Investigation of frustrated one-dimensional antiferromagnetic quantum chain systems and the rare earth intermetallic compound TmGa3

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Investigation of frustrated one dimensional antiferromagnetic quantum chain systems and the rare earth intermetallic compound TmGa$_3$

By
Michael George Banks

Doctoral Thesis

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY OF LOUTHBOROUGH UNIVERSITY FEBRUARY 22, 2007

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Maybe there is something!
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Abstract

My thesis concerns two areas of current research in magnetism, with the common experimental technique of elastic and inelastic neutron scattering on powders and single crystals. The first topic is concerned with rare earth intermetallic compounds with unfilled $4f$ shells. When a rare earth element with an unfilled shell is placed in an environment with surrounding charges, the crystal electric field acts to lift the $J$-fold degeneracy. Determination of the Crystal Electric Field (CEF) ground state and excited states are important to understand the complex and interesting low temperature phase diagrams these compounds exhibit. This will be discussed for the rare earth intermetallic compound TmGa$_3$. The other area of my thesis concerns one dimensional Heisenberg antiferromagnetic quantum chains systems. Due to the one dimensional lattice and low spin, quantum fluctuations play an important role in these systems. From the nature of the lattice, the interactions could give rise to magnetic frustration, resulting in interesting ground states. I will discuss results on the binary halides CuCl$_2$, CuBr$_2$ and on the quaternary oxide LiCuVO$_4$. To measure the thermal properties of the investigated systems, a quasi-adiabatic Nernst type calorimeter was constructed and commissioned. I will describe the design and the properties of the calorimeter.
Introduction

In $4f$ electron systems, determination of the crystal electric field level scheme in the paramagnetic phase is an important first step to understanding the rich variety of physical phenomena. In $4f$ systems, the coupling between the spin and orbital angular momenta is stronger than the crystal field due to the fact that the $4f$ orbital lies deep within the ion core and the other occupied orbitals screen out the potential of the surrounding ions. The ionic properties can therefore be described by the total angular momentum $J$, the degeneracy of which is then further split by the crystal field interaction. In rare earth intermetallic compounds a rich variety of magnetic and orbital ordering can occur. Recently, much interest has arisen due to the interplay of orbital and magnetic degrees of freedom in $f$ and also in $d$ systems. In $d$ transition metal oxides much of the unusual properties can be explained with the use of orbital ordering. In rare earth intermetallic systems, orbital ordering, through spontaneous lifting of the orbital degeneracy may manifest itself as a phase transition of quadrupole moments. This will concern the first part of my thesis on the investigation of the rare earth intermetallic compound TmGa$_3$.

Low dimensional magnetism has been an active area of research for both theoretical and experimental investigations ever since novel synthesis techniques, or natural compounds which exhibit low dimensional features have been found. Interest in low dimensional materials has increased by the discovery of high $T_c$ cuprates in which the Cu-O-Cu bond angle is close to 180°. The effect of this checkerboard geometry in two dimensions gives rise to large exchange integrals. Most of the focus has been on copper oxides, where the Cu-O-Cu
bond can either be 180° (corner sharing) or 90° (adjacent edge sharing). On the other hand 90° edge sharing compounds offer the possibility to study one dimensional compounds with frustrated magnetism since further neighbour interactions may become essential. Frustrated magnetism arises when all interactions across different bonds cannot be completely satisfied. I will present work on these frustrated 1D systems, which show a variety of effects at low temperature and in applied fields.

The thesis is made up of six chapters. The first describes the construction, testing and maintenance of a new quasi-adiabatic calorimeter for specific heat studies. The second chapter concerns the investigation of the rare earth intermetallic compound TmGa3. The third chapter gives an introduction to low dimensional magnetism. The fourth chapter consists of an investigation of the one dimensional compounds CuCl2 and CuBr2. The fifth chapter concerns an ideal one dimensional frustrated compound, LiCuVO4 and the features it shows at low temperatures. The final chapter shows the common properties that frustrated one dimensional spin 1/2 compounds exhibit.

The first Chapter is split into the following sections.

- Specific heat theory. Contributions from the lattice, electrons, spin waves and excitations of the spin energy levels are discussed.

- The design of the new quasi-adiabatic calorimeter is outlined and methods of how to experimentally obtain the specific heat of samples are examined.

- Testing a new experimental system is critical, and the various methods we used in order to assure we have a well calibrated system are presented.

The second chapter deals with the subject of rare earth intermetallic systems with emphasis on TmGa3. The chapter is presented in the following way

- An outline of crystal field theory is given in order to understand the importance of crystal electric field (CEF) effects in rare earth intermetallic compounds.
• Bulk measurements on TmGa₃ are shown including specific heat, susceptibility, magnetisation and resistivity.

• Crystal field parameters are presented for TmGa₃ derived from our inelastic neutron scattering investigations.

• The established CEF parameters are used to calculate thermodynamical properties such as the specific heat, susceptibility and magnetisation to compare these with experimental results.

The third chapter of the thesis presents the theory of one dimensional magnets and the difference between edge and corner sharing cuprates and why this is important to frustration in one dimensional magnets.

• The theory of magnetic models is discussed in terms of the spin degrees of freedom and the lattice dimensionality.

• The difference in edge and corner sharing cuprates is presented and how the physics changes from the corner sharing to edge sharing plaquette's giving rise to frustration.

In the fourth chapter of this thesis, I present work performed on the low dimensional compounds CuCl₂ and CuBr₂ which includes powder and single crystal measurements.

• The crystal structures of CuCl₂ and CuBr₂ are presented, including a description of the twinned nature of CuCl₂ single crystals.

• The magnetic properties are examined in terms of specific heat, susceptibility, Electron Spin Resonance (ESR) and high field measurements, for both powder and single crystal work.

• The theory of magnetic structure determination is presented.
• Investigations using elastic neutron scattering are examined for powder and single crystals, resulting in the magnetic structure of CuCl₂.

In the fifth chapter of this thesis, I present the investigation of an ideal frustrated one-dimensional magnet LiCuVO₄, which includes magnetisation and specific heat measurement.

• An introduction to previous work including elastic and inelastic neutron measurements.

• Measurements on single crystals of LiCuVO₄ such as specific heat, susceptibility and high field measurements in order to map out the low temperature phase diagram.

• Investigation of the two low temperature peak nature in the specific heat.

The final chapter shows the common properties of frustrated one dimensional spin chain compounds that are frustrated due to weaker nearest and stronger next nearest neighbour exchange. There are three appendices attached. Appendix A lists the program code used to calculate the heat capacity from the Einstein and Debye models, as well as program code to calculate the Chebychev coefficients to calibrate the thermometers used in the adiabatic calorimeter. Appendix B gives an example of an input and output file for usage in the program McPhase, that is used to calculate neutron scattering intensities originating from crystal field excitations. Appendix C lists the refined single crystal nuclear and magnetic structure data for CuCl₂ at room temperature and at 2 K, respectively.
Chapter 1

Specific heat measurements on a new calorimeter

1.1 Introduction

The study of low temperature physics is an important area not only for research, but also in the application of technology from rocket fuels to superconductors. Such studies have produced a clear manifestation of quantum effects and low temperature physics is one of the few areas where mankind has surpassed nature.

The wide range of temperatures available to experiments means that temperature is one of the most important parameters in the laboratory that we can vary in order to change the properties of matter, to understand it, and also to make practical use of it.

In this chapter, I will discuss specific heat theory, what is possible to measure using this technique, and demonstrate what a powerful technique it is to characterize samples. We have installed a new calorimeter for measuring the specific heat of samples in crystalline or powder form. Setting up a new system needs considerable calibration and testing, as well as in situ improving, which I will discuss in the following sections.
1.2 Specific heat theory

Specific heat is a powerful tool not only in connection with the refrigeration needed to take care of the thermal capacity of the system but also to study lattice vibrations, electronic distributions, energy levels in magnetic order and order-disorder phenomena in molecules.

In general, the specific heat of a substance is given as the quantity of heat required to raise the temperature of a unit mass of substance by a unit degree of temperature.

$$C_{x,y} = \lim_{dT \to 0} \left( \frac{dQ}{dT} \right)_{x,y}$$

(1.2.1)

In general, the total specific heat is the combination of lattice vibrations, electronic and magnetic contributions. I will examine the different contributions separately, how they are derived and in what way they affect the heat capacity of a system.

1.2.1 Lattice Heat Capacity

Ideally, the atoms in a solid are arranged in a regular lattice and held together by interatomic forces acting upon them. A simple example of a lattice would be a set of mass points which are held together by elastic springs. In this assumption, if the amplitude of the oscillations are small then interatomic spacing can be treated as a harmonic oscillators.

Each system can be treated as an assembly of harmonic oscillators with 6 degrees of freedom. By the equipartition theorem, the system has an internal energy of $3kT$, where $k$ is the Boltzmann constant and $T$ is the temperature. Therefore, the heat capacity at high temperatures is given by the Dulong-Petit value:

$$C_v = \left( \frac{\delta E}{\delta T} \right)_v = 3R \approx 24.94 \ [J/ \text{mol K}]$$

(1.2.2)

From experimental investigations this value is correct at high temperatures, but at lower temperatures the heat capacity is seen to fall below the $3R$ approximation, and so
classical statistical analysis was not sufficient to describe these findings. It was not until the development of quantum theory that an answer was suggested. These answers came from models proposed by Einstein and Debye, and are looked at in the next section.

Einstein's model

It was Einstein [25] who applied the atomic model to explain Brownian motion and confirmed our picture that matter is composed of atoms. In 1907 Einstein applied quantum theory outside the field of electromagnetic radiation to the thermal vibrations in solids. In his model, Einstein considered that each atom acts as a 3-D harmonic oscillator, so the atom is held in place by spring like forces in the x, y and z direction. It is also assumed that the atoms are described by quantum mechanics. The energies given for a simple harmonic oscillator are then

\[ \varepsilon_n = \hbar \omega_E (n + \frac{1}{2}) \]  

(1.2.3)

where \( \hbar \) is the Planck constant divided by \( 2\pi \) and \( \omega_E \) is the angular frequency of the lattice vibrations. If we apply statistical mechanics we can derive the thermodynamic properties of our model. The partition function for a single simple harmonic oscillator is

\[ Z = \sum_{n}^{\infty} e^{-\beta \varepsilon_n} \]  

(1.2.4)

where \( \beta = 1/k_B T \), \( k_B \) is the Boltzmann constant and \( T \) is the temperature. Substituting equation 1.2.3 into the above equation and expanding the summation gives,

\[ Z = \frac{e^{-1/2\beta \hbar \omega_E}}{1 - e^{-\beta \hbar \omega_E}} \]  

(1.2.5)

The average energy of an ensemble of \( N \) such oscillators is given as

\[ E = 3N\varepsilon \]  

(1.2.6)
where

$$\varepsilon = \frac{-1}{Z} \frac{\delta Z}{\delta \beta}$$  \hspace{1cm} (1.2.7)

Differentiating equation 1.2.5 with respect to $\beta$ and substituting into equation 1.2.7 gives

$$\varepsilon = -\frac{1}{Z} \left( \frac{-\frac{1}{2} \hbar \omega E Z - Z(e^{-\beta \hbar \omega E})(\hbar \omega E)}{1 - e^{-\beta \hbar \omega E}} \right)$$  \hspace{1cm} (1.2.8)

$$\varepsilon = \frac{1}{2} \hbar \omega E + \frac{\hbar \omega E}{e^{\beta \hbar \omega E} - 1}$$  \hspace{1cm} (1.2.9)

Therefore, the energy using equation 1.2.6 is given by

$$E = 3N \left( \frac{1}{2} \hbar \omega E + \frac{\hbar \omega E}{e^{\beta \hbar \omega E} - 1} \right)$$  \hspace{1cm} (1.2.10)

with the specific heat given as in equation 1.2.2

$$C_v = \frac{\delta E}{\delta \beta} = \left( \frac{d \beta}{d T} \right) (\delta E) = -k\beta^2 \left( \frac{\delta E}{\delta \beta} \right)$$  \hspace{1cm} (1.2.11)

substituting equation 1.2.10

$$C_v = 3Nk\frac{\delta E}{\delta \beta} \left( \frac{\hbar \omega E}{e^{\beta \hbar \omega E} - 1} \right)$$  \hspace{1cm} (1.2.12)

$$C_v = 3Nk \left( \frac{(\hbar \omega E)^2 e^{\beta \hbar \omega E}}{(e^{\beta \hbar \omega E} - 1)^2} \right)$$  \hspace{1cm} (1.2.13)

The over-simplification in this model is such that in a lattice all the atoms vibrate independently of one another and at the same Einstein frequency, $\omega_E$. The Einstein relation using equation 1.2.13 is given below,
\[ C_v = \left( \frac{T_e}{T} \right)^2 \frac{e^x}{(e^x - 1)^2} \]  \hspace{1cm} (1.2.14)

where \( T_e \) is the Einstein temperature, and \( x \) is a variable, both respectively given by

\[ T_e = \frac{\hbar \omega_e}{k_B} \quad x = \frac{\hbar \omega_e}{kT} \]  \hspace{1cm} (1.2.15)

A derivation is also given in [26].

A program was written in FORTRAN which calculates the heat capacity from equation 1.2.14 as a function of temperature for given values of the Einstein temperature, \( T_e \). The program code is given in Appendix A1.

The Einstein theory leads to the Dulong-Petit value at high temperatures and shows that by the quantization of lattice vibrations there is a reduction in heat capacity at low temperatures. Therefore, the decrease in the heat capacity at low temperatures is originating from a quantum phenomenon.

To check the theory, calorimetric calculations were performed by Nernst and others. They found that the qualitative features of Einstein's theory were sound, but the quantitative agreement was not sufficient. Therefore, by allowing just one frequency \( \omega_e \) to represent all vibrations was over simplified, as in a tight system, the vibrations of the other atoms will affect all neighbouring atoms. Also atoms can vibrate at several frequencies.

As a result in 1912 Debye introduced a model which incorporated a better understanding of lattice vibrational frequencies. This model is taken up in the next section.

**Debye's model (see e.g. [27])**

By quantization at low temperatures only the low frequency modes of the lattice will be excited, the very low frequency vibrations are acoustic. In Debye's theory there is a dispersion relation \( \omega = \omega_s(k) \) where \( s \) denotes the different types of waves, acoustic, transverse
etc. The internal energy is given as

\[ u(T) = \frac{1}{V} \sum_{k,s} \left( n_{ks} + \frac{1}{2} \right) \hbar \omega_s(k) \]  

(1.2.16)

where \( V \) is the volume and \( n_{ks} \) is the average number of phonons with a momentum \( k \).

Then \( n_{ks} \) is given by

\[ n_{ks} = \frac{1}{Z} e^{-\beta \hbar \omega_s(k)} = \frac{1}{e^{\beta \hbar \omega_s(k)} - 1} \]  

(1.2.17)

Substituting this into equation 1.2.16 and differentiating with respect to temperature provides

\[ C_v = \frac{k_B}{V} \sum_{k,s} (\beta \hbar \omega_s(k))^2 \frac{e^{\beta \hbar \omega_s(k)}}{(e^{\beta \hbar \omega_s(k)} - 1)^2} \]  

with the density of states given as \( V/(2\pi)^3 \), equation 1.2.18 is therefore

\[ C_v = \frac{k_B}{(2\pi)^3} \sum_{k,s} (\beta \hbar \omega_s(k))^2 \frac{e^{\beta \hbar \omega_s(k)}}{(e^{\beta \hbar \omega_s(k)} - 1)^2} \]  

(1.2.19)

For this model a few assumptions were made by Debye: the dispersion relation did not depend on the direction of \( k \), and are only in the regime of the 3 acoustical branches. The speed of sound in these 3 branches is

\[ \omega_s(k) = ck \]  

(1.2.20)

Using this, equation 1.2.19 becomes

\[ C_v = \frac{3k_B}{(2\pi)^2} \int (\beta \hbar ck)^2 \frac{e^{\beta \hbar ck}}{(e^{\beta \hbar ck} - 1)^2} dk \]  

(1.2.21)

Using \( x = \beta \hbar ck \), and changing the variable from \( k \) to \( x \) gives
The final simplification is to add a cut-off to the integration, and restrict the integration of \( k \) between 0 and \( k_D \) (or \( x \) between 0 and \( x_D(= \hbar c k_D / k_B T) \)). We can introduce a Debye frequency \( \omega_D = c k_D \) and a Debye temperature \( x_D = \theta_D / T \), equation 1.2.22 then becomes

\[
 C_v = \frac{3k_B}{(2\pi^2)} \left( \frac{k_B T}{\hbar c} \right)^3 \int_0^{\omega_D / T} \frac{x^4 e^x}{(e^x - 1)^2} dx 
\]  

(1.2.23)

given that

\[
 N = \int \frac{V}{(2\pi)^3} dk = \frac{V}{2\pi^2} \int k^2 dk = \frac{V}{6\pi^2} k_D^3
\]

(1.2.24)

\[
 \rho = \frac{N}{V} = \frac{k_D^3}{6\pi^2}
\]

(1.2.25)

\[
 k_B = NR
\]

(1.2.26)

with \( \rho \) being the density and \( R \) the gas constant. Therefore, substituting this into equation 1.2.23

\[
 C_v = 9RN \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D / T} \frac{x^4 e^x}{(e^x - 1)^2} dx
\]

(1.2.27)

The heat capacity for temperatures \( T < \Theta_D \) is given by

\[
 C_v(T) = \left( \frac{12}{5} \right) \pi^4 RN \left( \frac{T}{\Theta_D} \right)^3
\]

(1.2.28)

Again a program was written in FORTRAN to calculate the specific heat using the Debye model, for different values of the Debye temperature, this can be done by using
equation 1.2.27. The program code is shown in appendix A2. Figure 1.1 shows a plot of $C_v/R$ against temperature for varying Debye temperatures.

This plot shows that by increasing the Debye temperature the temperature taken to reach the Dulong Petit limit $3R$, is also increased. The Debye model has been successful in describing the specific heat of solids, the $T^3$ dependence of $C_p$ at low temperatures was an early prediction of the theory. Debye's prediction was verified at first measuring the specific heat of many solids such as rocksalt and showed excellent agreement with the theoretical law.

**Comparison between Einstein and Debye models**

With the programs written to calculate the specific heat, these can be used to compare the two models by setting the Debye temperature and the Einstein temperature equal, and then calculating the specific heat as a function of temperature.
Figure 1.2 shows the plot for $T_E$ and $\Theta_D$ at 100K, this shows that at low temperatures the Einstein theory approaches zero before the Debye model. Also the Einstein model reaches the $3R$ value at a much higher temperature than the Debye model.

In the course of my work, the programs were used to convert the measured heat capacities to a 'fictitious' temperature dependant Debye temperature $\Theta_D^{eff}(T)$, which was chosen such that according to eqn 1.2.22, the heat capacity $C_v(T)$ is obtained. The advantage of this conversion procedure is similar to converting magnetic susceptibilities into an effective, temperature dependant magnetic moment, $\mu_{eff}(T)$. In general, an experimentally determined heat capacity covers several orders of magnitude. If converted, $\Theta_D^{eff}(T)$ mostly varies by less than a factor of 2, given that no magnetic anomalies etc, are seen.
1.2.2 Electronic Heat Capacity

In a metal there is also the contribution, as well as lattice vibrations, from the conduction electrons which can be thermally excited.

With the success of the free electron model also came a fundamental inconsistency in the classical theory. If the electrons in the metal are considered as particles freely moving through the lattice, then by the equipartition law, the internal energy that each electron has is given as $\frac{3}{2}kT$, associated with 3 translational degrees of freedom. Therefore, each electron would contribute $\frac{3}{2}R$ per mole to the specific heat.

Therefore, for $T \gg \Theta_D$, one would expect a $3R$ contribution from the lattice vibrations for insulators and an additional $\frac{3}{2}R$ contribution for metals, giving a total of $\frac{9}{2}R$ per mole. This estimate was inconsistent with all experimental observations.

Given this, the model of an electron gas in a metal explains the transport properties well, but the caloric behaviour was in complete disagreement with the equipartition theorem.

When Sommerfeld applied quantum statistics to the free electrons in a metal, the reason for the small electronic specific heat became immediately evident. It became clear that the electronic contribution could only be observed at low temperatures, in the liquid helium range.

A knowledge of the energy levels in a metal is not required for determining the specific heat of electrons in a metal, due to the fact that electrons follow the Fermi-Dirac distribution. It can be shown that only electrons within $k_BT$ of the Fermi surface may be excited. Therefore, knowledge of the number of energy states in the vicinity of the Fermi surface is required to calculate the electronic specific heat.

As electrons have spin $\frac{1}{2}$ and are fermions, they obey the Pauli exclusion principle. Each energy state can be occupied by at most 2 electrons with antiparallel spin. Putting all the electrons in energy states, we fill these states up to a limiting energy, the Fermi energy (at $T=0$), given as
where $T_F$ is the Fermi temperature. The Fermi-Dirac distribution function for the occupation of energy states of electrons at a finite temperature $T$ is given by

$$f_e(E) = \left(\frac{1}{\exp[(E - \mu)/k_BT] + 1}\right)$$

(1.2.30)

with the chemical potential, $\mu = E_F$ at $T = 0$. As the Fermi temperature is a high energy of typically a few eV, room temperature is still a 'low temperature', so that the electron gas is very close to the ground state.

The density of states for conduction electrons in the free electron model is given by

$$g_e(E) = \left(\frac{3N_0}{2E_F^{3/2}}\right) E^{1/2} = \frac{V_m}{2\pi^2} \left(\frac{2m_e}{\hbar}\right)^{3/2} E^{1/2}$$

(1.2.31)

$V_m$ is the molar volume and $m$ is the mass of the electrons. Therefore, to find the properties of the conduction electrons in a metal we must multiply $f_e$ and $g_e$.

