S, M, D)

XIV Isothermal remanent magnetization and the spin dimensionality of spin glasses  
R. Mathieu, M. Hudl, P. Nordblad, Y. Tokunaga, Y. Kaneko, Y. Tokura, H. Aruga Katori, and A. Ito  
Philosophical Magazine Letters 90 723-729 (2010)  
(S, M, D)

XV Hysteresis loops of model spin glass systems  
M. Hudl, R. Mathieu, H. Aruga Katori, A. Ito, Y. Tokunaga, Y. Kaneko, Y. Tokura and P. Nordblad  
To be submitted (2012)  
(S, M, A, D, W)
D) Other publications

XVI  **Magnetic properties of Fe/W\textsubscript{x}/Re\textsubscript{100-x} (001) Multilayers**
C. Bran, M. Hudl, M. Björck, V. Kapaklis, and G. Andersson
In manuscript (2012)
(M, A, D)

XVII  **Dielectric and magnetic properties of Pb\textsubscript{3}Mn\textsubscript{7}O\textsubscript{x} (x = 15, 16)**
M. Hudl, R. Mathieu, A. A. Bush, S. A. Ivanov, G. André, Y. Tokunaga, Y. Taguchi, Y. Tokura and P. Nordblad
In manuscript (2012)
(M, A, D, W)
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
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<tbody>
<tr>
<td>AC/DC</td>
<td>Alternating/direct current</td>
</tr>
<tr>
<td>AFM</td>
<td>Antiferromagnetic</td>
</tr>
<tr>
<td>AMR</td>
<td>Active magnetic regenerator</td>
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<tr>
<td>AT</td>
<td>de-Almeida-Thouless</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-centered cubic</td>
</tr>
<tr>
<td>bct</td>
<td>Body-centered tetragonal</td>
</tr>
<tr>
<td>BNFSO</td>
<td>Ba$_3$NbFe$_3$Si$<em>2$O$</em>{14}$</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>CMR</td>
<td>Colossal magnetoresistance</td>
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<tr>
<td>COP</td>
<td>Coefficient of performance</td>
</tr>
<tr>
<td>DAC</td>
<td>Diamond anvil pressure cell</td>
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<tr>
<td>DFT</td>
<td>Density functional theory</td>
</tr>
<tr>
<td>DM</td>
<td>Dzyaloshinskii-Moriya</td>
</tr>
<tr>
<td>EA</td>
<td>Edwards-Anderson</td>
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<tr>
<td>EPMA</td>
<td>Electron probe microanalyzer</td>
</tr>
<tr>
<td>ESMO</td>
<td>Eu$<em>{0.5}$Sr$</em>{1.5}$MnO$_4$</td>
</tr>
<tr>
<td>FC</td>
<td>Field-cooled</td>
</tr>
<tr>
<td>FCC</td>
<td>Field-cooled-cooling</td>
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<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>FE</td>
<td>Ferroelectric</td>
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<tr>
<td>FM</td>
<td>Ferromagnetic</td>
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<tr>
<td>FMTO</td>
<td>Fe$<em>{0.5}$Mn$</em>{0.5}$TiO$_3$</td>
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<tr>
<td>FOMT</td>
<td>First-order magneto-structural phase transition</td>
</tr>
<tr>
<td>f.u.</td>
<td>Formula unit</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
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<td>FZ</td>
<td>Floating zone</td>
</tr>
<tr>
<td>GDR</td>
<td>German Democratic Republic</td>
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<tr>
<td>GKA</td>
<td>Goodenough-Kanamori-Anderson</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>--------------</td>
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<tr>
<td>GT</td>
<td>Gabay-Toulouse</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal close packing</td>
</tr>
<tr>
<td>IC</td>
<td>Incommensurate</td>
</tr>
<tr>
<td>IR</td>
<td>Infra-Red</td>
</tr>
<tr>
<td>IRM</td>
<td>Isothermal-remanent magnetization</td>
</tr>
<tr>
<td>LCR</td>
<td>Inductance, capacitance, resistance</td>
</tr>
<tr>
<td>LRMO</td>
<td>Long range magnetic ordering</td>
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<tr>
<td>MC</td>
<td>Magnetocaloric</td>
</tr>
<tr>
<td>MCE</td>
<td>Magnetocaloric effect</td>
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<tr>
<td>ME</td>
<td>Magnetolectric</td>
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<tr>
<td>MFSO</td>
<td>Mn$_2$FeSbO$_6$</td>
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<tr>
<td>MPMS</td>
<td>Quantum Design - Magnetic property measurement system</td>
</tr>
<tr>
<td>NPD</td>
<td>Neutron powder diffraction</td>
</tr>
<tr>
<td>Ph.D.</td>
<td>Doctor of Philosophy</td>
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<tr>
<td>PLD</td>
<td>Pulsed laser deposition</td>
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<tr>