If we perform a calculation of the number of electrons that experience an energy change, $\Delta E$, when the temperature is raised by $\Delta T$, then the specific heat is given as

$$C_v(T) = \frac{\pi^2}{2} N_0 k_B \frac{T}{T_F} = \frac{\pi^2}{3} k_B^2 T N(E_F)$$

(1.2.32)

with $N(E_F)$ being the density of states at $E_F$. This prediction is in good agreement with experimental data and was a great achievement of quantum mechanics, the free electron model and the Fermi theory of spin $\frac{1}{2}$ particles.

1.2.3 Low temperature specific heat

At room temperature the electronic contribution to the heat capacity of a metal is insignificant compared to the phonon contribution, but at lower temperatures the situation is quite
Different.

Above \( T \approx \Theta_D/20 \), the lattice contribution to the specific heat rapidly dominates, while below, the electronic part is significant. In general, for liquid helium temperatures both parts are of comparable magnitude and the specific heat is of the form

\[
C(T) = \beta T^3 + \gamma T
\]  

(1.2.33)

For a free electron model, the coefficients \( \beta \) and \( \gamma \) are given as,

\[
\beta = \frac{12}{5} \pi^4 N_0 k_B \left( \frac{1}{\Theta_D(T = 0)} \right)^3 \approx 1944N \frac{1}{\Theta_D(T = 0)^3} \quad [\text{J/mol K}^4]
\]  

(1.2.34)

\[
\gamma = \frac{\pi^2}{2} N_0 k_B \left( \frac{1}{T_F} \right)
\]  

(1.2.35)

A plot of \( C/T \) against \( T^2 \) (Sommerfeld plot) using equation 1.2.33 at low temperatures will produce a straight line with the Sommerfeld coefficient as the intersection with the ordinate. From such a plot the Sommerfeld constant \( \gamma \), is readily obtained.

1.2.4 Ferro and antiferromagnetic contribution to the specific heat (see e.g. [1])

The contribution to the specific heat by ferromagnetic spin waves can be calculated by analogy to lattice vibrations. The density of states of spin waves modes with a wavenumber between \( k \) and \( k + dk \) is given by

\[
g(k)dk = \frac{V k^2}{2\pi^2} dk
\]  

(1.2.36)

At low temperatures only the low energy long wavelength modes will be excited. The quanta associated with the spin wave modes are called magnons. Like phonons these are
bosons. From the dispersion relation for spin waves near $k = 0$ the magnon energy e.g. for a simple ferromagnet is given by

$$\epsilon = \hbar \omega = 23S\alpha^2 k^2 \quad (1.2.37)$$

where $\mathcal{S}$ is the exchange energy between nearest neighbours, $\alpha$ is the lattice spacing and $S$ is the spin. The number of modes with frequency between $\omega$ and $\omega + d\omega$ being

$$g(\omega)d\omega = g(k)dk = \frac{V}{4\pi^2} \left( \frac{\hbar}{23S\alpha^2} \right)^{\frac{3}{2}} \omega^{\frac{1}{2}} d\omega \quad (1.2.38)$$

The Bose-Einstein distribution function gives the average number of magnons at a temperature $T$ as

$$n_\omega = \frac{1}{e^{\hbar \omega / k_B T} - 1} \quad (1.2.39)$$

The contributions of the magnons to the energy is

$$E = E_0 + \int_0^\infty \hbar \omega \cdot n(\omega)g(\omega)d\omega \quad (1.2.40)$$

Substituting equation 1.2.38 and equation 1.2.39 into equation 1.2.40 gives

$$E = E_0 + \frac{V}{4\pi^2} \left( \frac{\hbar}{23S\alpha^2} \right)^{\frac{3}{2}} \left( \frac{k_B T}{\hbar} \right)^{\frac{3}{2}} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx \quad (1.2.41)$$

where $E_0$ is the zero point energy and $x = \hbar \omega / k_B T$. The specific heat is therefore given by

$$C_v = \frac{dE}{dT} = \frac{1.11V}{\pi^2 \hbar} \left( \frac{k_B}{23S\alpha^2} \right)^{\frac{3}{2}} k_B T^{\frac{3}{2}} \quad (1.2.42)$$

Therefore, the magnon specific heat varies by $T^{3/2}$ at low temperatures. So in metals, the conduction electrons give a specific heat contribution proportional to $T$, the phonons
give a $T^3$ contribution and when the magnetic term is added, the low temperature specific heat is of the form

$$C = \gamma T + \beta T^3 + \delta T^{3/2}$$  \hspace{1cm} (1.2.43)

where $\beta$ and $\gamma$ are defined as before and

$$\delta = c_f N k \left( \frac{k}{2\pi} \right)^{3/2}$$ \hspace{1cm} (1.2.44)

$c_f$ is a constant depending on the crystal structure and for a cubic system it is typically given as $\approx 0.113$. A similar treatment gives $C \propto T^3$ for antiferromagnetic magnons. In general we can assign $C \propto T^{d/n}$, where $n$ is the power of the magnon dispersion relation and $d$ is the lattice dimensionality.

Next, we will consider the Schottky effect on the specific heat.

### 1.2.5 Schottky anomalies (see also [2])

A particle with spin $s\hbar$ has $(2s + 1)$ possible orientations of the spin. In a magnetic field the particle has a number of discrete energy levels. Thermal population of the spin energy levels add to the specific heat, for example say two levels are separated by $\Delta$. At $T \ll \Delta/k_B$ according to Boltzmann statistics, the upper level is hardly populated, but at $T \gg \Delta/k_B$ both levels are almost equally populated. This change in the internal energy produces a contribution to the specific heat which approaches zero in an experimental manner at low and high temperatures, but produces a ‘hump’ in the specific heat at higher temperatures which is usually superimposed on the lattice and other contributions.

The probability of a particle occupying the $r^{th}$ level is given by the Boltzmann factor, $\exp(-\epsilon_r/k_BT)$, if it contains $m$ levels separated by energies $\epsilon_1, ..., \epsilon_m$ and with degeneracies of $g_1, ..., g_m$ then
with $N$ independent particles the mean energy at a temperature $T$ is

$$E(T) = \frac{N \sum_{r=0}^{m} \epsilon_r g_r e^{-\epsilon_r / k_B T}}{\sum_{r=0}^{\infty} g_r e^{-\epsilon_r / k_B T}}$$  \hspace{1cm} (1.2.46)

For a two level system with degeneracies $g_0$ and $g_1$ and energies $\epsilon_0 (=0)$ and $\epsilon_1$, equation 1.2.46 becomes

$$E(T) = \frac{N \epsilon_1 g_1 e^{-\epsilon_1 / k_B T}}{g_0 + g_1 e^{-\epsilon_1 / k_B T}}$$  \hspace{1cm} (1.2.47)

Using eqn 1.2.47, the Schottky contribution to the specific heat is

$$C_{sch}(T) = \frac{N \epsilon_1^2 g_0}{k_B T^2} \frac{e^{\epsilon_1 / k_B T}}{g_1 [1 + (g_0 / g_1) e^{\epsilon_1 / k_B T}]^2}$$  \hspace{1cm} (1.2.48)

with $\delta = \epsilon_1 / k_B$, equation 1.2.48 becomes,

$$C_{sch}(T) = R \left( \frac{\delta}{T} \right)^2 \frac{g_0}{g_1} \frac{e^{\delta / T}}{g_0 [1 + (g_0 / g_1) e^{\delta / T}]^2}$$  \hspace{1cm} (1.2.49)

At high and low temperatures the above equation gives

$$C_{sch}(T) = R g_0 g_1 (g_0 + g_1)^{-2} \left( \frac{\delta}{T} \right)^2 \quad T \ll \delta$$  \hspace{1cm} (1.2.50)

$$C_{sch}(T) = R g_0 g_1 (g_0 + g_1)^{-2} \left( \frac{\delta}{T} \right)^2 \quad T \gg \delta$$  \hspace{1cm} (1.2.51)

When the system includes more levels the full equation 1.2.46 has to be used or alternatively using the partition function

$$C_{sch} = T \frac{d^2 (RT \ln Z)}{dT^2} = RT^{-2} \frac{d^2 \ln Z}{d(1/T)^2}$$  \hspace{1cm} (1.2.52)
where the partition function is

\[ Z = \sum_r g_r e^{-\varepsilon_r / kT} \]  

(1.2.53)

1.3 Principles of measuring the specific heat

1.3.1 Cryostat and apparatus

The cryostat used to thermalize the sample and to perform the heat capacity measurements is a Helium 4 Konti cryostat IT (continuous flow cryostat) manufactured by Cryovac Company, Troisdorf, Germany. The cryostat provides a temperature stabilized environment in a \( \approx 50 \) mm diameter bore to carry out heat capacity measurements with no magnetic field present. An outline is given below.

The variable temperature insert carries the heat shields and the sample platform. The sample probe contains heat baffles to reduce the effect of thermal radiation, and access to the sample space to evacuate the sample environment, as well as housing the copper wires used for the measurement. In the set-up we have two radiation shields, an outer shield constituted by a vacuum tight calorimeter can and an inner shield defining the sample temperature.

The inner heat shield carries a heater and a temperature sensor. The temperature is controlled via a LakeShore 340 temperature controller. In all, there are 3 CERNOX [28] temperature sensors, one which is custom calibrated by LakeShore Cryogenics Inc, and the other two which are calibrated to this standard during the set-up of the calorimeter. The calibration procedure is discussed in a later section. The sample is mounted on the sapphire platform (see fig 1.3), which is suspended by cotton ‘wires’ to reduce heat leaks. Another CERNOX temperature sensor is glued to the bottom side of the sapphire platform which is then read out by a LakeShore 370 resistance bridge. The sample space is under high vacuum.
approx $< 10^{-6}$ mbar provided by continuous pumping with a turbo molecular pump. To measure the heat capacity we supply an electrical heat pulse to the sample. We do this by providing an electrical current to a stainless steel film ($\sim 1.5$ k$\Omega$) evaporated also on the bottom of the sapphire platform. Fig 1.3 shows a picture of the sample environment for the quasi-adiabatic calorimeter. Mounted on the sapphire platform is a copper sample used to calibrate the system. As can be seen the platform is suspended by three cotton threads. A minute amount of Apiezon grease was used to thermally couple the copper sample to the platform.

Our Nernst calorimeter can be used to measure crystalline samples or powders. The method of measuring a single crystal or crystalline piece is to apply a minute amount of Apiezon N grease [29] ($m = 3$–$5$ mg) to the platform and then directly attach the sample. The role of the Apiezon grease is to provide a thermal coupling between the heater and the sample. The mass of the Apiezon must be determined beforehand. To estimate its
contribution to the heat capacity we take tabulated values [30]. If in the case of a powdered sample, the powder must be contained in a Duran glass ampoule under \( \sim 1 \) mbar of He gas to provide thermal coupling to the sample. As in the case of a crystalline piece, the glass ampoule is then attached to the platform with Apiezon grease. In a similar manner the Duran glass specific heat has been tabulated [30]. In this way we have the following contributions for polycrystalline samples

\[
C_{\text{total}} = C_{\text{sample}} + C_{\text{Apiezon}} + C_{\text{platform}}
\]

(1.3.1)

In the case of a powder encapsulated in a Duran glass ampoule attached with Apiezon grease used to couple the glass ampoule to the sapphire disc,

\[
C_{\text{total}} = C_{\text{sample}} + C_{\text{Apiezon}} + C_{\text{platform}} + C_{\text{Duran}}
\]

(1.3.2)

Therefore, the knowledge of the heat capacity of the Apiezon grease, Duran glass and in addition the addenda (platform and surroundings) is mandatory in order to calculate an accurate value of \( C_{\text{sample}} \).

The method employed to undertake data acquisition (and thus the determination of \( C_{\text{total}} \)) is by the Nernst heat pulse method which is described in the next section.

1.3.2 Methods used to deduce the heat capacity of a sample

There are various ways to calculate the specific heat and this has been a topic of many papers discussing how to calculate it to a good accuracy, and ways of calculating it [31, 32]. The important factors in establishing the specific heat are the relaxation time constants, that describe the equilibration of the system after the heat pulse has been applied. In a usual set-up one has the sample platform, sample, and then the surroundings which is held at constant temperature. There is an internal relaxation time describing how fast the sample equilibrates with the platform after a heating pulse has been applied, and an
external relaxation time describing how fast the system equilibrates with the surroundings viz. the inner shield, which is held constantly at the temperature before the heating pulse has been applied.

Experimentally, the heat pulse is supplied by an electrical heater for a time \( \Delta t \) and the heat capacity is given by

\[
C_p = \frac{\Delta Q}{\Delta T} = \frac{VI\Delta t}{\Delta T}
\]  

(1.3.3)

where \( V \) is the voltage, \( I \) is the current, \( \Delta t \) is the time duration which the heat pulse is applied. These parameters can be measured with sufficient precision. The key parameter is \( \Delta T \) which has to be determined experimentally. \( \Delta T \) should be sufficiently small with respect to the temperature \( T \) at which the heat capacity is measured. In general \( \Delta T/T \leq 0.1 - 1\% \). Particularly, for phase transitions with very sharp anomalies, \( \Delta T \) has to be carefully selected. At low temperatures our system allows to resolve heating pulses leading to a \( \Delta T \approx 1 \text{ mK} \).

An example of a sample heat pulse is shown in fig 1.4. The top part of the figure shows the adiabatic case in which we have no loss of heat to the surroundings as in case a), so the post heat pulse section is linear. Then we can extrapolate \( \Delta T \) easily by taking the midpoint in the heat pulse. The distance from the pre heating extrapolation to the post heating extrapolation is \( \Delta T \).

However, in the semi adiabatic case which is a more realistic experimental scenario, the calculation of \( \Delta T \) is not so simple. Determining \( \Delta T \) becomes more problematic if one has an exponential heat loss.

One way of obtaining the heat capacity of a sample is by using the differential equation describing the change of \( T \) with time \( t \), given by using the heat flow equation [31, 32]

\[
C_p \left( \frac{dT}{dt} \right) = P + \kappa(T - T_0)
\]  

(1.3.4)
Figure 1.4: Heat pulse in the case of adiabatic (top) and semi-adiabatic (bottom) relaxation. The heat pulse current is switched on at $t = 0$ and lasts until $t = t_H$. Taken from [4].
$P$ is the electrical power supplied by the heater during the pulse, $\kappa$ is the thermal conductivity describing the external relaxation, $T$ is the temperature, $t$ is the time and $T_0$ is the temperature of the surroundings. The following equation describes the temperature development of the heating and post heating parts.

$$T(t) = \frac{P}{C\beta}(1 - e^{-\beta t_h})e^{-\beta(t-t_h)} \quad (1.3.5)$$

where $\beta = C/\kappa = \tau^{-1}$ is the inverse of the relaxation time and $t_h$ is the interval the heat pulse is applied. Fitting eqn 1.3.5 to the experimental curve of $T$ against $t$, and extrapolating the mid of the heating time which is $T(t_h/2)$. The heat capacity is obtained by iterating the formula

$$T\left(\frac{t_h}{2}\right) = \frac{2P}{C\beta} \sinh\left(\frac{\beta t_h}{2}\right) \approx \frac{Pt_h}{C} \left(1 + \frac{1}{24}(\beta t_h)^2\right) \quad (1.3.6)$$

Then the temperature sweep commences and the specific heat is calculated for each temperature increment. The method we employed in our system is described in the next section. It is based on a single relaxation model.

### 1.3.3 Single $\tau$ relaxation model

This simplified model assumes that the sample and sample platform are in good thermal contact with each other, and are at the same temperature during data analysis i.e the internal relaxation time, $\tau_{int} \to 0$. Then the temperature of the platform, $T_p$, obeys the following differential equation

$$C_{total} \frac{dT_p}{dt} = -K_W(T_p - T_0) + H(t) \quad (1.3.7)$$

Where $C_{total}$ is the total heat capacity of the sample and the sample platform; $K_W$ is the thermal conductance of the connection wires; $T_0$ is the temperature of the thermal bath
and $H(t)$ is the heating power of the measurement and is given by

$$H(t) = \begin{cases} 
  H_0 & 0 \leq t \leq t_h \\
  0 & \text{otherwise}
\end{cases}$$  \quad (1.3.8)

Using the transformation

$$T^* = T_p - T_0$$  \quad (1.3.9)

Hence,

$$\frac{dT^*}{dt} = \frac{T_p}{C_p}$$  \quad (1.3.10)

Substituting these results in equation 1.3.7 and rearranging one obtains

$$\frac{dT^*}{dt} + \frac{K_W T^*}{C_p} = \frac{H(t)}{C_p}$$  \quad (1.3.11)

Introducing,

$$P(t) = \frac{K_W}{C_p}, \quad Q(t) = -\frac{H(t)}{C_p}$$  \quad (1.3.12)

Therefore,

$$(T^*)' + T^* P(t) + Q(t) = 0$$  \quad (1.3.13)

The solution of this first order inhomogeneous differential equation is given by

$$T^*(t) = \left[ - \int Q(t)e^{\int P(t)dt}dt + C \right] e^{-\int P(t)dt}$$  \quad (1.3.14)

To find the constant during the heat pulse, $(H(t) = H_0)$ is found by taking the expression in the square brackets and integrating this gives:
\[
\left[- \int Q(t)e^{P(t)dt}dt\right] = \int \frac{H_0}{C_p} e^{\frac{K_W}{C_p}dt} dt
\] (1.3.15)

\[
= \frac{H_0}{C_p} \int e^{\frac{K_W}{C_p}dt} dt = \frac{H_0}{C_p} \left[ \frac{C_p}{K_W} e^{\frac{K_W}{C_p}t} + C_1 \right]
\] (1.3.16)

\[
= \frac{H_0}{K_W} e^{\frac{K_W}{C_p}t} + C_1 \frac{H_0}{C_p}
\] (1.3.17)

Putting this back into equation 1.3.14 gives

\[
T^*(t) = \left[ \frac{H_0}{K_W} e^{\frac{K_W}{C_p}t} + C_1 \frac{H_0}{C_p} \right] e^{-\frac{K_W}{C_p}t}
\] (1.3.18)

Using the condition \(T^*(0) = 0\) we can evaluate the constant \(C_1\).

\[
T^*(0) = \left[ \frac{H_0}{K_W} + C_1 \frac{H_0}{C_p} \right] = 0
\] (1.3.19)

So that \(C_1\) is given as

\[
C_1 = -\frac{C_p}{K_W}
\] (1.3.20)

Giving the solution

\[
T^*(t) = \left[ \frac{H_0}{K_W} e^{\frac{K_W}{C_p}t} - \frac{H_0}{K_W} \right] e^{\frac{K_W}{C_p}t}
\] (1.3.21)

Introducing a characteristic time constant \(\tau = \frac{C_p}{K_W}\) and rearranging gives

\[
T^*(t) = e^{-t/\tau} \frac{H_0}{C_p} \left[ e^{t/\tau} - 1 \right] = \frac{H_0}{C_p} \tau \left[ 1 - e^{-t/\tau} \right]
\] (1.3.22)

\[
T^*(t) = \frac{H_0}{C_p} \tau \left[ 1 - e^{-t/\tau} \right]
\] (1.3.23)
Introducing $p_0 = H_0/C_p$ gives the final solution. The temperature dependence as a function of time can then be fitted to the experimental curve, to obtain the heat capacity.

$$T^*(t) = p_0 \tau \left[ 1 - e^{-t/\tau} \right]$$  \hspace{1cm} (1.3.24)

In this way we then measure the total heat capacity as described in equation 1.3.2, and subtraction of the other known heat capacities, e.g. addenda and Apiezon grease, allows us to get an accurate estimate of the samples heat capacity.

1.4 Calibration and testing

1.4.1 Calibration of thermometers

As the LakeShore temperature controller measures a resistance, a calibration curve is needed to convert the resistances into temperatures. As described before, one of the thermometers was custom calibrated by LakeShore, and the other two were calibrated in house to the same standard in the following way. For the interpolation we used a piecewise Chebychev polynomial procedure as also employed by LakeShore. Using a Chebychev interpolation has advantages over regular power series in that it converges more rapidly, and the best approximation is approached. The temperature of the sensor can be calculated using the resistance and the Chebychev coefficients from the formula as given in equation 1.4.1:

$$T(K) = \sum A_i \cos(i \cos(x))$$  \hspace{1cm} (1.4.1)

where $T$ is the temperature in Kelvin, $A_i$ are the coefficients were $i$ is the order of the coefficients, and $x$ is defined as:

$$x = \frac{(z - z_l) - (zu - z)}{(zu - z_l)}$$  \hspace{1cm} (1.4.2)
$z$ is the resistance, $zu$ is the upper resistance of the selected interval, $zl$ is the lower resistance in the interval. All are $\log_{10}$ of their respective resistance values.

The main point of the calibration is to obtain the Chebychev coefficients, $A_i$ for the uncalibrated sensors. A sample program code to calculate the coefficients is listed in appendix A3.

1.4.2 Testing

Testing was preformed on the low temperature part of the addenda, as at low temperatures the addenda becomes more important due to the low heat capacity of samples. The heat capacity of a sample at very low temperatures ($T \leq 5$ K) can be, in general, only a factor of 2-3 larger than the addenda, in comparison to intermediate temperatures where the sample heat capacity is at least one order of magnitude larger than the addenda. Therefore, accurate knowledge of the low temperature behaviour of the addenda is crucial. The results of addenda measurements are shown in Fig 1.7 at low temperatures. The full black squares and circles are different addenda measurements. High purity copper pieces are used as a standard to test the low temperature behaviour, one piece of information to extract from the heat capacity at low temperatures is the Sommerfeld coefficient, $\gamma$ of Cu given by equation 1.2.35. The standard literature value is $7.0 \times 10^{-4}$ J/moleK² [33]. Fig 1.5 shows the results of our measurements on high purity Cu, which are in excellent agreement with the literature values, the value we obtain is $\gamma_{Cu} = (6.97 \pm 0.06) \times 10^{-4}$ J/moleK².

The total heat capacity when a sample is coupled by Apiezon grease to the platform is given by

$$C_{total} = C_{sample} + C_{Apiezon} + C_{platform} \quad (1.4.3)$$

We used 4 copper samples of varying mass, 30 mg, 100 mg, 200 mg and 300 mg. From the data, the Apiezon grease heat capacity is taken from tabulated values [30]. Subtracting
Figure 1.5: $C_p/T$ as a function of $T^2$ for a 300 mg copper sample. Full Black squares: measured heat capacity, solid line: linear fit as described in the text.

Figure 1.6: $C_{\text{total}} - C_{\text{Apiezon}}$ as a function of copper mass. Open circles: experimental data, solid line: straight line fit of the data to obtain a platform estimation, given by the constant $A$. 

\begin{align*}
\gamma &= (6.97 \pm 0.06) \times 10^{-4} \text{ J/moleK} \\
\beta &= (3.9 \pm 0.5) \mu\text{J/K} \\
A &= (4.0 \pm 0.3) \times 10^{-2} \mu\text{J/mgK}
\end{align*}
From copper measurements
First addenda determination
Second addenda determination

Figure 1.7: Semi-log plot of the heat capacity as a function of temperature. Full black squares and circles: Addenda measurements, open circles: estimation of the addenda from the measurements of Cu samples with different masses.

this from the total heat capacity as given by eqn 1.4.3, gives the platform and sample contribution. Plotting the total heat capacity minus the Apiezon grease heat capacity at a fixed temperature as a function of the mass of the copper piece, should then give a straight line. From this straight line extrapolation to an effective zero mass, will give an estimation of the platform heat capacity at that specific temperature. Fig 1.6 shows an example obtained at 2.67 K using this technique. Fig 1.7 shows the addenda heat capacity as a function of temperature. The full black squares and circles are measured platform heat capacities as done for regular addenda measurements. Open circles are estimations of the platform as determined by the above method using copper. The agreement with the measured addenda and that deduced from copper is very satisfactory.
Superconducting transition temperatures of Lead and Tin

Following a measurement on TmGa₃ (see next chapter) there was a difference of 0.1 K between the transition temperatures as reported in the literature [34, 35] and what we obtained on our new calorimeter. To check the custom calibration thermometer we measured the superconducting transition of high purity Lead and Tin. The standard literature values of the superconducting transition temperatures are given as $T_c = 7.20$ K and $T_c = 3.70$ K for lead and tin respectively. The experimental procedure was to have both samples on the platform in the same experimental run. The purest commercially available samples were chosen, lead 99.9999% pure and a 99.9995% pure tin sample (source Alfa Aesar, Johnson Matthey). For the tin sample the transition was not as sharp as for the lead sample, but a good estimate of the transition was possible.

Fig 1.8 shows the plot of the $C_p/T \propto T^2$ for high purity tin. The transition temperature found in the literature is $T_c = 3.71$ K. The transition as shown in fig 1.8 is broad due to the fact that there is also a lead sample on the platform, which contributes nevertheless at these low temperatures. In any case the midpoint of the transition, which is a reasonable estimate of the transition temperature, is at $3.72 \pm 0.02$ K, which is in good agreement with the literature data.

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The first lead sample when on the platform together with the tin sample, showed a transition that was much broader than the resolution we need (< 0.1 K) in order to conclude that our temperature calibration is correct. Due to the larger lattice contribution at 7 K from the tin sample, we measured the lead sample again alone. The lead sample was melted and then slowly cooled to relax possible lattice strains. The temperature dependence of the specific heat is shown in fig 1.9. As is evident the transition is much sharper, with a width of 0.025 K, and the critical temperature is in excellent agreement with the literature value of 7.20 K.

In conclusion, it has been shown that the newly installed adiabatic calorimeter, which
Figure 1.8: $C_p/T$ against $T^2$ for high purity tin (99.999%, Alfa Aesar).

Figure 1.9: $C_p/T$ against $T$ for high purity lead (99.999%, Alfa Aesar). Insert: $T$ dependence from 2-9 K showing the small jump in $C_p$ due to the transition into the superconducting state.
can operate in the temperature range of 1.5 to 250 K, is calibrated correctly. With all these various checks of addenda and thermometers we can be sure that the data we obtain from our adiabatic calorimeter measurements are accurate and reliable.
Chapter 2

Investigation of the rare earth intermetallic compound TmGa$_3$

2.1 Introduction

In this chapter I will present details of the investigations undertaken on the rare earth intermetallic compound TmGa$_3$. TmGa$_3$ undergoes two first order transitions at 4.29 K (Antiferroquadrupolar) and at 4.26 K (Antiferromagnetic) which are clearly evident in the heat capacity by two remarkable anomalies. Due to the close vicinity of the first order transitions this offers an interesting interplay between charge and magnetic degrees of freedom in this compound. In some particular rare earth intermetallic systems as in TmGa$_3$, orbital ordering, through spontaneous lifting of the orbital degeneracy, manifests itself as a phase transition of quadrupole moments. A Ferroquadrupolar (FQ) transition results when the order parameter is uniform from site to site. On the other hand, an Antiferroquadrupolar (AFQ) transition occurs when the ordered phase has a staggered component. It was argued [36] that in insulating materials the interactions of the quadrupoles are mediated by phonons, and in metallic systems the quadrupolar interaction is mediated via a RKKY-like interaction through conduction electrons.

Although the list of systems with experimentally verified AFQ transitions is limited, the number is growing due to recent increasing interest in these systems. Among Tm
based compounds, TmZn [37], TmCu [38] and TmGa\textsubscript{3} were described to exhibit an AFQ order transition in the paramagnetic phase, followed closely by an antiferromagnetic (AFM) transition. TmCd [37], on the other hand, undergoes only a transition of AFQ nature, with no experimentally verified AFM transition down to 30 mK. TmTe, a divalent Tm\textsuperscript{2+} magnetic semiconductor, has been studied by inelastic neutron spectroscopy (INS) [39], in which a field induced magnetic superstructure was seen due to AFQ order at 1.8 K. CeB\textsubscript{6} was the first compound to be unambiguously defined by INS experiments [40] as having a low temperature AFQ character. CeB\textsubscript{6} shows a huge enhancement of the AFQ phase in a magnetic field. Recently a modulated AFQ structure was observed in the intermetallic compound PrPb\textsubscript{3} by INS experiments [41].

Rare earth moments are subject to the interactions with the surrounding charge distribution. In general, this gives rise to a lifting of the 2\textit{J}+1 fold degeneracy of the total angular momentum. The remaining degeneracies are determined by symmetry and the magnitude of the electrical field generated by the charges in the environment. The interplay of the crystal electric field as well as orbital and magnetic ordering makes TmGa\textsubscript{3} a very interesting compound and generates a complex low temperature phase diagram. This was first investigated by Czopnik \textit{et al.} [34] by specific heat, thermal expansion and susceptibility measurements. They found two close lying transitions at 4.26 K and 4.29 K. The first transition was attributed to, by a comparison with TmZn and TmCd, a structural transition driven by quadrupolar pair interactions at 4.29 K, followed by a second antiferromagnetic transition at 4.26 K. A \Gamma\textsubscript{3}^{(1)} crystal field ground state was concluded from the temperature dependance of the susceptibility. A \textsuperscript{169}Tm Möösbauer spectroscopy study [42] concluded crystal field parameters of \textit{x} = -0.38 (in the Lea, Leask and Wolf notation) and \textit{B}_2\textsuperscript{0} = -0.30 K by an iterative procedure by fixing \textit{W} = 1.0 K. The trivalent state of Tm\textsuperscript{3+}, 4f\textsuperscript{12} has a total angular momentum of \textit{J} = 6. A previous neutron study by Morin \textit{et al.} [10] concluded the crystal field parameters in the Lea, Leask and Wolf (LLW) scheme [5] to be \textit{x} = -0.32
and $W = 1.03$ K giving a CEF ground state as a $\Gamma_5^{(1)}$ triplet separated from the first excited state $\Gamma_3$ by 2.5 meV.

It is the purpose of this chapter to investigate, mainly in the paramagnetic phase, the CEF level scheme. To allow for a more detailed conclusion about the AFQ and AFM ordering, we decided to repeat and further the preceding experiment in order to see possible splitting of the $\Gamma_5^{(1)}$ ground state. In addition to this, to follow the temperature dependence of the low lying crystal field levels near the antiferroquadrupolar transition to see if there are any signatures of the transition in the CEF spectra. Surprisingly, our experiments reveal a level scheme very much different from that proposed by Morin et al. and a significantly reduced overall splitting of the Tm$^{3+}$ CEF states. In further electron paramagnetic resonance, specific heat and magnetisation experiments we obtained support for this interpretation. Also it will be discussed what effect this new level scheme has on the AFQ and AFM transitions. In the following section, we will review crystal field theory mainly in the cubic environment as in the case of TmGa$_3$.

### 2.2 Crystal field theory

Crystal field theory is concerned primarily with the study of the energy level degeneracies of electrons that are localized on the atom, which is situated in a crystalline solid. Crystal field theory is a model for the calculation of the eigenvalues and the matrix elements of transitions between the CEF levels.

The Hamiltonian of a 4f electron, is such that it is a combination of the Hamiltonian of the bound ion, and an electrostatic potential of the surrounding atoms which satisfies the Laplace equation, $\Delta V = 0$.

$$\mathcal{H} = \mathcal{H}_0 + V$$

(2.2.1)
\( \mathcal{V} \) can be expanded in terms of spherical harmonics \( Y^m_l(\theta, \varphi) \)

\[
\mathcal{V}(r) = \sum_l \sum_m A^m_l Y^m_l(\theta, \varphi) r^l
\]  

(2.2.2)

The eigenvalues and eigenfunctions of an electron must belong to the irreducible representations of the group of the symmetry operations of the Hamiltonian, in which the electron finds itself, according to Wigner's theorem [43]. In the case of the free atom (or ion) the symmetry operations are 3-dimensional rotations. However as described above, when the environment in which the ion finds itself is in a crystalline solid, the ion will no longer experience a spherically symmetric potential, but the electrostatic potential which is experienced by the \( 4f \) electrons will have the symmetry of the crystallographic point group. In this way symmetry alone plays an essential role. Group theory allows to predict the remaining degeneracies of the energy levels. The wave function of the electron must belong to one of the irreducible representations of the point group, and thus the degeneracies of the energy levels will depend on the dimension of the irreducible representations.

To determine the irreducible representations by a given basis, we must determine the conjugacy classes, which are described by symmetry operations that are the same in the case of the point group. The character of a representation can be defined by considering one element from each conjugacy class, which is given by

\[
\chi_J(\varphi) = \frac{\sin[(J + 1/2)\varphi]}{\sin(\varphi/2)}
\]  

(2.2.3)

The irreducible representation can occur \( a_{\Gamma_i} \) times given as

\[
a_{\Gamma_i} = \frac{1}{\hbar} \sum_i \chi_R^{*\Gamma_i}(R) \chi_R(R)
\]  

(2.2.4)

For a free \( 4f \) ion, the degenerate ground states would span a \( (2J+1) \) dimensional representation of a symmetry group. This is normally too large to be the dimension of any
Table 2.1: Stevens operator equivalents expressed in terms of angular momentum operators [3].

<table>
<thead>
<tr>
<th>Notation</th>
<th>Operator equivalents</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_0'$</td>
<td>$3J_z^2 - J(J + 1)$</td>
</tr>
<tr>
<td>$O_2'$</td>
<td>$\frac{1}{2}(J^2_z + J^2_z)$</td>
</tr>
<tr>
<td>$O_4'$</td>
<td>$35J_z^2 - (30J(J + 1) - 25)J_z^2 - 6J(J + 1) + 3J_z^2(J + 1)^2$</td>
</tr>
<tr>
<td>$O_6'$</td>
<td>$\frac{1}{3}(J^4_z + J^4_z)$</td>
</tr>
<tr>
<td>$O_8'$</td>
<td>$231J_z^2 - 105(3J(J + 1) - 7)J_z^2 + (105J^2(J + 1)^2 - 525J(J + 1) + 294)J_z^2 - 5J^3(J + 1)^2 + 40J^2(J + 1)^2 - 60J(J + 1)$</td>
</tr>
<tr>
<td>$O_{10}'$</td>
<td>$\frac{1}{4}[(11J_z^2 - J(J + 1) - 38)(J^4_z + J^4_z) + (J^8_z + J^8_z)(11J_z^2 - J(J + 1) - 38)]$</td>
</tr>
<tr>
<td>$O_{12}'$</td>
<td>$\frac{1}{6}(J^4_z + J^4_z)$</td>
</tr>
</tbody>
</table>

irreducible representation of a point group, and the crystal field acts to split the $(2J+1)$ degenerate levels into sublevels.

Using some of the properties of spherical harmonics, it is already possible to limit how $V(r)$ acts within a subspace, because of the addition properties of angular momenta, $l$. For $d$-states the matrix element vanishes for $l > 4$, similarly for $f$ states it is only needed to consider $l \leq 6$. Due to parity, all odd-parity components can also be taken out of the expansion of $V(r)$. Therefore, the only contributions to the expansion of $V(r)$ come from the terms $l = 0, 2, 4, 6$.

In terms of a cubic crystal field, $l = 0, 4, 6$ contribute to the total energy of the crystal. Therefore we can expand $V$ as

$$V = V_0 + V_4 + V_6$$

(2.2.5)

The Hamiltonian in a cubic crystal field environment can be written as

$$H_{CEF} = B_4(O_4' + 5O_4') + B_6(O_6' - 21O_6')$$

(2.2.6)

The so called $O_m'$ are Stevens operator equivalents [44] of the corresponding spherical harmonics which are listed in table 2.1. $B_4$ and $B_6$ are coefficients that scale the crystal
field splitting, and can be shown to be related to \(< r^4 >\) and \(< r^6 >\), the expectation values of \(r^n\) calculated from the radial distribution \(r\) of the 4f wavefunction. \(B_4\) and \(B_6\) are given as

\[
B_4 = \beta A_4 \langle r^4 \rangle \quad (2.2.7)
\]
\[
B_6 = \gamma A_6 \langle r^6 \rangle \quad (2.2.8)
\]

where the radial part of the 4f wavefunction, \(\rho_{4f}(r)\) is used to calculate the expectation of \(r^n\) according to

\[
\langle r^n \rangle = \int_0^\infty |\rho_{4f}(r)|r^{l+\frac{3}{2}}dr
\]

(2.2.9)

The terms \(A_4\langle r^4 \rangle\) and \(A_6\langle r^6 \rangle\) are the fourth and sixth order crystal field parameters given e.g. by [45]. \(\beta\) and \(\gamma\) are reduced matrix elements which are listed for each rare earth element in e.g. [46].

Lea, Leask and Wolf [5] conveniently transformed the \(B_4\) and \(B_6\) parameters into parameters of \(x\) and \(W\) by the following relations to display and tabulate in a convenient form the normalized eigenvectors and eigenvalues acting on a \(J\)-manifold.

\[
B_4 F(4) = W x
\]

(2.2.10)

\[
B_6 F(6) = W (1 - |x|)
\]

(2.2.11)

where \(-1 \leq x \leq 1\) and \(F(4)\) and \(F(6)\) are common factors, which in this way are conveniently separated out of the calculation. Rewriting 2.2.6 in terms of \(x\) and \(W\) yields

\[
\frac{H_{CEF}}{W} = \left[ x \left( \frac{O_4}{F(4)} \right) + (1 - |x|) \left( \frac{O_6}{F(6)} \right) \right]
\]

(2.2.12)

with
If a cubic crystal undergoes a further distortion e.g. to tetragonal symmetry [34, 42] a further term has to be added to the Hamiltonian in 2.2.12:

\[ H_{QP} = B_2^0 O_2^0 + B_2^2 O_2^2 \]  

(2.2.15)

Diagonalization of the Hamiltonian 2.2.12 in the range \(-1 \leq z \leq 1\) gives the eigenvalues and energies belonging to the irreducible representations, \(\Gamma_i\). An example for \(J = 6\) is given below

\[ J = 6 \rightarrow \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5^{(1)} + \Gamma_5^{(2)} \]  

(2.2.16)

The degeneracy of each irreducible representations is: \(\Gamma_1\) and \(\Gamma_2\) are singlets, \(\Gamma_3\) and \(\Gamma_4\) are doublets and \(\Gamma_5^{(1)}\) and \(\Gamma_5^{(2)}\) are triplets. Lea, Leask and Wolf [5] diagonalized the Hamiltonian 2.2.12 for all values of \(z\), with the energy scaled by \(W\), this is shown in fig 2.1 for \(J=6\). The value of \(z = -0.32\), \(W = 1.03\) K that Morin et al. [10] found in TmGa\(_3\) is shown as giving a \(\Gamma_5^{(1)}\) triplet ground state followed by a \(\Gamma_3\) doublet first excited state. The overall splitting of the crystal field levels according to Morin's suggestion would amount to \(\approx 20\) meV.

The most powerful way to obtain the energy level diagram for a \(J\) manifold split by a crystal field is by inelastic neutron spectroscopy. Inelastic neutron spectroscopy is unique in that it probes the eigenvalues of the hamiltonian through the transition energies and the eigenfunctions through the transition intensities. Trammell [6] obtained the neutron cross section. If we limit to small momentum transfers it is then given as [47]
Figure 2.1: Diagonalization of eqn 2.2.12 for the full range of $x$, according to [5].

\[
\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{1.91 e^2}{2mc^2}\right)^2 \frac{k_f}{k_i} f^2(Q) \sum_{nm} \rho_{nm} |\langle n|J_\perp|m\rangle|^2 \delta \left(\frac{E_n - E_m}{\hbar} - \omega\right) \tag{2.2.17}
\]

The effect of increasing the momentum transfer $|\vec{Q}|$ is to decrease the magnetic dipole transition intensities via the form factor $f(Q)$. $k_f$ and $k_i$ are the final and initial state of the neutron. $n$ and $m$ are the states belonging to a given $J$ multiplet. $J_\perp$ is the component of the total angular momentum operator perpendicular to the scattering vector $|\vec{Q}|$. From the $Q$ and temperature dependance the crystal field transitions can be distinguished from phonon excitations which may occur in the same energy range. Phonon peak intensities vary as $Q^2$ whereas crystal field peaks follow $f^2(Q)$. Phonons obey Bose statistics whereas crystal field levels obey Boltzmann statistics.

Birgeneau [6], calculated for integer and half integer $J$ in a cubic crystal field the appropriate matrix elements $|\langle \Gamma_i|J_\perp|\Gamma_j\rangle|^2$ for a transition from crystal field level $\Gamma_j$ to $\Gamma_i$. An
example for $J = 6$ as a function of the LLW parameter $x$ is shown in figure 2.2.

2.3 Crystal growth and structure

TmGa$_3$ crystallises in the AuCu$_3$ type cubic structure with space group $Pm\bar{3}m$. Fig 2.3 shows a unit cell of TmGa$_3$.

The growth of single crystals was facilitated from a Ga flux as described in more detail in [48]. All samples were characterized by X-ray diffraction to make sure that no other phases were present and had the correct AuCu$_3$ structure. In addition, Scanning electron microscopy (SEM) was performed on single crystals of TmGa$_3$ and revealed an atomic percentage of 74.95 for Ga, and 25.05 for Tm, showing unambiguously the high quality of the crystals and powders. A picture of a TmGa$_3$ single crystal can be seen in fig 2.8.

2.4 Specific heat, susceptibility and resistivity

2.4.1 Ordering in TmGa$_3$ shown in the specific heat

Due to the closeness of the antiferroquadrupolar and antiferromagnetic transitions in TmGa$_3$, specific heat measurements is a very approximate method to determine the transitions in zero field accurately. We therefore performed specific heat measurements on our single crystals of TmGa$_3$. In addition, we measured the heat capacity of the isostructural nonmagnetic LuGa$_3$ by the quasiadiabatic heat pulse (Nernst) method as described in the previous chapter. Using our newly built calorimeter we separated for the first time the two transitions in TmGa$_3$ in zero field. Fig 2.4 shows $C_p$ against $T$ in the vicinity of the two transitions. The transitions give a remarkable anomaly in $C_p$ with a peak value which is of the order of 1000 J/moleK. The transitions are just seen to be separated, this reflects a good resolution in temperature of our calorimeter.

Our results show that the transitions occur at a different temperature than what has
Figure 2.2: Transition probability matrix elements as a function of the LLW parameter $x$, for $J = 6$, taken from [6].
been reported in the literature, which is $\text{AFQ} = 4.29 \text{ K}$ and $\text{AFM} = 4.26 \text{ K}$ [34]. Our results indicate that the AFQ transition rather occurs at $4.40 \text{ K}$ and AFM at $4.38 \text{ K}$. Our calorimeter has gone through numerous temperature checks, as described in chapter 1 so we are confident that our temperature calibration is correct for this temperature range. From now on we will quote these transitions happening at $\text{AFQ} = 4.40 \text{ K}$ and $\text{AFM} = 4.38 \text{ K}$.