<td>PM</td>
<td>Paramagnetic</td>
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<tr>
<td>PT</td>
<td>Phase transition</td>
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<tr>
<td>PPMS</td>
<td>Quantum Design - Physical properties measurement system</td>
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<tr>
<td>RA</td>
<td>Raman-active</td>
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<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>RKKY</td>
<td>Ruderman-Kittel-Kasuya-Yosida</td>
</tr>
<tr>
<td>RSB</td>
<td>Replica symmetry breaking</td>
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<tr>
<td>SF</td>
<td>Spin-flop</td>
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<td>SG</td>
<td>Spin glass</td>
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<tr>
<td>SHG</td>
<td>Second harmonic generation</td>
</tr>
<tr>
<td>SK</td>
<td>Sherrington-Kirkpatrick</td>
</tr>
<tr>
<td>SOMT</td>
<td>Second-order magnetic phase transition</td>
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<tr>
<td>SQUID</td>
<td>Superconducting quantum interference device</td>
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<td>SRMO</td>
<td>Short range magnetic ordering</td>
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<tr>
<td>TRM</td>
<td>Thermoremanent magnetization</td>
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<tr>
<td>VSM</td>
<td>Vibrating sample magnetometer</td>
</tr>
<tr>
<td>XMCD</td>
<td>X-ray magnetic circular dichroism</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>ZFC</td>
<td>Zero-field-cooled</td>
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## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Denotation</th>
<th>SI unit*</th>
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<tbody>
<tr>
<td>α</td>
<td>Polarizability</td>
<td>$A^2 \cdot s^4 \cdot kg^{-1}$</td>
</tr>
<tr>
<td>B, B</td>
<td>Magnetic induction</td>
<td>T (G)</td>
</tr>
<tr>
<td>$B_{HF}$</td>
<td>Hyperfine field</td>
<td>T</td>
</tr>
<tr>
<td>β, γ</td>
<td>Critical exponents</td>
<td>1</td>
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<tr>
<td>χ</td>
<td>Magnetic susceptibility</td>
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</tr>
<tr>
<td>(emu⋅cm$^{-3}$Oe$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>Specific heat</td>
<td>J⋅kg$^{-1}$K$^{-1}$</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
<td>F</td>
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<tr>
<td>D</td>
<td>Electric displacement</td>
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<tr>
<td>$ΔS_M$</td>
<td>Magnetic entropy change</td>
<td>J⋅kg$^{-1}$K$^{-1}$</td>
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<tr>
<td>$ΔT_{ad}$</td>
<td>Adiabatic temperature change</td>
<td>K</td>
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<tr>
<td>ΔT</td>
<td>Temperature change</td>
<td>K</td>
</tr>
<tr>
<td>E</td>
<td>Energy</td>
<td>J</td>
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<tr>
<td>$E_a$</td>
<td>Anisotropy energy</td>
<td>J</td>
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<tr>
<td>E, E</td>
<td>Electric field</td>
<td>V⋅m$^{-1}$</td>
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<td>H, H</td>
<td>Magnetic field</td>
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<tr>
<td>$H_C$</td>
<td>Coercivity field</td>
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<tr>
<td>$\mathcal{H}$</td>
<td>Hamiltonian</td>
<td>J</td>
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<tr>
<td>γ</td>
<td>Grüneisen parameter</td>
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<tr>
<td>I</td>
<td>Intensity</td>
<td>W⋅m$^{-2}$</td>
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<td>J</td>
<td>Exchange constant</td>
<td>J</td>
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<tr>
<td>j</td>
<td>Current density</td>
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<tr>
<td>K</td>
<td>Anisotropy constant</td>
<td>J⋅m$^{-3}$</td>
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<tr>
<td>k, k</td>
<td>Propagation vector</td>
<td>m$^{-1}$</td>
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<tr>
<td>λ</td>
<td>Wavelength</td>
<td>m</td>
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* For the magnetic quantities cgs units are added in parenthesis.
## Symbol Denotation SI unit*