To estimate the magnetic contribution to the specific heat we performed a subtraction of the heat capacity of LuGa$_3$ by scaling the high temperature ($T \geq 250 \text{ K}$) Debye temperatures of LuGa$_3$ such that this coincides with TmGa$_3$. From the scaled Debye temperature of LuGa$_3$ a lattice reference is calculated using the program ‘Debye model’ listed in appendix A2. This allows us to estimate the lattice and electronic contribution by subtraction from the total $C_p$ of TmGa$_3$ and thus obtain the magnetic contribution including any possible contribution of a Schottky anomaly due to the thermal excitation of the higher CEF levels. The magnetic entropy can then be estimated from eqn 2.4.1.
Figure 2.4: Semi-log plot of $C_p$ against $T$ showing the resolution of the AFQ and AFM transitions in TmGa$_3$ at 0 T. The solid line is a guide to the eye. Insert: A plot showing the the two transitions on a linear scale.

\[ S = \int_0^T \frac{C_p(T)}{T} dT' \]  

(2.4.1)

As shown in the insert of figure 2.5 the entropy contained in each anomaly is approximately $\ln(2)$. The total entropy accumulated up to 40 K, at which the entropy saturates is approximately $3\ln2$. The phase diagram for the [001] crystallographic direction is shown in fig 2.6 and it is taken from [7]. The nature of the two transitions is such that the first transition has a very large re-entrant feature, which goes to a maximum of around 5 K for a maximum field of 5 T along [0 0 1]. Then it decreases in temperature with increasing field. This is displayed in the insert of fig 2.6. The transition is of an antiferroquadrupolar nature, and one of its signatures is a re-entrant phase diagram. The second antiferromagnetic transition decreases in temperature on applying a magnetic field.
Figure 2.5: Plot of the magnetic entropy against temperature for TmGa₃. Insert: entropy released at the AFM and AFQ transitions.

Figure 2.6: Phase diagram for TmGa₃ along [001] near the AFM and AFQ phase transitions. Insert: full phase diagram along [001]. Taken from [7].
2.4.2 Magnetic susceptibility

Magnetic susceptibility measurements were performed from 2 - 330 K using a Quantum Design MPMS SQUID magnetometer [49]. Figure 2.7 shows the susceptibility as a function of temperature for a magnetic field of 0.1 T near the AFQ, AFM transitions showing a drastic upturn of the susceptibility at the transition temperatures. The insert of figure 2.7 shows the temperature dependant susceptibility for the whole measured temperature range. The first transition at 4.4 K is in agreement with the ordering temperature obtained by heat capacity.
2.4.3 Resistivity

Resistivity measurements were performed using a Quantum Design PPMS [50] system using the four point technique. Figure 2.8 shows a picture of the four point technique on two TmGa₃ crystals.

Figure 2.9 shows the resistivity of TmGa₃ for different fields applied along the [001] direction. The transition is seen to be washed out with the application of a stronger field, until at 9 T it is nearly flat. The field dependence of the AFQ transition in the resistivity qualitatively confirms the phase diagram in fig 2.6. The insert of figure 2.9 shows the resistivity up to room temperature. The room temperature resistivity for zero field has a value of $\rho_{rt} \sim 17 \, \mu\text{ohm-cm}$, indicating a good metal and is approximately the value found for Nb metal [51]. Also a hump is seen in the resistivity at about 30 K in zero field. Such a feature was also seen by Z. Kletowski et al. [52] which they assumed was a Kondo type anomaly due to covalent interactions of the crystal field split $4f$ state with conduction
Figure 2.9: Plot of the resistivity of TmGa$_3$ for different fields close to the transition temperature. Insert: full temperature dependance of the resistivity giving a room temperature value of $\rho_{rt} \sim 17 \, \mu$Ohm-cm.

electrons. We also investigated the knee type anomaly. The anomaly quickly disappeared with only a small field, 10 - 50 G. Our conclusion came from a report by Quantum Design [53] about a distorted low level signal readback of A-C signals in the PPMS, in the range of our anomaly in the resistivity. This feature is due to the inconel electrical feedthrough at the bottom of the PPMS sample chamber that the puck interface plugs into. Our conclusion was that this effect was due to the measurement setup of the PPMS rather than an intrinsic property of the sample.
2.5 Deduction of CEF parameters

2.5.1 Electron paramagnetic resonance (EPR) on $\text{Lu}_{1-x}\text{Er}_x\text{Ga}_3$

Searching for the correct crystal field parameters involves determining for the cubic case, two variables, $B_4$ and $B_6$ or $x$, $W$ in the LLW notation. A way to perform a first estimation of these parameters is to perform a scaling, assuming that $A_4$ and $A_6$ do not vary significantly across the rare earth series. In a previous study on $\text{ErGa}_3$ by Murasik et al. [54] the crystal field parameters were deduced from the Schottky anomaly in the specific heat and from an inelastic neutron spectroscopy investigation. A clearly defined Schottky anomaly provided a good basis for the determination of $x$ and $W$ parameters, and the final evaluation from fitting inelastic spectra gave $x_{\text{Er}} = +0.195$ and $W_{\text{Er}} = +0.022$ meV. With the assumption that $A_4^{\text{Er}} \approx A_4^{\text{Tm}}$ and $A_6^{\text{Er}} \approx A_6^{\text{Tm}}$ and by using the appropriate values for $r^4(\text{Tm,Er})$ and $r^6(\text{Tm,Er})$ as given by Freeman and Watson [45] we can estimate $x_{\text{Tm}}$ and $W_{\text{Tm}}$ from the values of $\text{ErGa}_3$. If we convert $x_{\text{Er}}$ and $W_{\text{Er}}$ to the corresponding parameters for Tm we arrive at $x_{\text{Tm}} = -0.382$ and $W_{\text{Tm}} = -0.44$ K. These parameters suggest a CEF which is completely different from that suggested by Morin et al. [10].

EPR (Electron Paramagnetic Resonance) was performed on diluted Er powder samples, in order to obtain the ground state from the resonance position, as well as the energy gap between the ground state and the nearest excited states. Under special conditions it is possible to extract from the linewidth broadening with increasing temperature the energy separation of near lying states. Upon agreement with the results obtained in [54] we can then scale $x$ and $W$ obtained by inelastic neutron spectroscopy of Er to that of Tm. This provides a rough first approximation of the crystal field parameters for $\text{TmGa}_3$.

EPR was performed using a X-band spectrometer on $\text{Er}^{3+}$ in diluted $\text{Lu}_{1-x}\text{Er}_x\text{Ga}_3$ ($x=0.005, 0.01, 0.03$) powder samples. EPR is a very sensitive technique (an introduction to the EPR technique is shown in a later chapter), so a diluted sample can be used with
the advantage that in general, with dilution, the linewidth decreases due to the reduced magnetic interaction. A magnetically diluted sample minimizes exchange effects that result between coupled Er ions, as the sample is so dilute in Er, this effect is in principle zero. There may be clusters of Er ions, but in a first approximation this is taken as negligible and merely adds to the broadening of the resonance signal. Spectra were taken at low temperatures as to populate the ground state, and with increasing temperature populate also excited CEF states. By studying the relaxation processes via the excited states we can extract information about the nature of the excited state and the energy gap to the ground state.

An example spectrum for a sample of Lu_{0.95}Er_{0.05}Ga_3 at 5 K is shown in fig 2.10. The spectrum was fitted to a Lorentzian line including absorption and dispersion signals and also included the effect of hyperfine splitting. In metallic samples the EPR line is a combination of an absorption and a dispersion signal. As a consequence the EPR line of a metal is asymmetric. EPR with the standard effect modulation technique (100 kHz in our spectrometer) measures the first derivative with respect to the external field. An EPR resonance signal of a metal can in general rather well approximated by

$$\frac{dI}{dH} = \frac{V}{\Delta H} \left( \frac{-2x + \alpha(1-x^2)}{(1+x^2)^2} \right)$$

(2.5.1)

where $\alpha$ is the dispersion, $x$ is given by

$$x = \frac{H - H_{res}}{\Delta H}$$

(2.5.2)

The $g$ factor of this given field is the calculated by $g\mu_B H = h\nu$ or,

$$g = \frac{0.71449 \times \nu[\text{MHz}]}{H_{res}[\text{G}]}$$

(2.5.3)

The raw data in fig 2.10 shows deviations from a single Lorentzian line. This comes
from the hyperfine splitting which is caused by the dipole interaction between the nuclear spin moment and a magnetic field i.e. Zeeman splitting. In the case of natural Er this is a mixture of different isotopes as shown in table 2.2. Only the isotope $^{167}$Er has a non-zero nuclear spin of 7/2, this means that in the ESR measurement it may be possible to see the $(2I+1)$ hyperfine lines. In fig 2.10 we have taken into account the effect of the hyperfine lines and calculated the resonance positions of the hyperfine satellites with the 'Breit-Rabi' formula [55]:

$$H_{res} = H_0 - A m_I \left( 1 + \frac{A^2}{2H_0} \right)^2 \frac{1}{2H_0} \left( I(I + 1) - m_I^2 \right)$$  (2.5.4)

where, $H_0$ is the resonance field strength with $I = 0$, $m_I$ is the magnetic moment quantum number representing the $z$ component of $I$ and $A$ is the hyperfine constant which was fitted to $A^{(167}\text{Er}) = 72 \pm 1$ Oe. The hyperfine constant may vary as well and depend on...
Table 2.2: Isotopes of natural Er.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Abundance (%)</th>
<th>Nuclear spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{162}$Er</td>
<td>0.14</td>
<td>0</td>
</tr>
<tr>
<td>$^{164}$Er</td>
<td>1.61</td>
<td>0</td>
</tr>
<tr>
<td>$^{166}$Er</td>
<td>33.61</td>
<td>0</td>
</tr>
<tr>
<td>$^{167}$Er</td>
<td>22.93</td>
<td>$7/2$</td>
</tr>
<tr>
<td>$^{168}$Er</td>
<td>26.78</td>
<td>0</td>
</tr>
<tr>
<td>$^{170}$Er</td>
<td>14.93</td>
<td>0</td>
</tr>
</tbody>
</table>

the particular host. Since we could not resolve the hyperfine satellites, fitting the hyperfine constant did not converge to reasonable parameters for $A^{(167)}$Er. We therefore fixed $A^{(167)}$Er to a value which has been observed in other metallic phases [56].

Given the fitted resonance field ($I = 0$), represents $g = 6.803$, which indicates a $\Gamma_7$ ground state as found by Murasik et al. [54]. To obtain information about the excited states and the energy gap, the linewidth as a function of temperature is given by

$$\Delta H = a_0 + a_1 T + \frac{a_2}{\exp(\Delta/k_B T) - 1}$$  \hspace{1cm} (2.5.5)

The linewidth of the fitted Lorentzian as a function of temperature was fitted for Er dopings of 1 and 3%. The corresponding fit according to 2.5.5 gives the first excited state at 3.0(5) meV away from the ground state and a Korringa relaxation rate of 30 G/K. All the results from our EPR investigation on doped Er samples support the findings obtained by Murasik et al. [54] by inelastic neutron scattering and heat capacity measurements.

Using these results from Murasik et al. [54] for ErGa3, we can then scale the $x$ and $W$ parameters to that of TmGa3 using the following relations
Figure 2.11: Linewidth as a function of temperature for 1 and 3\% doped Er samples. Solid red line is a fit as described in the text \((x \Gamma / (\exp(35K / \Gamma) - 1))\). Open circles, triangles and squares are the collected data.

\[
Wx = B_4 = A_4 \langle r^4 \rangle \beta_f \tag{2.5.6}
\]

\[
W(1 - |x|) = B_6 = A_6 \langle r^6 \rangle \gamma_f \tag{2.5.7}
\]

Using the assumption that \(A_4\) and \(A_6\) do not vary significantly from Er to Tm. From this procedure we arrive at \(x_{Tm} = -0.382\) and \(W_{Tm} = -0.44\) K. We would then expect \(x, W\) for TmGa$_3$ to be negative and approximately in this range given above. The assumption that \(x\) and \(W\) should be negative already contradicts the results of Morin et al. [10]. Therefore, to test the level scheme for TmGa$_3$ further we performed inelastic neutron investigations which are discussed in the next section.
2.5.2 Inelastic Neutron spectroscopy

Experiments on the spectrometer IN4 (ILL)

First, neutron crystal field spectroscopy was performed on the thermal neutron time-of-flight spectrometer IN4 at the ILL, Grenoble, France, which works in the thermal neutron energy range 10-100 meV. A suitable energy is selected from the thermal spectrum with a crystal monochromator. An outline of the experimental set up is shown in fig 2.12. Experimental data on IN4 was taken with a powder sample of Ti$_3$Ga$_3$ at 5, 10, 30, 50, 100K at a wavelength of 3.4 Å.

With reference to the previous report on the crystal field excitations, as large an excitation of 17 meV was expected. Using IN4 we discovered that all transitions above 4 meV are not due to crystal field transitions, but arise from phonon excitations (see fig 2.13 for the high energy transfer spectra). This was achieved by studying the Q dependance for all transitions. Indeed, there is no thermal effect seen on the high energy transfer excitations, $\Delta E \geq 10$ meV which we would expect if they arise due to crystal field excitations. We
saw one broad excitation centered at 2.5 meV that was due to a crystal field transition and also one at around 0.5 meV. Due to the limited resolution of IN4 at low energy transfer, it was not possible to fully resolve the low energy excitations. Searching with $\Delta E \geq 5$ meV did not produce any evidence for further crystal field excitations. Therefore, we were led to conclude that all CEF excited states are bunched together in an energy regime $E \leq 3$ meV. This conclusion was supported by the extrapolation from the results obtained for ErGa$_3$ and Lu$_{0.9}$Er$_{0.1}$Ga$_3$. In addition as shown by fig 2.14 we performed inelastic neutron scattering on ErGa$_3$ in which we saw evidence for a CEF excitation at 10 meV in agreement with the earlier work of Murasik [54]. In addition as concluded from the work of Murasik all excitations above 10 meV are due to phonon excitations in correspondence with our measurements and conclusions on TmGa$_3$.

Using the results from the EPR experiment, and scaling to that of TmGa$_3$, provides us with a preliminary set of starting values of our $x$ and $W$ parameter search. Using the IN4 data a least square fitting procedure was carried out on the 5 and 10 K spectra. Although the 0.3 meV excitation is not clearly resolved, the relative intensities of the peaks at 0.3 meV and 2.5 meV enable us to get a first set of parameters. The program Mcphase [57] was used to calculate the intensities and energies of the allowed transitions for a set temperature and $x$ and $W$ values. An additional program was written to fit the spectra using a wide range of $x$ and $W$, using Gaussian lineshapes for the excitations. We also included an elastic peak, because of the closeness of the 0.3 meV peak to the elastic peak.

Given an $x$ and $W$ we could fit the spectra using the intensities and energies given by a program cfield in Mcphase. The program gives the total intensity in (barn/ion) for a set temperature and $x$ and $W$ according to equation 2.5.8

$$I_{E_n \rightarrow E_m} = 4\pi \left( \frac{\hbar^2 e^2}{mc^2} \right)^2 \sum_n \exp\left(\frac{E_n}{k_BT}\right) \times \frac{2}{3} \sum \left| n \left| J \right| m \right|^2$$

(2.5.8)

An example input file is given in appendix B1 and an example output file listing the
Figure 2.13: IN4 spectra for TmGa$_3$ at 1.1 Å for three different temperatures 3 K, 10 K and 20 K. All transitions above 10 meV have been identified as phonon excitations.

Figure 2.14: IN4 spectra for ErGa$_3$ at 1.1 Å at 10 K and whilst cooling the sample from room temperature.
Table 2.3: Transition probabilities according to equation 2.5.8 for \( x = -0.44 \) and \( W = -0.22 \) K of the crystal field states of Tm\(^{3+}\) in TmGa\(_3\). transitions and intensities is given in appendix B2. An example of the transition intensities for the most intense excitations for \( x = -0.44 \) and \( W = -0.22 \) K is shown in Table 2.3.

The best approximation was obtained for \( x = -0.42 \) and \( W = -0.222 \) K, this is shown in figure 2.15. The elastic peak at approximately zero energy transfer, is the most distinct feature, as well as the excitations at \( \approx 2.5 \) meV. The observed accuracy was estimated by allowing small variations to these values, and to see the effect on peak positions and relative intensities. In this way we fitted every peak that has a non zero probability regardless of the magnitude of the relative probability, so that every possible transition was accounted for, even when \( \Gamma_n = \Gamma_m \). Only in this way is it certain that correct parameters can be taken from such a small energy range, and with so many different transition probabilities being so similar.

<table>
<thead>
<tr>
<th>( \Gamma_n \rightarrow \Gamma_m )</th>
<th>( \Delta E ) (meV)</th>
<th>5K</th>
<th>10K</th>
<th>15K</th>
<th>20K</th>
<th>30K</th>
<th>50K</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_2 \rightarrow \Gamma_2^{2} )</td>
<td>0.4</td>
<td>7.14</td>
<td>5.07</td>
<td>4.30</td>
<td>3.86</td>
<td>3.37</td>
<td>2.94</td>
</tr>
<tr>
<td>( \Gamma_1 \rightarrow \Gamma_4 )</td>
<td>0.34</td>
<td>6.75</td>
<td>5.37</td>
<td>4.73</td>
<td>4.33</td>
<td>3.85</td>
<td>3.41</td>
</tr>
<tr>
<td>( \Gamma_2^{2} \rightarrow \Gamma_2 )</td>
<td>-0.4</td>
<td>2.85</td>
<td>3.20</td>
<td>3.17</td>
<td>3.07</td>
<td>2.89</td>
<td>2.68</td>
</tr>
<tr>
<td>( \Gamma_4 \rightarrow \Gamma_1 )</td>
<td>-0.34</td>
<td>3.08</td>
<td>3.63</td>
<td>3.64</td>
<td>3.56</td>
<td>3.38</td>
<td>3.15</td>
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<tr>
<td>( \Gamma_2^{2} \rightarrow \Gamma_3 )</td>
<td>2.41</td>
<td>1.35</td>
<td>1.52</td>
<td>1.50</td>
<td>1.46</td>
<td>1.37</td>
<td>1.27</td>
</tr>
<tr>
<td>( \Gamma_2^{2} \rightarrow \Gamma_5^{1} )</td>
<td>2.63</td>
<td>0.79</td>
<td>0.88</td>
<td>0.87</td>
<td>0.85</td>
<td>0.80</td>
<td>0.74</td>
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<tr>
<td>( \Gamma_4 \rightarrow \Gamma_3 )</td>
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<td>0.52</td>
<td>0.52</td>
<td>0.51</td>
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<td>( \Gamma_4 \rightarrow \Gamma_5^{1} )</td>
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<td>1.07</td>
<td>1.08</td>
<td>1.05</td>
<td>1.00</td>
<td>0.93</td>
</tr>
<tr>
<td>( \Gamma_2 \rightarrow \Gamma_5^{1} )</td>
<td>3.03</td>
<td>1.34</td>
<td>0.95</td>
<td>0.8</td>
<td>0.72</td>
<td>0.63</td>
<td>0.55</td>
</tr>
</tbody>
</table>
Figure 2.15: IN4 spectra of the scattering cross section for various energy transfers at 3.4 Å. Solid line is a fit as described in the text. Open circles are the measured data. Insert: excitations at ≈ 2.5 meV.
Figure 2.16: Experimental setup of IN6 at the ILL [9].

Experiments on the spectrometer IN6 (ILL)

Further measurements on the cold neutron time-focussing time-of-flight spectrometer IN6 also at the ILL, Grenoble, provides quasielastic and inelastic scattering for incident wavelengths in the range of 4 to 6 Å. The monochromator can deliver four wavelengths: 4.1, 4.6, 5.1, and 5.9 Å. The second order reflection from the graphite monochromator is removed by a beryllium-filter cooled to liquid nitrogen temperature. The elastic energy resolution at 4.1 Å is 170 μeV and at 5.9 Å, 50 μeV. An outline of the set up is given by fig 2.16. Measurements on IN6 with TmGa3 at wavelengths of 4.1 and 5.1 Å were taken at 5, 10, 15, 20, 30 and 50 K.

Further experiments on IN6 enabled us to fully resolve the excitations at ≈ 0.3 meV which are clearly seen in both energy loss and gain. Further excitations at 2.5 meV were also seen on both sides of the elastic peak. Upon raising the temperature the effect of thermally populating higher CEF levels gives the effect of lowering the transition probability of excitations from the lower levels to the higher levels and this was observed in all spectra.
Figure 2.17: Semi-log plot of the IN6 spectra taken at 5, 10, 15, 20, 30 and 50 K for TmGaO. Solid red line represents the fit as described in the text. Green lines are the individual lorentzian profiles. Open circles are the experimental data.

Fitting the IN6 spectra was done using Lorentzian profiles as this was found to fit the spectra much better than Gaussians. Using the intensities and energies from McPhase we fitted the elastic line to a Lorentzian with 3 parameters, and then one Lorentzian for each of the -0.4 and 0.4 meV peaks, and one for the 2.5 and 2.6 meV transitions. The fits for all temperatures taken on IN6 are shown in fig 2.17. Due to the existence of many transitions very close to each other (see table 2.3) the peaks at 2.37 and 2.41 meV were merged into one Lorentzian, and also the peaks at 2.59 and 2.61 meV and ±(0.34 and 0.40 meV). In addition, the transition at 3.03 meV was increasingly intense at lower temperatures (see table 2.3) and this was included into the fit at 5 and 10 K. It should be noted that all plots in fig 2.17 are semi-log plots, which due to CEF transitions near to the elastic line, were necessary in order to see the full spectrum in a clear way. This shows in more details the closeness of the fit at the transition energies and also highlights the parts of the spectrum which are not in close agreement with the fit.
Figure 2.18: IN6 spectrum of TmGa3 at 50 K. Crystal field transitions are shown for $x = -0.44$ and $W = -0.222$ K for the low energy excitations only. Insert: 2.5 meV peak shown to consist of 4 transitions. Red line is the fit from fixing the intensities and transition energies from the program cfield.
Further analysis of the transitions shows that at high temperatures, 30 K and 50 K, the agreement with the fit profiles and the measurement is always close even on a log scale. At lower temperatures it became increasingly difficult to fit the energy part between the transitions at 0.3 meV and 2.5 meV. One can see at 20 K the agreement with the data and fit is good for the position of the transition energies and around, but for the part of the spectrum 1 meV ≤ E ≤ 1.5 meV there is a gap between the fit and data and this persists from 20 K to 5 K. The reason for this discrepancy may be due to a quasielastic contribution which one would expect to decrease with increasing temperature. This could explain why it disappears above 30 K. A quasielastic line was not included in the fits due to the requirement to include an elastic line in the fitting procedure. Also at this low energy transfer, there could be possible broadening due to magnetic dispersion.

The 50 K spectrum and fit is shown in more detail in fig 2.18. The transition positions are shown as according to table 2.3. The overall level scheme is bunched together in a very small energy range, with small transition energies between levels. The final level scheme is shown in fig 2.19. The most intense transitions (Γn ≠ Γm) are shown for energy gain and loss. The comparison with the former level scheme is shown, which highlights the different energy scale of the crystal field splitting from the previous estimate.

**Experiments on the spectrometer IN12 (ILL)**

To resolve the first CEF excitation at around 0.3 meV additional measurements on the cold neutron three-axis spectrometer IN12 at the ILL with a diluted Tm0.1Lu0.9Ga3 sample were performed. The experimental outline of IN12 is shown in fig 2.20.

Measurements on IN12 on the diluted Tm sample Tm0.1Lu0.9Ga3, provides us with the single ion properties of Tm. Dilution reduces magnetic interaction and reduces line broadening due to possible dispersion in the CEF levels that could be evident in the IN6 spectra. Heat capacity measurements shown in fig 2.21 indicate no magnetic or quadrupole
Figure 2.19: Level scheme proposed by Morin et al. [10] (left). New level scheme (right), note that the ground state ($\Gamma_2$) has been shifted down to -0.3 meV so to be clearly seen from the $\Gamma_1$ which is only 0.09 meV away. Solid arrows represent energy gain transfer, dash dot arrows energy loss. Only the most intense transitions have been shown for $\Gamma_n \neq \Gamma_m$. 

\[
x = -0.32 \\
W = 1.03K
\]

\[
x = -0.44 \\
W = -0.222K
\]
order down to 1.7 K in Tm_{0.1}Lu_{0.9}Ga_3. A difference between Tm_{0.1}Lu_{0.9}Ga_3 and LuGa_3 at $T < 10$ K is seen due to a Schottky anomaly emerging from the CEF excitations.

The spectrum at 2 K is shown in fig 2.22 as a semi-log plot with a fit of three gaussian profiles. The transitions at $E \sim \pm 0.3$ meV can be clearly resolved and they are well separated from the elastic peak. The insert of fig 2.22 shows the full spectrum at 2 K. The transition at 2.5 meV is also seen but seems to be as broad as in the case of the time of flight (TOF) data. Additionally, which is not seen in all other data on IN4 and IN6, is a small peak at 1 meV. Data taken on IN12 at 10 K also showed the same features as that of 2 K, including the peak at 1 meV. We propose that this extra feature comes from a splitting of the $\Gamma_5^{(2)}$ third excited state, which may be caused by some slight distortion from cubic symmetry. This slight deviation may arise from the substitution of Lu on most of the Tm sites and the difference in atomic radii. Such a splitting could also describe some of the features of the 2.5 meV transition which is very broad. This could arise from the new degenerate levels caused by the splitting of the $\Gamma_5^{(2)}$ triplet to higher excited states. By observing the relative

Figure 2.20: Experimental setup of IN12 at the ILL [11].
Figure 2.21: Heat capacity for $\text{Tm}_{0.1}\text{Lu}_{0.9}\text{Ga}_3$ (closed squares) and $\text{LuGa}_3$ (open circles). Insert: difference between the heat capacity of $\text{Tm}_{0.1}\text{Lu}_{0.9}\text{Ga}_3$ to that of $\text{LuGa}_3$.

Intensities and also positions, we find slight deviations in $x$ and $W$ from the pure $\text{TmGa}_3$ case, which can be expected. The best fit values are obtained for $x = -0.44$, $W = -0.17\,\text{K}$, which give the same level scheme as before, but with a slightly modified energy scale.

2.6 Testing the CEF parameters with specific heat, susceptibility and magnetisation

To test the derived CEF level scheme heat capacity measurements on $\text{TmGa}_3$ were carried out and compared with the heat capacity of the non magnetic isotropic compound $\text{LuGa}_3$ (see fig 2.23 for the superconducting transition at $T_c = 2.45 \pm 0.02\,\text{K}$ in slight disagreement with reported literature values of $T_c = 2.3 \pm 0.1\,\text{K}$ [58]). The heat capacity of $\text{LuGa}_3$ can be taken as an adequate representation for the phonon contribution to the heat capacity.
Figure 2.22: Semi-log plot of the IN12 data for Tm$_{0.1}$Lu$_{0.9}$Ga$_3$ at 2 K. Open black circles are the data points, solid line represents the fit as described in the text. Insert: full IN12 spectrum from -0.6 meV to 3.5 meV.

Figure 2.23: Superconducting transition of LuGa$_3$ at 2.45 ± 0.02 K. Open circles represent the data.
(lattice reference). The maximum of the Schottky anomaly in TmGa₃ is very near to the ordering temperature, and thus is not clearly defined. Using the results of the neutron spectroscopy we calculated the resulting Schottky specific heat from the CEF energy levels. Experimentally, we performed heat capacity measurements on TmGa₃ and LuGa₃ from 2 K - 250 K. By scaling and matching at high temperature (scaling factor 0.97) and then subtracting the isostructural LuGa₃ gives the magnetic contribution containing the Schottky anomaly and the first order transitions. Fig 2.24 shows $C_p$ against $T$ in the range of 6 K to 40 K, therefore being just above the AFQ and AFM transitions, meaning that the initial slope of the anomaly is smeared out by the oncoming transitions at 4.3 K. Although the $T^2$ dependance of the Schottky anomaly is not clearly defined, the peak is seen at 11 K. Our calculations also show the peak clearly defined at 11 K and the corresponding decay after the peak. In addition, the anomaly as calculated using the results of Morin also give a peak at around 10 K, but also an additional contribution centered at 32 K which is not confirmed by our data.

Calculation of the temperature dependant susceptibility is also a method of determining or testing the crystal field parameters. Fig 2.25 shows a semi-log plot of the inverse susceptibility in the range of 2 K to 200 K. The susceptibility calculated from the crystal field parameters as obtained by inelastic neutron spectroscopy agree well with the experimental data above the transition temperatures. The difference with the results using the previous values of $x$ and $W$ from Morin et al. [7] further confirm the agreement with experiments using the new values obtained by our neutron scattering study.

The magnetisation in the various crystallographic directions was also calculated in the paramagnetic phase to check for consistencies in the proposed CEF model. We checked the calculations against results obtained by Morin et al. [7] for the [001] and [110] directions. These are shown in fig 2.26 and 2.27. The calculation of the specific heat and susceptibility was done using the mean field Monte Carlo program implemented in McPhase [57].
Figure 2.24: Schottky anomaly in the specific heat after subtraction of the isostructural LuGa$_3$. Open circles represent the data. Solid black line the calculation using the new crystal field parameters. Dashed line calculation with the parameters of Morin et al. [7].

Figure 2.25: Semi-log plot of the temperature dependence of the inverse susceptibility of TmGa$_3$. Open circles represent the data. Solid black line the calculation using the new crystal field parameters. Dashed line calculation with the parameters of Morin et al. [7].
Figure 2.26: Magnetisation at 10 K for TmGa$_3$ along [001]. Data taken from Morin et al. [7].

Figure 2.27: Magnetisation at 10 K for TmGa$_3$ along [110]. Data taken from Morin et al. [7].
2.7 Discussion and further work

We have obtained a new set of crystal field parameters from inelastic neutron scattering which are in stark contrast to those given by Morin and used as a basis for the interpolation of the AFQ order parameter in TmGa₃. When the new CEF parameters are used to calculate thermodynamic properties they agree well when compared to experimental data. We have shown that the previous study by Morin et al. which gave $x = -0.32$ and $W = 1.03$ K does not agree with our new values and indeed when compared to experimental data, is in stark disagreement. As the 13 crystal field levels in TmGa₃ are very close to each other and bunched to an energy range $E < 3$ meV, there exist no excitations above 4 meV. To resolve such a level scheme by neutron scattering is difficult. To trust that we have the correct parameter set, we have performed a number of further tests. First testing the assumption of Murasik et al. [54] for the CEF parameters of ErGa₃, by EPR measurement on doped Er samples. We have confirmed that for Er³⁺ in LuGa₃ the ground state is a $\Gamma_7$ doublet and the level scheme by Murasik appears to be correct. We have then scaled these values to provide an approximation of where in the parameter space the correct values of $x$ and $W$ for TmGa₃ could be. As neutron spectroscopy is the best means to determine such parameters, we have fitted numerous spectra and reached $x$, $W$ parameters that best fit all spectra. These values were taken to calculate thermodynamic properties, such as the Schottky anomaly in the specific heat and the temperature dependant susceptibility as well as the magnetisation in several crystallographic directions. The agreement with the values obtained by inelastic neutron spectroscopy and the thermodynamic properties enable us to conclude that we have obtained the correct parameter set. One may speculate whether other compounds showing an AFQ transition like TmCd and TmZn, also have a different level scheme to the ones proposed in the literature [37], as indeed the level scheme for TmGa₃ was proposed to be the same as that of TmCd and TmZn. Therefore,
there is a possibility that due to the limited spectra collected for TmCd and TmZn the results given are not correct. Based on these results, order parameters were calculated and fitted to experimental behaviour [59]. Although the transition at low temperature gives the indication that they are due to antiferroquadrupolar and antiferromagnetic ordering. The role of the ordering in TmGa$_3$ is given by a transition induced mixing of CEF levels, due to the small energy range of the whole CEF level scheme. The results that I presented here can then be used for further measurements in the ordered phase to understand the complex and interesting competition between orbital and magnetic ordering in this compound and also other compounds such as TmCd and TmZn which could be revisited. Due to the fact that all CEF are bunched together into an energy interval $E \leq 3$ meV, we could not resolve any effect which points to quadrupolar splitting of the CEF levels.
Chapter 3

One dimensional $S = 1/2$ frustrated antiferromagnetic quantum chain compounds

3.1 Introduction to low dimensional magnetism

One dimensional magnetism originated in 1925, when Ernst Ising first investigated a one-dimensional model of magnetism [60]. He studied a model which is now known as the model of a one-dimensional Ising chain. He assumed ferromagnetic nearest neighbour interactions between magnetic moments which can either point up or down and had to conclude, somewhat disappointedly, that long range order disappeared at any finite positive temperature. In 1931 a major step in the theoretical understanding of a chain system came from Bethe [61], which is now known as the Bethe ansatz. The Bethe ansatz provides a method to obtain the exact quantum mechanical ground state of the antiferromagnetic Heisenberg model, which was proposed by Heisenberg [62] in 1928. The interest in this field was rather that there was an exact solution of the eigenfunctions and energies of the model, rather than any novel behaviour being found. Indeed, the model was first found to be more useful as a stepping stone to more difficult 3D models, rather than any interest in itself. Today, 1D magnetism is one of the most active areas in research, both in theory and experiment.
Figure 3.1: Different magnetic models in 1D and for $S = 1/2$. $a$ is the Ising model and $b$ is the planar $xy$ model. $c$ and $d$ are the antiferromagnetic and ferromagnetic Heisenberg models respectively. Taken from [12].

Experimentally, it was not until the mid of the 1960's that any interest in the field of 1D magnetism was initiated, mainly due to the invention of novel synthesis methods or the discovery of natural compounds which show 1D characteristics. For a review of the early experimental work see e.g. L. J. De Lough and A. R. Miedema [12]. A magnet with restricted dimensions can be realized in bulk, if the exchange interactions which leads to magnetic coupling are much stronger in 1 or 2 spatial dimensions. Therefore, the experimental realization of bulk materials with 1D magnetic characteristics means that their properties can be probed and compared to theoretical results.

The general Hamiltonian assuming nearest neighbour exchange between spins $S_i$ and $S_j$ is
\[ H = -2 \sum_i J_{ij} \left( a S_i^x S_j^x + b (S_i^y S_j^y + S_i^z S_j^z) \right) \]  \hspace{1cm} (3.1.1)

The summation in this case is taken only over nearest neighbour spins. \( J_{ij} \) represents the nearest neighbour exchange constant. Obtaining different models of magnetism is given by changing the values of \( a \) and \( b \). For the isotropic Heisenberg model, we would set \( a = b = 1 \). The Ising model results when \( a = 1 \) and \( b = 0 \). Another limiting case is when \( a = 0 \) and \( b = 1 \), this provides the XY model, or planar Heisenberg model. These models give certain degrees of freedom to the spins, and where they can point spatially, in the classical sense. For example, Heisenberg spins can point anywhere in 3 dimensional space and the exchange energy depends only on the angle they enclose with respect to each other. For Ising spins, they are restricted to either pointing up or down. For XY or planar spins they are confined to lie in the \( xy \) plane. Figure 3.1 shows the heat capacity as a function of reduced temperature for the three different models in one dimension and with spin 1/2.

As well as the magnetic dimensionality, one may also choose the lattice dimensionality. In real materials, we may say that the magnetic interaction, if limited to within a cluster, represents \( d = 0 \). For exchange preferentially along one lattice direction, \( d = 1 \), and within a plane \( d = 2 \). It is shown that the dimension of the magnetic lattice has a profound effect on thermodynamic quantities of all spin models. The interest in this, is the clear breakdown of mean field theory, which can not predict the behavior of low dimensional systems. A clear indication of this is seen in fig 3.2. Here the Heisenberg model for spin 1/2 is shown for different lattice dimensions and the expectation within mean field theory.

The breakdown of the mean field model, means that studying the correlations between a spin and its neighbour must be taken into account. Fisher [63] considered the static pair correlation function \( \Gamma_r(T) \)
Figure 3.2: Lattice dimensionality effects on the heat capacity of the Heisenberg model. For \( d = 1, 2, 3 \) and the mean field (MF) approximation. Taken from [12].

\[
\Gamma_r(T) = \frac{\langle S_0^z S_r^z \rangle}{\frac{1}{2} S(S + 1)}
\]  

The denominator of eqn 3.1.2 is a normalization factor. From this expression thermodynamic quantities can be related to \( \Gamma_r \) for a general magnetic model. The temperature dependence of the magnetic energy of a system with nearest neighbour interactions can be expressed as

\[
U_m(T) = -N_0 z |J| \langle S_0^z S_1^z \rangle
\]

\( N_0 \) is the number of spins, \( z \) is the number of nearest neighbours and \( J \) is the exchange constant. The heat capacity is then given by the derivative of \( U_m \) with respect to temperature. The magnetic susceptibility according to the fluctuation theorem of statistical mechanics is given in terms of the correlation function by
\[ \chi = \frac{C}{T} \left( 1 + \sum_{r 
eq 0} \Gamma_r(T) \right) \]  

(3.1.4)

where \( C \) is the Curie constant. For a paramagnetic system, \( \Gamma_r \)'s \( \rightarrow 0 \), giving just the famous Curie's law. For an antiferromagnet, the sign of the summation alternates. It was given by Fisher that equation 3.1.4 can be represented by

\[ \chi \approx \frac{C}{T} (1 - |U_m(T)|) \]  

(3.1.5)

Figure 3.3 shows the effect of equation 3.1.2, 3.1.3 and 3.1.5 as a function of reduced temperature. In Fig 3.3a, the correlation function is plotted as a function of reduced temperature, the solid lines represent \( \Gamma_\infty \) and \( \Gamma_1 \). \( \Gamma_\infty \) is an infinite range correlation which corresponds to long range order. The dotted line represents an intermediate value of \( r \) which is intermediate between the two solid lines. In Fig 3.3b the dashed line represents the MF result, in which \( \Gamma_\infty \sim M_r^2 \sim U_m \). The solid line is for \( U_m \approx -|\Gamma_1| \). Fig 3.3c shows the temperature dependence of the heat capacity, the MF result is shown as the broken line. Fig 3.3d shows the antiferromagnetic susceptibility.

The important difference between the mean field approximation and the pair correlation function approach is that the former does not account for short range correlations, which shows up e.g. in the heat capacity before the transition to long range order takes place (see Fig 3.3c). So that in reduced dimensionality systems, the effect of short range interactions which act to remove an essential fraction of the entropy, are more and more important. All the magnetic models in one dimension never have long range order at a non-zero temperature, (see e.g. Mermin and Wagner [64]) and the entropy is then removed by short range order by a maximum in the specific heat or susceptibility. In all real one dimensional materials, however, long range (3D) order arises due to interchain coupling. So that in reality, a material will show a broad short range maximum in the susceptibility.
Figure 3.3: (a) Correlation function according to eqn 3.1.2. (b) magnetic energy from eqn 3.1.3: broken curve represents $\Gamma_{\infty}$, solid curve: $U_m = -|\Gamma_1|$. (c) specific heat: broken curve is the mean field result. (d) susceptibility according to eqn 3.1.5. Taken from [12], after Fisher [13].

and heat capacity at some temperature which is greater than the 3D ordering temperature. The rest of this chapter will be concerned with the discussion of one dimensional spin 1/2 Heisenberg magnets.

The interest in one dimensional magnetism developed into a field of its own, generally due to the possibility of the exact solution of the Hamiltonian in 3.1.1 and also because of the rich variety of ground and excited states of quantum models. Due to compounds that have magnetic ions with a low spin i.e. Cu$^{2+}$, 3d$^{9}$, $S = 1/2$, the interplay between quantum fluctuations and thermal fluctuations becomes more important. Theoretically, the field is very broad even when restricted to the one dimensional Heisenberg model. The exact solution provided by the Bethe ansatz, and the rapid development in Quantum Monte Carlo (QMC) simulations enable interesting Hamiltonians to be studied which will be explained more fully in the next sections.
3.1.1 Examples of low dimensional compounds

The first compound to be experimentally verified to be a low dimensional magnet was CuCl$_2$·2NC$_5$H$_5$ (CPC) [65] which long range orders at 1.13 K, with a broad short range maximum in the susceptibility at 17.5 K. (CH$_3$)$_4$NMnCl$_3$ (TMMC) [66] was one of the first 1D compounds to be investigated by neutron scattering. Today there exists an increasing number of verified one dimensional chain systems. To find new one dimensional systems, first one has to search for compounds with very anisotropic chemical bonding properties. In a second step, testing the magnetic susceptibility and the magnetic contribution to the heat capacity. If both quantities show typical features and long range ordering appears at significantly lower temperatures, one may have a good realization of a one dimensional magnetic system. In a further step, detailed comparisons with theoretical predictions are necessary to reveal the special character of the magnetism. Magnetic long range order is primarily due to interchain interactions, i.e. interactions to other neighbouring chains. Schulz [67], using a mean field approximation provided a relation between inter- ($J_\perp$) and intra- ($J$) chain interactions given as

$$|J_\perp| = \frac{T_N}{4A \sqrt{A \cdot J/T_N}} \quad (3.1.6)$$

where $A = 0.32$ and $A = 5.8$ are numerical constants. Using this relation, from the antiferromagnetic ordering ($T_N$) and the exchange integral ($J$) one can obtain an estimation of the interchain interactions, $J_\perp$.

At low temperatures, the ground state of a one dimensional spin chain compound can be antiferromagnetic or a spin-Peierls ground state. The antiferromagnetic state is most common and comes from interchain coupling, so that most compounds exhibit long range order at a finite temperature. Some compounds may also undergo a transition to a spin-Peierls state, which is a consequence of a structural dimerisation leading to a gap opening.
in the magnetic excitation spectrum. The first inorganic material to exhibit this behaviour was CuGeO$_3$ [68]. This material is driven to a spin-Peierls state at 14 K. KCuF$_3$ is another good realization of a spin 1/2 Heisenberg antiferromagnet, although it has a relatively high transition to 3D order of $T_N = 39$ K. The exchange integral is quite large and of the order of 200 K [68].

3.1.2 Cuprate based magnetism and the realization of frustration in one dimension

Due to the discovery of high $T_c$ cuprate superconductors, where it is commonly thought that the cuprate 2-dimensional layers (CuO$_4$) carry the superconductivity, the interest in low dimensional magnetism has rapidly grown in the last two decades. There are two basic building blocks in cuprates. When the copper oxide squares are corner sharing, which gives a Cu-O-Cu bond of $\approx 180^\circ$, such bonds give rise to very large exchange integrals of the order of 100 meV as found in undoped high temperature superconductors. A second case results when the copper oxide squares are edge sharing, this leads to a Cu-O-Cu bond enclosing an angle of $\sim 90^\circ$. This gives rise to smaller exchange integrals and as discussed later, possible magnetic frustration. Examples of the different types of cuprate building blocks are shown in fig 3.4. Fig 3.4a shows the corner sharing cuprate, realized for example in the parent high-$T_c$ compounds such as in Sr$_2$CuO$_3$. Fig 3.4b shows the CuO topology which is the main part of this thesis and is realized in edge sharing cuprates. Known examples of these are LiCuVO$_4$, LiCu$_2$O$_2$, CuGeO$_3$ and NaCu$_2$O$_2$. The third type, fig 3.4c is a mixture of the edge and corner sharing cuprates which is realized in SrCuO$_2$. This type of configuration is called a zigzag chain. For reasons shown in the next section, the next nearest neighbour coupling (180° bond) is around 10 times larger than the diagonal Cu-O-Cu bond enclosing an angle of 90°.