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<thead>
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<th>Symbol</th>
<th>Denotation</th>
<th>SI unit*</th>
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<tbody>
<tr>
<td>( \mathbf{M} ), ( M )</td>
<td>Magnetization</td>
<td>( \text{A} \cdot \text{m}^2\text{kg}^{-1} ) ((\text{emu} \cdot \text{g}^{-1}))</td>
</tr>
<tr>
<td>( M_R )</td>
<td>Remanent Magnetization</td>
<td>\text{idem}</td>
</tr>
<tr>
<td>( M_S )</td>
<td>Saturation Magnetization</td>
<td>\text{idem}</td>
</tr>
<tr>
<td>( \mathbf{m}, \mu )</td>
<td>Magnetic moment</td>
<td>( \text{A} \cdot \text{m}^2 ) ((\text{emu}))</td>
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<tr>
<td>( N )</td>
<td>Demagnetization factor</td>
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<tr>
<td>( \mathbf{P}, P )</td>
<td>Electrical Polarization</td>
<td>( \text{C} \cdot \text{m}^{-2} )</td>
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<tr>
<td>( p )</td>
<td>Dipol moment</td>
<td>( \text{C} \cdot \text{m} )</td>
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<tr>
<td>( P )</td>
<td>Pressure</td>
<td>( \text{Pa} )</td>
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<td>( \Phi )</td>
<td>Order parameter</td>
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<td>( Q )</td>
<td>Heat</td>
<td>( \text{J} )</td>
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<td>( q )</td>
<td>Refrigeration capacity</td>
<td>( \text{J} \cdot \text{kg}^{-1} )</td>
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<td>( S )</td>
<td>Entropy</td>
<td>( \text{J} \cdot \text{K}^{-1} )</td>
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<td>( \mathbf{S}, s )</td>
<td>Spin moment</td>
<td>( \hbar/2 )</td>
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<tr>
<td>( \sigma, q )</td>
<td>Charge</td>
<td>( \text{C} )</td>
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<tr>
<td>( T )</td>
<td>Temperature</td>
<td>( \text{K} )</td>
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<td>( T_C )</td>
<td>Curie (critical) temperature</td>
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</tr>
<tr>
<td>( T_F )</td>
<td>Freezing temperature</td>
<td>( \text{K} )</td>
</tr>
<tr>
<td>( T_G )</td>
<td>Spin-glass temperature</td>
<td>( \text{K} )</td>
</tr>
<tr>
<td>( T_N )</td>
<td>Néel temperature</td>
<td>( \text{K} )</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
<td>( \text{s} )</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Life time</td>
<td>( \text{s} )</td>
</tr>
<tr>
<td>( \theta )</td>
<td>Curie-Weiss temperature</td>
<td>( \text{K} )</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Frequency</td>
<td>( \text{Hz} )</td>
</tr>
</tbody>
</table>

* For the magnetic quantities cgs units are added in parenthesis.

## Physical constants

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name</th>
<th>Value</th>
<th>Unit (SI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varepsilon_0 )</td>
<td>Vacuum permittivity</td>
<td>( 8.85 \cdot 10^{-12} )</td>
<td>( \text{F} \cdot \text{m}^{-1} )</td>
</tr>
<tr>
<td>( k_B )</td>
<td>Boltzmann constant</td>
<td>( 1.38 \cdot 10^{-23} )</td>
<td>( \text{J} \cdot \text{kg}^{-1} )</td>
</tr>
<tr>
<td>( \mu_0 )</td>
<td>Vacuum permeability</td>
<td>( 4\pi \cdot 10^{-7} )</td>
<td>( \text{V} \cdot \text{s} \cdot \text{A}^{-1} \cdot \text{m}^{-1} )</td>
</tr>
<tr>
<td>( \mu_B )</td>
<td>Bohr magneton</td>
<td>( 9.27 \cdot 10^{-24} )</td>
<td>( \text{A} \cdot \text{m}^2 )</td>
</tr>
</tbody>
</table>
REFERENCES


REFERENCES


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STATEMENT

I hereby declare that the contents of this thesis entitled "Magnetic materials with tunable thermal, electrical, and dynamic properties" is the result of investigation carried out during my time as a PhD candidate in the Department of Engineering Sciences at Uppsala University, Uppsala, Sweden, under the supervision of Prof. Per Nordblad and Doc. Roland Mathieu.

The general practice of reporting scientific observations and results made in collaboration with other investigators was obeyed and their work and contributions have been acknowledged. Any omission which might be caused by oversight or error in judgement is regretted.

In agreement with academic practice at Uppsala University, chapter 3 of this thesis is based on my licentiate thesis, entitled "The magnetocaloric effect in Fe$_2$P-based alloys", which was defended 21$^{st}$ May 2010. The licentiate thesis is intended as a half-time report and corresponds to approximately 50% of the work for a doctoral thesis. It is therefore expected that there is an overlap with regard to contents and textural parts.

Matthias Hudl
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