If we take this view a step further and apply the orbital configurations, i.e. the oxygen
2p and the copper 3d orbitals, we see how the different fundamental cuprates differ in the magnitude and sign of the exchange integrals and how this gives rise to frustration. If we take the case of the parent high $T_c$ superconductors, which is represented in fig 3.5a, we see that the large dominant nearest neighbour exchange integrals can be understood by a large orbital overlap between the Cu 3d and the O 2p giving rise to large exchange integrals. For example in Sr$_2$CuO$_3$ the exchange integral $J$ is antiferromagnetic and around 2100 ± 200 K [69]. The case of edge sharing cuprates as shown in fig 3.5b, represents a more complicated situation. A special situation arises due to the nature of the overlap of the d and p orbitals. Due to the 90° Cu-O-Cu bond angle the Cu 3d hybridizes with the nearest O 2p. However, unlike in the case of the corner sharing cuprate, the O 2p orbital is then orthogonal to the next Cu 3d orbital, meaning that the exchange interaction between nearest neighbours is weak. Due to these structural reasons and degeneracies, the next O 2p orbital hybridizes with the third Cu 3d orbital as shown in fig 3.5b. In terms of the
orbital configurations the nearest neighbour Cu-O-Cu interaction is either ferromagnetic or antiferromagnetic and is much smaller than the more dominant antiferromagnetic Cu-O-O-Cu superexchange pathway to next nearest neighbours. Regardless of the nearest neighbour sign (i.e. ferromagnetic or antiferromagnetic) we then have a scenario of magnetic frustration. The next section will give an introduction to frustration in different lattices.

3.1.3 Frustration in low dimensional magnets

Frustration in magnetism arises when a magnetic system cannot satisfy all interactions simultaneously. The most common type of frustration is geometrical frustration as in triangular or Kagomé 2D lattices, or with a pyrochlore lattice in 3D. These types of configurations are shown in fig 3.6b,c. For a review of geometrical frustration see e.g. Ramirez [14]. Therefore, in edge sharing one dimensional compounds, when the Cu-O-Cu bond is 90 degrees one may find a playground of model systems for frustrated low dimensional spin 1/2 quantum antiferromagnets and novel quantum behaviour such as frustration which is
intimately related to quantum criticality.

Theoretically, the frustrated Hamiltonian 3.1.7 was first studied by Majumdar and Ghosh [70, 71] in which they considered a Hamiltonian of a chain with $N$ spin $1/2$ particles.

$$H = J \sum_{i} S_i S_{i+1} + J\alpha \sum_{i} S_i S_{i+2}$$  \hspace{1cm} (3.1.7)

They considered the effect of the parameter $\alpha$ (the frustration parameter, given as $J_2/J$, where $J_2 = \alpha J$ is the next nearest neighbour coupling) for 4 cases. They found: 1) $J < 0$, $\alpha > 0$, so that all interactions are ferromagnetic, with a stable ground state. 2) $J > 0$, $\alpha < 0$, nearest neighbour interaction is antiferromagnetic, while next nearest interaction is ferromagnetic, again a stable ground state. An interesting question came in the next case, 3) $J < 0$, $\alpha < 0$, so that the nearest neighbour interaction is ferromagnetic, with the next nearest neighbour interaction being antiferromagnetic. This configuration causes an unstable ground state. The fourth case, 4) $J > 0$, $\alpha > 0$, the alignment of the next nearest neighbour is opposing that of the nearest neighbour, this gives the ground state to be different to that of the classical analogue by symmetry. Bursill [15] continued using Density-Matrix Renormalization Group theory (DMRG) with the following Hamiltonian

$$H = J_1 \sum_{i} S_i S_{i+1} + J_2 \sum_{i} S_i S_{i+2} = \cos \omega \sum_{i} S_i S_{i+1} + \sin \omega \sum_{i} S_i S_{i+2}$$  \hspace{1cm} (3.1.8)

This Hamiltonian was studied for the range of $\alpha = J_2/J_1 = \sin \omega / \cos \omega = \tan \omega$. Fig 3.7 shows the $T = 0$ phase diagram for classical spin systems and the quantum analogue. In classical magnets competing interactions with strong frustration often result in helimagnetic ground states with incommensurate long range order. In the quantum case, strong frustration can suppress long range order and create gapped spin liquid phases and other states with local spin correlations.
Figure 3.6: Types of geometrical frustration. a) One dimensional chain, nearest neighbour is ferromagnetic, while the next nearest neighbour is antiferromagnetic and stronger. b) Two dimensional triangle, all interactions are equal and antiferromagnetic. c) 3D case for an antiferromagnetic coupled tetrahedra as e.g. in the pyrochlore lattice [14].
The classical case gives three distinct phases, a ferromagnetic ground state, antiferromagnetic ground state, and also helical order for a frustrated region of the exchange parameters. In the quantum case, the antiferromagnetic regime is suppressed, so it extends from \(-\pi/2 < \omega < \omega_{MG}\), where \(\omega_{MG} = \tan^{-1}(1/2)\). This point is represented by the Majumdar-Ghosh (MG) Hamiltonian \([70, 71]\) in which there are dimerised singlets as the ground state, with an energy gap to excited states. The frustrated regime is given by \(\omega_{FF} < \omega < \omega_{MG}\), where \(\omega_{FF} = \tan^{-1}(1/4)\). Novel and interesting ground states exist in this phase diagram. A cross over point occurs when the gapped spin liquid phase changes into a gapped MG dimer type ground state. The question arises to which extent quantum fluctuations are present around this area. This area of the phase diagram has no classical analog.
3.1.4 Examples of low dimensional Heisenberg $S = 1/2$ quantum chain systems with a weaker nearest and stronger next nearest neighbour interaction

Gibson and collaborators first showed that LiCuVO$_4$ represents a one dimensional system with competing nearest and next nearest neighbour interactions. An incommensurate antiferromagnetic ground state was found by single crystal neutron diffraction [72] and it was first proposed that a scenario of competing nearest and next nearest neighbour interactions giving rise to magnetic frustration could be valid in this compound. Subsequent inelastic neutron scattering [21] found that the nearest neighbour exchange is $J_1 = -15$ K, and the next nearest neighbour exchange is $J_2 = 40$ K, thus confirming unquestionably this scenario of frustration. This will be discussed in more detail in chapter 5. A similar scenario was proposed to hold for LiCu$_2$O$_2$[73] and more recently for NaCu$_2$O$_2$[74]. Chapter 6 will summarize the main findings of the currently available one dimensional frustrated chain compounds. The next chapter is the investigation of two new low dimensional compounds which are magnetically frustrated due to a weaker nearest and stronger next nearest neighbour interaction.
Chapter 4

Investigation of \( \text{CuCl}_2 \) and \( \text{CuBr}_2 \): Possible systems with a frustrated \( S = 1/2 \) Heisenberg chain

Historically, \( \text{CuCl}_2 \) and \( \text{CuBr}_2 \) belong to compounds that have been analyzed in terms of one dimensional chains (see e.g. L. J. De Longh and A. R. Miedema [12] and references therein) as early as 1962. The first susceptibility measurements [75, 76] performed on \( \text{CuCl}_2 \) and \( \text{CuBr}_2 \) showed a transition at 23.9 K and 73.4 K respectively which indicated antiferromagnetic interactions via superexchange through the halogen atom. Above the ordering temperature, a broad maximum is seen which is a general characteristic of low dimensional antiferromagnetic spin systems. NQR (Nuclear Quadrupole Resonance) [77] on \( \text{CuBr}_2 \) showed a sudden decrease in the \(^{81}\text{Br} \) NQR signal at 74 K, the copper resonance disappeared sharply at 82 K. Heat capacity measurements on \( \text{CuBr}_2 \) showed a clear transition at 74 K. Preliminary powder neutron data was taken at 293 and 4.2 K on \( \text{CuBr}_2 \). These revealed only one possible weak, not clearly resolved, magnetic reflection which was on the shoulder of the lowest angle nuclear reflection [78].
CuCl$_2$ has received more attention due to the possible preparation of CuCl$_2$ single crystals [79]. Heat capacity [80, 81] measurements on powders showed the Néel temperature at 23.9 K and a broad short range maximum around 40 K, although the absence of an adequate lattice reference made it difficult to estimate a more precise magnetic contribution to the heat capacity. A detailed analysis of the magnetic ground state and the character of the short range ordering process above the Néel temperature is missing so far. In this chapter, it will be shown that these compounds can be understood by a one dimensional Heisenberg model with competing interactions giving rise to magnetic frustration. As both compounds exhibit 3D order at a considerable Néel temperature they are possibly far from representing ideal low dimensional systems.

4.1 Crystal structures of CuCl$_2$ and CuBr$_2$

The binary divalent Cu halides crystallize in a layered structure with Cu$^{2+}$ ($3d^9$ configuration, $S = 1/2$) in a Jahn-Teller distorted octahedral halogen atom environment. Each CuX$_6$ (X = Cl,Br) octahedron shares two X-X equatorial edges with adjacent octahedra. The apical halogen atoms are equatorial ligands for adjacent octahedra. As a result, the structures contain chains of Cu$^{2+}$ ions extending along (010) coupled by superexchange via halogen bridges.

The chemical structure can be described within the monoclinic space group $C\ 2/m$ [82, 83] with the Cu$^{2+}$ ion occupying Wyckoff position 2a and Cl$^{1-}$ or Br$^{1-}$ occupying position 4i. Fig 4.1 shows the crystal structure of CuCl$_2$ and CuBr$_2$ which clearly shows the chain structure extending along $b$. Table 4.1 shows the lattice parameters and monoclinic angle for both compounds as well as the Cu-X-Cu bond angle.
Figure 4.1: Crystal structure of a) CuCl₂ and b) CuBr₂. Larger atoms represent the halide, small green atoms are copper. c) Shows the CuX₄ squares extending along the crystallographic b direction and the Cu-X-Cu bond angle.

Table 4.1: Lattice parameters, monoclinic angle and Cu-X-Cu bond angle for CuCl₂ and CuBr₂ at room temperature.

<table>
<thead>
<tr>
<th>Compound</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Cu-X-Cu angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl₂</td>
<td>6.9038(9)</td>
<td>3.2995(4)</td>
<td>6.824(1)</td>
<td>122.20(1)</td>
<td>92.03</td>
</tr>
<tr>
<td>CuBr₂</td>
<td>7.2096(5)</td>
<td>3.4742(2)</td>
<td>7.0475(6)</td>
<td>119.61(0)</td>
<td>93.64</td>
</tr>
</tbody>
</table>
4.2 Specific heat measurements

Specific heat measurements were performed on powder samples of CuCl₂ and CuBr₂ by the quasi adiabatic (Nernst) heat pulse method as described in the first chapter. The powder samples were contained in Duran glass ampules under ~ 1 bar of He gas to provide thermal coupling. A minute amount of Apiezon N grease was used to attach the ampule to the sapphire platform, which has a stainless steel heater and a CERNOX CX 1050 thermometer (LakeShore). The platform thermometer is read out by a LakeShore 370 resistance bridge. A single $\tau$ relaxation method (as described in chapter 1) is used by applying a heat pulse to the sample and measuring the relaxing temperature. Fitting the relaxation to the single $\tau$ model gives the temperature difference brought about by the electrical heat pulse. The heat capacity of the ampule, Apiezon and sample holder was subtracted after measurement. The temperature range was 2 - 250 K.

4.2.1 CuCl₂

Fig 4.2 shows the heat capacity as a function of temperature for powder samples of CuCl₂ (black open circles) and MgCl₂ (open red circles). MgCl₂ is chosen as an initial lattice reference which one can subtract in order to obtain the magnetic contribution to the specific heat of CuCl₂. At 23.9 K one can see a small hump in the heat capacity of CuCl₂ due to long range ordering. MgCl₂ is not perfectly suited to be used as a direct lattice reference as subtraction leads to a much higher magnetic entropy than expected. Indeed, the structure of MgCl₂ is different from that of CuCl₂ due to the Jahn-Teller distortion which the copper halogen octahedra undergo. Therefore, we can expect a somewhat altered phonon spectra for MgCl₂. In addition, the mass of Mg is much smaller than that of Cu, so MgCl₂ was not used as a lattice reference in which to obtain the magnetic contribution to the specific heat of CuCl₂. As there are no available phonon spectra for CuCl₂, we constructed a lattice
Figure 4.2: Specific heat of CuCl$_2$ (open black circles). Specific heat of MgCl$_2$ (red open circles). The magnetic contribution to the specific heat for CuCl$_2$ (open blue circles). Dashed black line estimated lattice contribution for CuCl$_2$ (details in text). Red solid line is a two $J$ model fit as described in the text.

reference using an extended Debye method. The black dashed line in fig 4.2 shows a lattice estimation based on an extended Debye model. The lattice contribution was estimated from

$$C_{lat}(T) = \beta_1 T^3 - \beta_2 T^5 + \beta_3 T^7 - \beta_4 T^9 + \ldots$$

(4.2.1)

For $T \leq 150$ K, the best description was found using $\beta_1 = 0.55$ mJ/molK$^4$, $\beta_2 = 1.7 \times 10^{-7}$ J/molK$^6$, $\beta_3 = 0.5 \times 10^{-12}$ J/molK$^8$ and $\beta_4 = 6.00 \times 10^{-15}$ J/molK$^{10}$. Using $\beta_1$ and three atoms per formula unit, we arrive at a Debye temperature $\Theta_D(T = 0) \approx 250$ K.

The lattice contribution shows that there is still a magnetic contribution to the heat capacity of CuCl$_2$ even up to 150 K. The entropy of the magnetic contribution to the specific heat gives $R \ln 2$ as expected for Cu$^{2+}$ ($S = 1/2$). The blue open circles in fig 4.2 show the subtracted lattice contribution from CuCl$_2$. The magnetic contribution contains the long
range ordering temperature which is shown as a \( \lambda \)-type anomaly at 23.9 K and also the broad short range maximum which is shown in more detail in fig 4.3.

The broad maximum indicates that this compound is a low dimensional system, with a large amount of entropy released via short range correlations above the Néel temperature. Using only a nearest neighbour interaction, \( J_{nn} \), on a one dimensional \( S = 1/2 \) chain, the heat capacity was calculated using the ALPS libraries [84] according to

\[
H = J_{nn} \sum_i S_i S_{i+1} \tag{4.2.2}
\]

The best value of \( J_{nn} \) which fits the experimental data is an exchange parameter of \( J_{nn} = 110 \) K (see fig 4.3). If we use the relation from Johnston et al. [85] obtained for the Bethe ansatz calculation

\[
k_B T_{\text{max}} = 0.48028487 J \tag{4.2.3}
\]

Using the temperature \( T_{\text{max}} \), where the maximum in the magnetic heat capacity occurs, for \( \text{CuCl}_2 T_{\text{max}} \sim 54 \) K (see fig 4.3). Equation 4.2.3 gives a uniform nearest neighbour exchange integral of \( J_{nn} = 112 \) K. Using the relation given by Schultz [86] for an estimation of the interchain coupling, \( J_\perp \)

\[
|J_\perp| = \frac{T_N}{1.28 \sqrt{5.8 J_{nn}/T_N}} \tag{4.2.4}
\]

Via a crude nearest neighbour only model, a coupling ratio can be estimated as \( R_c = J_\perp/J_{nn} = 1 \times 10^{-1} \). Comparing with \( T_N/J_{nn} = 0.3 \), both values are quite large for one dimensional systems, but are nevertheless comparable to that of KCuF\(_3\) (\( J_{nn} \approx 400 \) K) [87].

If the idea is taken further it is possible to estimate the effect of a two \( J \) model, as shown in the previous chapter. In a lattice geometry such as \( \text{CuCl}_2 \) we could expect nearest and next nearest neighbour exchange interaction. The red solid line in fig 4.2 and fig 4.3 shows
Figure 4.3: Magnetic specific heat of CuCl$_2$ (open circles). Solid black line is a fit to a $S = 1/2$ with uniform nearest neighbour coupling only ($J_{nn} = 110$ K). Solid red line is a two $J$ model fit as described in the text ($J_1 = 30$ K, $J_2 = 120$ K).

the calculation for a two $J$ model. The best agreement with the subtracted contribution is obtained for $J_1 = 30$ K and $J_2 = 120$ K. This results in a signature of a magnetic frustrated system with competing exchange integrals.

4.2.2 CuBr$_2$

Fig 4.4 shows the heat capacity as a function of temperature for CuBr$_2$. The onset of long range antiferromagnetic order is at 73.4 K which is shown as a $\lambda$-type anomaly in the specific heat. In a similar manner to CuCl$_2$ the broad short range maximum is seen in the specific heat above the transition at 73.4 K. Unfortunately, as the transition temperature to 3D order is so high, the short range order maximum is approximately at 120 K. At such temperatures it is difficult to estimate the magnetic heat capacity due to the difficulty in the lattice estimation at high temperatures. However it is possible to fit the magnetic
susceptibility which will be shown in the next section.

4.3 Magnetisation and susceptibility

Susceptibility measurements were performed using a Quantum Design MPMS SQUID magnetometer. Fitting of the data is done to the theoretical prediction of the susceptibility of an antiferromagnetic Heisenberg spin 1/2 chain with uniform nearest neighbour coupling [85] and a two $J$ model, with $J_1$ and $J_2$ representing the nearest and next nearest neighbour interaction respectively.

The fits have been performed in two ways. One by full diagonalization using both a nearest and next nearest neighbour interaction defined as
\[ H = J_1 \sum_i S_i S_{i+1} + J_2 \sum_i S_i S_{i+2} \] (4.3.1)

Second, assuming that the experimental data can be described by the susceptibility of a uniform antiferromagnetic $S=1/2$ Heisenberg chain with additional terms taking into account a Curie-Weiss susceptibility contribution arising from quasi-isolated magnetic entities, e.g., from magnetic impurities. An additional temperature independent contribution \( \chi_0 \) is added to take into account the diamagnetic susceptibilities of the closed core electronic shells of the Cu\(^{2+} \) and Br\(^{-} \), Cl\(^{-} \) ions. In this case using one exchange integral, \( J \), for a next nearest interaction. The susceptibilities were fitted to a model including the effect of the interchain interaction treated in a mean field approach

\[ \chi_{\text{mole}} = \frac{\chi^{ch}_{\text{mole}}}{(1 + \chi^{ch}_{\text{mole}}(z'J'/J))} + \frac{\chi^{\text{imp}}}{(T - \Theta)} + \chi_0 \] (4.3.2)

with \( \chi^{ch}_{\text{mole}} \) as defined in equation 54 of ref [85] (parameters are given in Table I of ref [85]). \( z'J' \) represents the interchain coupling, \( \chi^{\text{imp}} \) is a low temperature impurity contribution and \( \Theta \) is the paramagnetic Curie constant of the impurities.

### 4.3.1 CuCl\(_2\)

The temperature dependent susceptibility of CuCl\(_2\) is shown in fig 4.5. As expected for a one dimensional chain, there is a broad short range maximum clearly seen in the susceptibility with a maximum centered at 71 K. The onset of 3D antiferromagnetic order is indicated at 23.9 K by a kink in the susceptibility, in excellent agreement with the results from the heat capacity measurement. The open circles are the data points and the solid line is a fit to equation 4.3.2. The parameters obtained from the fits are listed in table 4.2. Attempts to add additional temperature dependent terms \( a_0 + a_1 T + a_2 T^2 \) to the exchange parameter \( J \) converged to very small values for \( a_1 (i\neq0) \) and in turn the fits were performed using only eqn 4.3.2.
Figure 4.5: Open circles: powder susceptibility of CuCl$_2$, solid line: fit to equation 4.3.2.

The resulting fit of the exchange parameter $J = 103$ K agrees well with what one would expect just taking into account the maximum in the susceptibility, using the formula given by Johnston et al. [85].

$$k_B T_{\chi}^{\text{max}} = 0.6408510 J$$  \hspace{1cm} (4.3.3)

Using the maximum in the susceptibility at 71 K, equation 4.3.5 provides a nearest neighbour exchange of 110 K.

If we extend the fitting to include a two $J$ model with the Hamiltonian given in equation 4.3.1 we can obtain an estimate of the nearest neighbour and next nearest neighbour exchange integrals. Fig 4.6 shows the experimental data. The dashed line is a fit using only a nearest neighbour interaction, $J_{nn}$. The solid line is the full diagonalization of the Hamiltonian 4.3.1 for a nearest neighbour exchange integral of $J_1 = 30$ K and a next nearest neighbour interaction of $J_2 = 120$ K, both being antiferromagnetic. Using only a nearest
neighbour interaction does not fit the high temperature susceptibility well with large deviations whereas the two $J$ model with the exchange parameters given above fits the whole experimental curve.

The values that fit the susceptibility best to a two $J$ model are very close to those found in the analysis of the magnetic heat capacity. The finding from the detailed analysis of both quantities results in a consistent set for $J_1$ and $J_2$. This can be taken as a first evidence of a frustration scenario in CuCl$_2$, by having a weaker antiferromagnetic nearest neighbour and a much stronger antiferromagnetic next nearest neighbour interaction, thus providing magnetic frustration in one dimension. Later in this thesis, I present neutron scattering results on CuCl$_2$ where the realization of frustration is shown in terms of the magnetic structure.
The temperature dependent susceptibility of CuBr$_2$ is shown in fig. 4.7. As in CuCl$_2$, there is a broad short range maximum clearly seen in the susceptibility with the maximum centered at 220 K. The onset of 3D antiferromagnetic order is seen at 73.4 K by a kink in the susceptibility, in excellent agreement with the results from the heat capacity measurements.

The low temperature susceptibility vs. $1/T$ dependance indicates a negative Curie-Weiss temperature ($\Theta = -1.2 \pm 0.2$ K). The origin of this negative $\Theta$ indicates some antiferromagnetic exchange.

The susceptibility was simulated by fixing the $g$-factor to 2.06. This is a standard value for a powder, as well as $\chi_0$ to $-83 \times 10^{-6}$, as calculated from Sellwood's table [88] (fit parameters shown in table 4.2). In addition, we assumed a smooth temperature dependence of $J$ according to a polynomial to second order and allowed the variation of the coefficients $a_i$ (e.g. Johnston et al. [85]).
\[ J(T) = J(1 - 0.00006947T - 0.0000086T^2) \] (4.3.4)

The resulting fit was largely insensitive to the choice of \( z'J'/J \) and we consequently fixed \( z'J'/J \) to 0.035 or equivalently \( T_N = 74 \text{ K} \). The fit was improved with a slightly reduced value of \( J \) \((T = 0 \text{ K})\) and negative coefficients \( a_1 \) and \( a_2 \) (with \( a_0 = 1 \)). Negative values for \( a_1 \) induce a smooth increase of \( J \) from room temperature to low temperatures of about 14\% (see fig 4.8). An increase of \( J \) with decreasing temperature can easily be attributed to a contraction of the lattice causing an increasing overlap of the wavefunctions. If we reasonably assume a lattice contraction of about 1\% and the superexchange to depend on the distance \( d \), like \( d^{\alpha} \) \((\alpha \approx 10-15)\) we arrive at the experimental value given above.

In a similar manner to CuCl₂. The resulting fit of the exchange parameter \( J = 322 \text{ K} \) agrees well with what one would expect just taking into account the maximum in the
Figure 4.9: Open circles: susceptibility of CuBr₂, solid line: full diagonalization of the Hamiltonian 4.3.1 for \( N = 20 \) lattice sites. Dashed line: is a calculation of a \( S = 1/2 \) model with uniform nearest neighbour coupling only (\( J_{nn} = 340 \) K).

Using the maximum in the susceptibility at 220 K, results in a nearest neighbour exchange integral of 340 K. If we extend the fitting to include a two \( J \) model as described by equation 4.3.1 we can get an estimate of the nearest neighbour and next nearest neighbour exchange integrals. Fig 4.9 shows the powder susceptibility of CuBr₂. The solid line is the full diagonalization of the Hamiltonian 4.3.1 for a nearest neighbour exchange integral of \( J_1 = 85 \) K and a next nearest neighbour interaction of \( J_2 = 340 \) K, both being antiferromagnetic as in the case of CuCl₂. On the other hand, as in the case of CuCl₂, using only a nearest neighbour interaction does not agree well with the measured data in the high temperature regime of the magnetic susceptibility and a two \( J \) model produces a much better
Table 4.2: Parameters of the fits according to eqn 4.3.2 to the susceptibilities of CuBr₂ and CuCl₂. Letters (f) and (v) indicate whether the respective parameters were fixed or varied in the fitting procedure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CuCl₂</th>
<th>CuBr₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J / K )</td>
<td>103(1) (v)</td>
<td>322(5) (v)</td>
</tr>
<tr>
<td>( g )</td>
<td>2.06(0) (f)</td>
<td>2.06 (f)</td>
</tr>
<tr>
<td>( z'J'' / J ) (mol/cm³)</td>
<td>-0.0113(1) (v)</td>
<td>-0.014 (f)</td>
</tr>
<tr>
<td>( \chi_0 ) (10⁻⁶ cm³/mole)</td>
<td>-83 (f)</td>
<td>-83 (f)</td>
</tr>
<tr>
<td>( C_{imp} ) (10⁻³ cm³K/mole)</td>
<td>1.43(1) (v)</td>
<td>1.25(1) (f)</td>
</tr>
<tr>
<td>( \Theta ) (K)</td>
<td>0.65(1) (v)</td>
<td>-1.2(2) (f)</td>
</tr>
</tbody>
</table>

agreement.

The results of the susceptibility fits for both CuCl₂ and CuBr₂ in terms of a nearest neighbour model based on the Bethe Ansatz is shown in table 4.2. The result of both the susceptibility and magnetic specific heat fits in terms of a two \( J \) model are summarized in table 6.2 of chapter 6.

### 4.4 Crystal growth of CuCl₂

Single crystals of CuCl₂ were grown according to a previous report by Billerey et al. [79]. The crystals were grown from the melt. Special precaution must be taken due to the high chlorine vapor pressure close to the melting point. By this method, single crystals of max 2x10x2 mm³ could be grown in quartz glass tubes by slowly cooling the melt. Fig 4.10 shows a picture of a 1x5x1 mm³ CuCl₂ single crystal. The single crystals are kept in inert conditions (dry argon gas) due to them being moisture sensitive. Crystals treated in air show an additional ordering feature at low temperatures (\( \sim 3 \) K) which can be attributed to antiferromagnetic order of CuCl₂·2H₂O [89]. When left in air for over 20 minutes the effect is more visible by a light green colour emerging on the edges of the crystal. With time the crystal deteriorates. As it will be shown later CuCl₂ crystals are inherently twinned in
Figure 4.10: 1x10x1 mm³ Single crystal of CuCl₂ enclosed in argon atmosphere.

the ac plane.

4.5 High Field magnetization and phase diagram

A further test of the magnetic behaviour and the exchange integrals in the previous section can be made from high field magnetisation. At sufficiently high fields saturation may be expected when the Zeeman energy is of the order of the exchange energy. In this section, I will provide the phase diagram of CuCl₂ using high field measurements. High field measurements were carried out using a non destructive technique at the Laboratoire National des Champs Magnétiques Pulsés Toulouse, France. The large magnetic fields are produced in pulses lasting not more than 1s. In this way, fields of up to 60 T can be produced, while maintaining longer coil survival times i.e. increasing the number of pulses. We measured a single crystal of CuCl₂ along the chain axis, b. The results up to 55 T are shown in fig 4.11.

There are two main conclusions that can be drawn from fig 4.11. The first is the
Figure 4.11: High Field response for single crystals of CuCl$_2$ with $H \parallel b$ for 1.4 and 4.2 K. Insert: Spin flop transition at $H_{SF} \sim 4$ T.

occurrence of a step in the magnetisation at 4 T possibly due to a spin flop transition. The other conclusion is that there is no saturation seen up to 55 T. In the first case, the occurrence of a magnetisation jump indicates a sudden change in the magnetic structure, by possibly a spin flop transition. The lack of saturation effects supports the view of the susceptibility and heat capacity fits, that a field of over 100 T would be needed in order to break the exchange field. Measurements up to 150 T at the MegaGauss facility in Berlin, via a destructive method [90], showed a possible saturation at approx 200 T ($\sim 120$ K, see fig 4.12) in agreement with the exchange integrals fitted above. However, due to experimental problems the result was not conclusive due to the small signal coming from the sample just above noise levels.

With all the information collected above, a $H - T$ phase diagram can be constructed for $H \parallel b$. This is shown in fig 4.13. There are two clear phases as we go below the long range order temperature, one is with helicoidal long range order, as will be discussed in the next
Figure 4.12: Field pulse $H(t)$ (solid blue line), time derivative $dH/dt$ (solid red line) for single crystals of CuCl$_2$ with $H \parallel b$ at 2 K. Black straight lines show changes in the gradient of the time derivative and show small kinks at fields of $\sim 200$ T.

A second phase is seen with the application of a magnetic field. Above 4 T, CuCl$_2$ undergoes a spin flop phase where there is a rearrangement of the spin structure due to local anisotropies, in agreement with previous brief reports [91, 92]. The field dependance of the phase boundary increases slowly with increasing temperature until 5 T with a tricritical point at 23.4 K and 5.24 T. The next section will show elastic and inelastic neutron scattering results in the two main areas of the phase diagram as presented in fig 4.13.

4.6 Neutron scattering

Neutron scattering is a fundamental experimental technique in magnetism. It provides, via elastic and inelastic diffraction, a probe of the static and dynamic spin structures. The first magnetic structure to be solved by elastic neutron scattering was MnO by C. Shull [93] which earned him the Nobel prize by confirming the idea of antiferromagnetism proposed
Figure 4.13: Phase diagram of CuCl$_2$ with $H \parallel b$. Open circles from susceptibility measurements.
by Néel [94]. Ever since, the plethora of magnetic structure that nature offers has been investigated using the powerful technique of neutron scattering. In the next section, I will report on powder and single crystal neutron diffraction on CuCl$_2$ and powder neutron scattering investigation on CuBr$_2$.

4.6.1 Powder neutron scattering on CuCl$_2$ and CuBr$_2$

Powder neutron diffraction was performed on polycrystalline samples of CuCl$_2$ and CuBr$_2$ on ILL's high flux two-axis powder diffractometer D20 (see fig 4.14 for an outline) at a wavelength of 1.88 Å (high resolution option) and 2.5 Å (high intensity, low resolution). The refinements of the chemical structures were done using the program FULLPROF [95].

Powder neutron diffraction was undertaken in order to obtain the magnetic structure and to follow the structural properties as a function of temperature. Due to the very small ordered moment in both CuCl$_2$ and CuBr$_2$, only a few very weak magnetic Bragg reflections were seen below the Néel temperature. The temperature dependance of these reflections identifies them unambiguously as magnetic reflections. This is demonstrated for both compounds in fig 4.19. Both reflections disappear at 23.9 and 73 K for CuCl$_2$ and CuBr$_2$, respectively. These temperature are in excellent agreement with thermodynamic properties. Full profile refinements (see fig 4.15, 4.17 and 4.16) using FULLPROF [95] to the diffraction patterns collected in a temperature range of 2 - 100 K for CuBr$_2$ indicate structural anomalies close to $T_N$ due to magnetoelastic coupling. This is most pronounced in the lattice parameter $b$ which is the along the chain, and also in the monoclinic angle $\beta$. This is shown in fig 4.19h and j.

Due to the occurrence of magnetic reflections in the diffraction patterns below the ordering temperatures (see the difference pattern for CuCl$_2$, fig 4.18), it is possible to define a propagation vector by indexing the positions in the scattering angle $2\Theta$. For CuCl$_2$ a
Figure 4.14: Experimental setup of D20 at the ILL [16].
Figure 4.15: Powder neutron diffraction at 42 K for CuCl$_2$ on D$_2$O ($\lambda = 1.88$ Å). Closed circles: raw data, black solid line: calculated pattern, blue solid line: difference of the calculated and observed patterns with a $\chi^2 = 87.60$.

Figure 4.16: Powder neutron diffraction at 2 K for CuCl$_2$ on D$_2$O ($\lambda = 2.50$ Å). Closed circles: raw data, black solid line: calculated pattern, blue solid line: difference of the calculated and observed patterns with a Bragg $R$ factor = 12.0.
magnetic Bragg reflection is clearly seen in the neutron data and is shown in the temperature dependance in fig 4.19 is at $\approx 22$ degrees in $2\Theta$. Using this reflection we arrive at a tentative propagation vector of $k = [0.5, -0.224, 0]$ for CuCl$_2$, which suggests an incommensurate structure along $b$, and gives a possible helicoidal order along the chain. Likewise, we see reflections at 25.3 and 41 degrees in $2\Theta$ for CuBr$_2$ which we tentatively index to a propagation vector $k = (0.5, -0.245, 0)$. It is reasonable that the two propagation vectors do not differ greatly, as we would expect them to give similar results given the closeness of the chemical cell.

Figure 4.17: Powder neutron diffraction at 120 K for CuBr$_2$ on D20 ($\lambda = 1.88$ Å). Closed circles: raw data, black solid line: calculated pattern, blue solid line: difference of the calculated and observed patterns with a $\chi^2 = 15.78$. 
4.7 Magnetic structure determination from single crystal diffraction

Every magnetic structure is described by the superposition of the basis functions of the irreducible representation in the magnetic representation of the crystal symmetry group [96]. The determination of a magnetic structure requires the propagation vector, which describes the relation between orientations of moments of equivalent magnetic atoms in different nuclear cells. Also a knowledge of the form of the basis vectors that make up an irreducible representation is needed.

A central concept in the symmetry analysis of magnetic structures is the little group $G_k$ which contains all the symmetry elements that leave $k$, the propagation vector, invariant. There exists matrix sets that describe how the moments transform under all the operations
Figure 4.19: Magnetic and structural properties for CuCl$_2$ and CuBr$_2$. For CuCl$_2$: a) magnetic reflection at $2\theta = 22^\circ$ indexed as [0.5,0.224,0]. Lattice parameters: b) $a$, c) $b$, d) $c$. e) monoclinic angle, $\beta$. For CuBr$_2$: f) magnetic reflection at $2\theta \approx 25.3^\circ$ indexed as (0.5,-0.245,0). Lattice parameters: g) $a$, h) $b$, i) $c$. f) monoclinic angle, $\beta$. 
of $G_k$, these can be separated orthogonally into irreducible representations. The real power of group theory comes from the Landau theory of second order phase transitions [97]. This states that when a second order transition occurs, this involves the build up of magnetic fluctuations that have the symmetry of only one irreducible representation. As a result of the Landau theory this implies that the resulting magnetic structure can be described by the basis vectors associated with that irreducible representation. In this way, all the other basis vectors associated with the irreducible representations that are not involved in the transition are zero. This, in many cases, considerably reduces the number of possibilities of magnetic models. However, in the case of both CuCl$_2$ and CuBr$_2$, using the space group and propagation vector, as obtained from power neutron scattering, symmetry analysis does not help to reduce the number of magnetic models.

4.7.1 Single crystal neutron diffraction - magnetic structures

Single crystal neutron diffraction was performed on CuCl$_2$ using the four-circle diffractometer D10 at the Institute Laue-Langevin, Grenoble, France. An instrument outline is given in fig 4.20. A wavelength of $\lambda = 2.34$ Å provided by a Cu[200] monochromator was chosen for the experiment because this instrument setting provides optimal flux conditions. Low temperatures were provided by a helium-flow cryostat. Using CuCl$_2$ single crystals on D10 at the ILL, nuclear structure data were taken at 300 K and magnetic structure data at 2 K.

Magnetic reflections were identified by searching many directions in the Brillouin zone and then comparing with the response at 30 K, above the magnetic ordering temperature. The propagation vector was successfully identified by centering a magnetic reflection in reciprocal space. This gave a propagation vector of $\tau = [0.5 \ 0.224 \ 0]$ as shown in fig 4.21 in excellent agreement with the powder study. The refinement of the crystallographic and magnetic structure was done using the standard routines of the Cambridge Crystallographic Subroutine Library (CCSL) [98] and the Rietveld analysis FULLPROF suite [95]. The
Figure 4.20: Experimental setup of D10 at the ILL [17].

Figure 4.21: CuCl$_2$ single crystal neutron diffraction on D10. Closed circles: raw data at $\sim$82 K along [0.5 0]. Open circles: Magnetic reflection at 1.7 K fitted to a Gaussian (solid line). The center of the magnetic reflection indicated by an arrow is at $+0.776$ in $k$. 
Figure 4.22: Observed and calculated nuclear integrated intensities for CuCl$_2$ single crystal neutron diffraction on D10. Closed circles: results of the refinement giving a $\chi^2 = 15.9$. Solid line: $F^2_{\text{obs}} = F^2_{\text{calc}}$. 
program SFTWIN in CCSL was used in order to explain and refine the twinned structure of CuCl₂ using the space group C 2/m and the twin matrix of equation 4.7.1.

$$T = \begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$ (4.7.1)

When applied to a $hkl$ reflection, this matrix changes the $h$ and $l$, and leaves $k$ opposite in sign. No twinning in CuCl₂ has been reported before, and it was first observed by the occurrence of forbidden reflections in the single crystal neutron data when given the above space group. X-ray analysis on small crystals (2x5x2 mm²) confirmed by the twin matrix given above. Further investigations with Electron Spin Resonance (ESR) also revealed two signals coming from both twin domains as discussed in detail in a later section. The best refinement of the nuclear data is shown in fig 4.22.

The final structure refinement gave a $\chi^2 = 15.9$ using SFTWIN for 86 unique reflections. The domain population of the twin was refined to 58% and 42%. See Appendix C1 for a complete reflections list. The magnetic structure was refined using FULLPROF by selecting the magnetic reflections that correspond to the nuclear structure of one domain i.e. from the nuclear refinement one can separate the domain reflections, then from this, picking out the magnetic reflections that arise from the nuclear reflection. This gave 15 unique reflections that belonged to only one domain. The best refinement of the magnetic structure factors gave a polarized magnetic helix in the $ab$ plane. This magnetic structure model gave a $\chi^2$ of 7.3 (see appendix C2 for a list of integrated intensities). The refined Cu moment is $\mu_{Cu} = 0.63(1) \mu_B$. The refined magnetic structure of CuCl₂ is shown in fig 4.23. Only the copper atoms are shown with the arrows which represent the moment direction.

The incommensurability in the magnetic structure indicates that there is a considerable degree of frustration in the system. Similar results have been seen for other frustrated one
Figure 4.23: Magnetic structure of CuCl$_2$ showing only the copper positions. Five nuclear unit cells are shown along $b$, and two along $a$ to give one magnetic unit cell. Arrows show the direction of the moments.

dimensional spin chain systems [72, 73, 74]. The pitch angle between spins given by the propagation vector is $\phi_r = 80.6^\circ$. Using the classical prediction of the frustration parameter $\alpha$, we arrive at a frustration ratio $\alpha = J_2/J_1 = -1.53$. The propagation vector is similar to that found for other frustrated quasi one dimensional spin systems that undergo Néel ordering (see chapter six).

Further single crystal experiments on E6 (see fig 4.24) at the HMI were performed to get a temperature dependence of a selected magnetic reflection, to allow an estimation of the critical exponent, $\beta$ of the order parameter. We found by fitting the integrated intensity to the following formula

$$I = I_0(1 - T/T_N)^{2\beta} + BG$$  \hspace{1cm} (4.7.2)

where $I$ is the intensity, $I_0$ is the intensity at $T = 0$ and BG is the background. The best fit as shown in fig 4.25, revealed a critical exponent $\beta = 0.26 \pm 0.05$. 

Figure 4.24: Experimental setup of E6 at HMI, Berlin [18].

Figure 4.25: Critical exponent estimation for CuCl$_2$. Open circles represent the raw data. Solid line is a fit to eqn 4.7.2.
4.7.2 Neutron diffraction in an applied field

In addition to zero field measurements resulting in the magnetic structure, first measurements were carried out in an applied field to test the nature of the propagation vector in the spin flop phase. Fig 4.26 shows the magnetic field dependence of a strong magnetic peak at \([0.5 \kappa -1]\). It is evident that there is a sudden decrease in the intensity of the magnetic peak which could indicate that the spin flop transition involves only a small change in the magnetic structure and not a full phase transition. Therefore, this supports the view that there is only change in the helix in this phase. The nuclear peaks at \([0 \ 0 \ 4]\) and \([2 \ 0 \ 0]\) showed no change in the integrated intensity when passing through the spin flop transition. We also found when increasing the field above 4 T that there was no change in the propagation vector, therefore the magnetic structure appears to remain incommensurate in the spin flop phase.
4.7.3 Single crystal inelastic neutron scattering

Inelastic neutron diffraction was done on IN12 and IN20. Fig 4.27 shows the experimental setup of IN20, the setup of IN12 was discussed in a previous chapter. IN20 is a thermal beam three-axis spectrometer equipped for inelastic scattering experiments. The energy transfer range accessible in the present configuration of IN20 extends to 100 meV with a maximum incident neutron energies reaching up to 150 meV. The typical energy widths (FWHM) measured with a reference vanadium sample at the graphite filter wave-numbers $k_i = 2.66 \ \text{Å}^{-1}$ and $4.1 \ \text{Å}^{-1}$ are 0.82(3) meV and 3.05 (15) meV, respectively. However, due to the small crystals and low moment, it was difficult to measure the spin dispersion and long scan times were required. In addition, due to the low signal, also the inclusion of water in the sample during the aligning procedure created dominant incoherent scattering.
from hydrogen. Therefore, at present a conclusive result was not obtained. However, the initial dispersion ($E < 10 \text{ meV}$) could be mapped out from the ordered structure $k = 0.22, 0.77$ (see fig 4.28). It was seen that the initial dispersion from the ordered $k$ vector was very steep, when going along $k$. Although the signal at the zone boundary was too weak to be mapped out, we can conclude support for the large integrals obtained by susceptibility measurements.

### 4.7.4 Discussion from bulk and neutron investigations

From the results of our powder and single crystal neutron diffraction experiments and bulk properties, we have shown that both CuCl$_2$ and CuBr$_2$ represent another example of a 1D Heisenberg antiferromagnetic chain. Specific heat measurements and susceptibility show that there is a sizable interchain interaction for both CuCl$_2$ and CuBr$_2$ as they undergo
a transition to long range antiferromagnetic order at $T_N = 73.4$ and 29.3 K respectively. Both compounds can be shown to be quasi-1D as the broad short range correlations are clearly seen in both compounds above the ordering temperature.

Our neutron diffraction results indicate that the magnetic order is incommensurate along the chains, and will be described as helicoidal ordering. Sizable magneto-elastic coupling is seen in the temperature dependence of the lattice parameter $b$ and the monoclinic angle $\beta$ for CuBr$_2$. We ascribe the incommensurability to competing interactions along the chain directions due to a ferromagnetic nearest neighbour and an antiferromagnetic next nearest neighbour coupling, as provided by the two $J$ fit to the susceptibility and magnetic specific heat. This is in analogy to LiCuVO$_4$, for which details will be discussed in a later chapter. The next section looks further into the twinned nature of CuCl$_2$ by Electron spin resonance measurements.

4.8 The Electron Spin Resonance technique and principles

Electron Spin Resonance (ESR) deals with the interaction of electromagnetic radiation with magnetic moments. It remains until now one of the experimental techniques in condensed matter which gives clear insights into the concepts of quantum mechanics. In most spectroscopic studies absorption occurs when the energy of a quantum of radiation ($h\nu$) corresponds to the separation between energy levels.

Fig 4.29a shows the basic setup of a continuous wave EPR spectrometer. The source of electromagnetic radiation in our case is a microwave klystron source providing high frequency radiation with a frequency of 9.5 GHz (wavelength of approx 30 mm). The sample is located in a resonating cavity where at resonance the energy density is significantly enhanced. The magnetic field must be very stable, as any variations in the field represent variation in the resonance field, or energy separation. As a detector, a solid state diode is
Figure 4.29: Experimental basics of EPR. a) Basic experimental setup of a continuous wave EPR spectrometer. b) Energy level diagram of a free electron system as a function of an applied magnetic field. By varying the static field, $B$, we can reach resonant absorption when the separation of the two energy levels is equal to the energy $h\nu$ of an incident microwave photon, denoted as $B_r$. 

Resonance field $\Delta U = h\nu$

$B = 0 \quad B \rightarrow$
used which is sensitive to microwave energy. The external field is modulated by a small high
frequency (typically 100 kHz) field of $\approx 10$ Oe amplitude. The diode signal is detected by a
lock-in amplifier. Considering the case as shown in fig 4.29b, a simple energy level diagram
of a spin 1/2 particle in a magnetic field. The energy levels are shown by $\alpha$ and $\beta$. By
varying the static field, $B$, we can reach resonant absorption when the separation of the two
energy levels is equal to the energy $h\nu$ of an incident microwave photon. The absorption of
photons is indicated by a change in the detector current. The derivative of the resonance
signal $dP_{abs}/dH$ is obtained using the lock-in technique described above. The important
parameter in ESR is the Zeeman splitting $g$-factor defined as

$$g = \frac{h\nu}{\mu_B H}$$ \hspace{1cm} (4.8.1)

For a free electron the $g$-factor amounts to $g = 2.002319304386(2)$ which is one of the
most accurately known physical constants. For a single crystal material, ESR can reveal
anisotropy, leading to a dependance of the resonance line position on the crystal orientation
relative to the magnetic field. A system will have three mutually perpendicular inherent
directions, called the *principle axes*, which are the principle axes of the $g$-tensor describing
the Zeeman splitting in an external magnetic field, which describes the anisotropic properties
of the crystal. For an isotropic system the $g$-tensor is diagonal with all diagonal tensor
elements equal

$$g_a = g_b = g_c = g$$ \hspace{1cm} (4.8.2)

Likewise for an anisotropic system with orthorhombic or lower symmetry the $g$-tensor
can be diagonalized with the individual $g$-factors, $g_i$, along the principle axes

$$g_a \neq g_b \neq g_c$$ \hspace{1cm} (4.8.3)
4.8.1 Electron Spin Resonance in one dimensional spin chains

The discovery of the Electron Spin Resonance (ESR) technique in 1945 by E. Zavoisky [99] prompted the use of this technique to understand many interesting properties of a material by this microscopic probe. Many studies proceeded on salts containing Mn$^{2+}$ or Cu$^{2+}$ [100, 101] which were shown to exhibit characteristic line broadening of the resonance line. Theoretical analysis followed from Van Vleck [102] and Anderson [103] in which the linewidth broadening was related to dipole-dipole interaction. Extensive studies on the behaviour of one dimensional magnets came with the discovery of the Heisenberg magnet (CH$_3$)$_4$NMnCl$_3$ (TMMC) which showed no long range ordering down to 1.1 K [104]. ESR investigations [105] demonstrated that the role of reduced dimensionality can be understood by the long time persistence of spin correlations. It was shown that the linewidth as a function of angle did not follow the $(1+\cos^2(\theta))$ dependance predicted from previous exchange-narrowing theories. In the former theory, an exponential time dependance of the relation function would give a Lorentzian lineshape. However, if long term diffusive behaviour is found in low dimensional magnetic systems, then the lineshape is an intermediate between a Lorentzian and Gaussian. The lineshape is determined by the Fourier transform of $e^{-A/t^{3/2}}$, where $A$ is a scale parameter. In addition, the angular dependance of the linewidth is given by $|3\cos^2(\theta) - 1|^{4/3}$. At $\approx 54.7$ degrees from the chain axis, the lineshape is a pure Lorentzian. This angle is the so-called ‘magic angle’ and the linewidth assumes a minimum.

Recent studies on low dimensional compounds such as CuGeO$_3$ have shown that other effects such as the Dzyaloshinsky-Moriya interaction may give rise to large broadening at room temperature [106, 107] but further investigation on CuGeO$_3$ proved that the anisotropic exchange interaction is indeed the major cause of line broadening [108]. We note that most of the effects that are characteristic of one dimensional compounds e.g. the so called ‘half field resonance’, are rarely seen in quasi-one dimensional compounds which undergo long
range order at low temperatures [24].

4.8.2 Crystal considerations of CuCl$_2$

In this section, the principle axis is defined, in terms of the normal crystal axis and the twin axis. The twinning in this compound comes from the fact that the lattice parameters $a$ and $c$ are quite close and that the monoclinic angle $\beta \approx 120$ degrees. Interchanging $a$ and $c$ results in a 'mirror twin'. This was first concluded as shown in the previous section by elastic neutron studies, for which the creation of many forbidden reflections in the $ae$ plane was observed. The principle axes of the $g$ tensor forms an orthonormal system. By chemical reasons, in CuCl$_2$ one may expect principle directions along $b$ and $c$. The third principle direction along $a$ would be $\approx 30$ degrees away from $a$ towards $c$. As the angle from $a$ to $c$ ($\beta$) is 122.2 degrees, this would give the a principle axis at 90 degrees from $c$ and 32.2 from $a$. Fig 4.30 shows the crystallographic structure, as well as the principle axes as defined by symmetry.

The twinning is defined such that the $a$ and $c$ lattice parameters are interchanged, and
Figure 4.31: ac plane of CuCl₂. Black axes as defined for the normal structure, with $a'$ the principle axis. Red axes: The twin structure axes is defined by $a^t$ and $c^t$ with $a''^t$ the principle axis of the twin.

the chain axis, $b$ of the mirror twin are antiparallel. Therefore the effect this leaves on the principle axis $a'$ is shown in fig 4.31. The axes in fig 4.31 are colour coded so when we discuss the angular dependance from individual lines later, the red colour is the line originating from the twin axis and the black from the normal axis.

4.8.3 Angular dependance

In a single crystal of CuCl₂ we have only one Cu crystallographic position. One would therefore expect only a single resonance line at a resonance given by eqn 4.8.6 and 4.8.7. Experimentally however, one finds a superposition of several lines, two rather intense with a pronounced angular dependance and a third resonance line which is considerably weaker in intensity and which shows a weaker angular dependance of the resonance position not immediately related to the two symmetric lines. These three lines are clearly resolved only at temperatures of 100 K and below. Above $\sim 100$ K relaxation processes cause a rapid broadening and the lines in general can not be resolved any more.

Due to the appearance of three signals in the ESR spectra, the linewidth of each signal
Figure 4.32: 3D plot of the ESR resonance ($\nu = 9.34$ GHz) signal, magnetic field and rotation when going from the $a$ axis to the $c$ axis in CuCl$_2$ at 25 K. Crosses are the experimental data and solid lines represent a three line fit as described by eqn 4.8.4. The development of the three signals varies strongly going from one axis to another.
broadens at high temperature due to the perturbations of the dipole-dipole, anisotropic or antisymmetric interactions to the Heisenberg operator. This causes a single broad signal at room temperature, and it is not possible to resolve individual lines without the introduction of unreasonable errors. With this in mind, cooling down to intermediate temperatures (100 - 50 K) gives three separable lines. Two are clearly seen at all angles in the rotation. Only at certain angles does the other third line appear. At these angles it is not possible to fit the spectrum with two lines, even with the introduction of a dispersive contribution to the linewidth, i.e. allowing deviations from a pure lorentzian absorption signal by admixture of a dispersive part as is seen e.g. in metallic samples (Dyson lineshape). Therefore as a result, three lines were taken into consideration to fit the spectra. The spectra were fitted to the following equation containing the derivatives of a Lorentzian resonance line

\[
\frac{dP}{dH} = a_0 + a_1 H - \frac{4}{\pi} \sum_{i=1}^{3} \frac{I_i}{\omega_i (1 + x_i^2)^2} x_i
\]  (4.8.4)

where \(a_0\) and \(a_1\) are introduced to describe a linear background signal, \(\omega_i\) is the individual linewidth, and \(I_i\) the intensity of the Lorentzian, the parameters \(x_i\) are given by

\[
x_i = \frac{H - H_{ci}}{w_i}
\]  (4.8.5)

\(H\) is the magnetic field which is scanned during the measurement, \(H_{ci}\) is the resonance position of the individual line, which is identical with the point where the derivative of the signal changes sign. Example scans are shown in figures 4.32, 4.33 and 4.34, the best three line fit is shown by the red solid line. From fitting we obtain three parameters from each line, the resonance position, linewidth and the intensity.

In the case of twins, it is important to know which axis and twin is the source of the resonance signal. We can fit the \(g\) factors as a function of angle using the following equation for a single line
Figure 4.33: ESR signal at 100 K for 90 degrees from $a$ to $c$ in an ac plane rotation. Closed squares are data points, solid line is the best fit with 3 lines.

$$g = \sqrt{g_1^2 \cos^2(\varphi - \varphi_0) + g_2^2 \sin^2(\varphi - \varphi_0)}$$  \hspace{1cm} (4.8.6)

where, $g_1$ and $g_2$ are $g$ factors associated to the different principle axes in the rotation, and $\varphi$ is the angle between the field and the principle axis, $\varphi_0$ is an offset angle. The conversion between the $g$ factor and the resonance field is made by $g\mu_B H = h\nu$ or in convenient units

$$g = \frac{0.71449 \times \nu [MHz]}{H_{res}[G]}$$  \hspace{1cm} (4.8.7)

Angular dependance in the $ac$ plane

Due to the size of the sample space in the cavity, and the needle shape of the single crystals of CuCl$_2$, it is difficult to mount a large crystal for a rotation of the field in the $ab$ plane. Fortunately, the $ac$ plane does not have the same problem, as the $b$ axis is then perpendicular
to the field direction and selected well shaped large crystals can be mounted without cutting. Cutting the crystals very often leads to a separation of the crystals into a frayed like sample. Two crystals were investigated in this manner. The domain population in the twin is expected to be approximately equal in a large crystal. In a smaller crystal, the domain population of the twin could be imbalanced, and this was indeed the case when several small crystals were checked by X-ray diffraction. In this way we can test our interpretation by performing ESR on both type of crystals.

The dimensions of the single crystal used for ESR was $b \approx 10 \text{ mm}$, $a \approx 2 \text{ mm}$ and $c \approx 2 \text{ mm}$. The crystal was aligned such that the $b$ axis was perpendicular to the field, and the $a$ axis was approximately aligned to be parallel to the field at zero degrees ($\varphi = 0$). The angular dependence was investigated at 100 K. The temperature was stable within 0.1 K during the measurement.
The plots of the resonance position and linewidth as a function of angle are shown in fig 4.35 and 4.36 respectively. Let us first address the resonance position. The black squares in fig 4.35 represent the data points which results from the fit of eqn 4.8.4. The solid lines are a fit of eqn 4.8.6 to these data points. From the data it is evident that two resonance lines exist with a similar angular dependance but shifted in their resonance position by about 30 degrees. A third line considerably less intense is also visible, but the resonance position has a much smaller dependance on angle. At present we attribute this line to intergrown crystallites or from deteriorated crystallites at the crystals surface. The fitting of the $g$ factors to the lines involved 4 parameters, two $g$ factors, $\varphi$ and an offset angle ($\varphi_0$) according to equation 4.8.6. The intensities of the three lines is such that the signal coming from the normal axis is the same as the twin axis. The intensity of the third line from intergrown crystallites is around 30% that of the normal and the twin axes.

When going from one principle axis to another, gives the effect of going from a maximum in the resonance to a minimum. To deduce which signal comes from the twin or normal axis, it is important to define the starting conditions. We will always talk in terms of the axis as defined in fig 4.31. The sample was mounted such that the $a$ axis (the cleavage plane is the $ab$ plane, so that $a$ is $\perp$ to $b$) was at zero degrees. In the twin this corresponds to the $c'$ axis. As $a$ is not a principle axis, we can distinguish between the twin and the normal part in the following way. There are two conditions which indicate that the crystal was aligned at zero degrees along $c$ in the twin, $c'$, or along $a'$ in the untwined axis being 30 degrees away from $a$ towards $c$. The condition is that the first two axis come from the same principle axis. It can be shown that the only way this is justified is if we start with $c'$ at zero, then a rotation in the $ac$ plane would produce $c$ at 60 degrees, $a''$ at 90 degrees and $a'$ at 150 degrees given that no offset is present ($\varphi_0 = 0$). As shown in fig 4.35 the resonance positions of the two intense lines can be fitted with these assumptions allowing an offset (= misalignment) of $\varphi_0 \approx 15^\circ$. The phase difference in this case would be $\approx 30$
Figure 4.35: Resonance position as a function of angle for the rotation in the ac plane. Black squares represent the data points. Lines are the fit according to eqn 4.8.6. Three lines are shown, the black dashed line is from a polycrystalline piece. The solid black line is from the normal axes and the solid red line is the signal from the twin axes.

degrees and this is the offset parameter. As zero degrees in the rotation is between $a'$ and $c'$ the offset in each case is $\pm 15^\circ$. The results for the $g$ factor is such that along the principle axis $c$, the best fit gives $g_c = 2.273 \pm 0.001$ and along the principle axis $a'$, $g_{a'} = 2.065 \pm 0.001$.

This procedure allows us to separate which signal comes from which axes (the twin or normal) so then we can look at the linewidth of these signals. The linewidth of both the normal and twin axes are given in fig 4.36. The signal from the normal axis of the crystal gives a clearer angular dependence than the twin part. A maximum is seen in the normal
Figure 4.36: Experimental linewidth as a function of angle for the rotation in the $ac$ plane. Closed squares: signal from the normal axis. Red closed squares: signal from the twin axis. Solid line are connecting the data points. Solid lines are the calculation of $\Delta(1 + \cos^2\Theta)$ showing the approximate cosine dependence.
part along the c axis, and a minimum is seen along the a' axis. The apparent fluctuations at other angles (around 40 and 220 degrees) arise when lines merge and problems arise to deconvolute the spectrum. Difficulties with the deconvolution could also be the origin for the different amplitude of the linewidth of the the mirror twins.

The dependance on temperature will be analyzed in a later section. Next we look at the rotation of the crystal in the ab plane.

**Angular dependance in the ab plane**

In this section the angular dependance of the lines is shown in the ab plane. The crystal, with dimensions b ≈ 2 mm a ≈ 0.5 mm and c ≈ 0.5 mm was mounted such that in the initial position (φ = 0), the chain axis (b) was chosen to be approximately aligned with the magnetic field. Therefore at 90 degrees, this should correspond to the c' axis which is perpendicular to b, or the a' axis. The a' axis is not perpendicular to the chain axis in the rotation, but is ≈ 30 degrees towards c. This could be the case if the crystal is not perfectly aligned flat in the ab plane, but is slightly elevated so that it is in the a'b plane. This is feasible since the alignment was done by visual inspection only. The rotation and data collection was done at 50 ± 0.1 K. Fig 4.37 and 4.38 shows the angular dependance for the resonance position and the linewidth, respectively. Let us first address the resonance position. There exist three lines as in the ac plane rotation. As there is no twinning along the b axis, we would expect there to be one signal, but given the intergrowth and polycrystal pieces in the sample, this means that other g factors will be present. From the analysis of this crystal in the ac plane, we would expect one signal to come from the normal structure, to give a characteristic dependance at b and at a'. By fitting all three lines, it is clear that varying the g factors only one line exactly matches that found for the ac rotation along a, which gives the minimum along b. The g factors given in this case are $g_{a'} = 2.065 \pm 0.001$ along a' and along b, $g_b = 2.235 \pm 0.001$. The other two lines represented by a maximum
Figure 4.37: Resonance position as a function of angle for the rotation in the $ab$ plane. Black squares represent the data points. Solid lines are the fit according to eqn 4.8.6. Three lines are shown, the black dashed line one is from the polycrystalline piece. The black solid line originates from the normal axis and the red solid line from the twin axis.

along $b$ and minimum along $a$ also have an angular dependance. Interestingly, the line with the minimum along $a'$ with respect to the normal crystal has a $g$ factor of $g_{pol} = 2.19 \pm 0.01$, which is the average of all the $g$ factors found along, $a'$, $b$ and $c$, indicating that this is indeed could be a polycrystalline piece with some preferred orientation. Therefore, we expect that the crystal was aligned in the $a'b$ rather than the $ab$ plane.

The linewidth dependance on angle is shown in fig 4.38, the open squares represent the signal from the normal crystal. It is shown that the linewidth is constant as it passes through the $b$ axis, and there is a minimum along the $a'$ axis, as seen also in the $ac$ plane rotation. The final $g$ factors coming from each principle axes are

$$g_{a'} = 2.065 \pm 0.001$$  \hspace{1cm} (4.8.8)
Figure 4.38: Linewidth as a function of angle for the rotation in the \(ab\) plane. Lines connecting the data points are a guide for the eyes. The open squares are originating from the polycrystalline piece. Black closed circles is the signal originating from the normal axis. Open red circles are from the twin axis. Solid lines are the calculation of \(A(1 + \cos^2\Theta)\) showing the approximate cosine dependence.
\[ g_b = 2.235 \pm 0.001 \]  
\[ g_c = 2.273 \pm 0.001 \]

4.8.4 'De-twinning' the twin

In this section we will deal with only the signal from the normal part of the crystal and compare each rotation. This was done by taking the results of the fits from the previous section for the lines that correspond to the so-called normal part of the crystal, so that the twin signal and the intergrowth part are not discussed further. Even though the rotation in the \( ac \) and \( ab \) planes were done at different temperatures, at 100 and 50 K respectively, this should not give much difference in the \( g \)-factors. However, in the case of the linewidth, we could see differences as the temperature at 50 K is where the maximum lies in the heat capacity and susceptibility, which would yield a different value than at 100 K. Next, we will compare the signal from the \( ac \) and \( ab \) plane rotation.

Fig 4.39 shows the resonance position for the \( ac \) (closed green squares) and \( ab \) (open blue circles) plane rotation. The extra features on the \( ab \) plane at 65 and 150 degrees, could come from fit deconvolution problems in the fit procedure, as lines merge at these angles. In fig 4.40 the linewidth is plotted as a function of angle, with the \( a \) axis located at 0 degrees. It can be seen that at the \( a' \) axis there is a minimum in both rotations, followed by a relatively flat region going to \( b \), and a maximum going to \( c \). The \( c \) axis is well defined probably because of the large crystal that was chosen for the \( ac \) rotation, so there is no ambiguity in the line. The \( ab \) plane rotation is not as well defined due to the smaller signal which was half of the signal from the polycrystalline pieces. The solid lines in figure 4.40 are a calculation of the function \( A(1 + \cos^2(\Theta)) \) which describes qualitatively the cosine dependance on the angle. The constant \( A \) is a scaling quantity.
Figure 4.39: Measured resonance position as a function of angle for the rotation in the \( ab \) plane (open circles) and \( ac \) plane (closed squares).

Figure 4.40: Linewidth as a function of angle for the rotation in the \( a'b \) and \( a'c \) plane. The solid lines are a fit to the function \( A(1 + \cos^2(\Theta)) \) showing the cosine dependance.
4.8.5 Estimation of the major perturbations causing the ESR line broadening in CuCl$_2$

The Hamiltonian due to an exchange coupled magnetic system can be described as

$$ H = H_0 + H' $$

(4.8.11)

$H_0$ consists of the isotropic exchange between spins and the Zeeman interaction given by

$$ H_0 = J \sum_i S_i \cdot S_{i+1} - \mu_B \sum_i S_i \cdot g \cdot h $$

(4.8.12)

where $g$ is the $g$-factor, $J$ is the exchange interaction along the chain assuming nearest neighbour interactions only, $h$ is the applied field and $\mu_B$ is the Bohr magneton. The perturbation $H'$ comprises of all the terms which may cause line broadening. Line broadening can be caused by dipolar interactions, anisotropic exchange, antisymmetric exchange, single ion anisotropy and hyperfine interactions. The first three contributions in general are much larger, and the rest can usually be neglected. The perturbation term, $H'$ in eqn 4.8.11 can be written as (see e.g. [24])

$$ H' = H_{DD} + H_{AE} + H_{DM} $$

(4.8.13)

The effect of the line broadening of the three perturbations can be calculated by the second moment [102] as given by Yamada et al. [109]

$$ M_2^{DD} = \frac{3g^2\mu_B^2}{2} \left( \sum_{i>j} \frac{1}{r_{ij}^3} \right)^2 S(S+1)(1+\cos^2(\theta)) $$

(4.8.14)

$$ M_2^{AE} = \frac{3}{2g^2m\mu_B^2} |A_{i,i+1}|^2 S(S+1)(1+\cos^2(\theta)) $$

(4.8.15)
\[ M_{2}^{DM} = \frac{1}{3g^{2}m_{u}^{2}}|d_{i,i+1}|^{2}S(S+1)(1 + \cos^{2}(\theta)) \]  
\eqref{eq:4.8.16}

where \( r \) is the Cu-Cu distance, \( \theta \) is the rotation angle when going from one principle axis to the other, \( |A_{i,i+1}| = (\Delta g/g)^{2}|J| \), \( |d_{i,i+1}| = (\Delta g/g)|J| \) with \( \Delta g = |g - 2| \). Each of these terms will be analyzed for the \( b \) axis (chain axis) of CuCl\(_{2}\).

**Dipole-dipole exchange perturbation**

The only parameter in eqn 4.8.14 is the Cu-Cu distance, \( r \) and the \( g \) factor along the chain. In the case of CuCl\(_{2}\), \( r = 3.30 \) Å and from ESR measurements at high temperature \( g_{b} = 2.235 \). The angular variation \( (1 + \cos^{2}(\theta)) \) is fixed to 1 \( (\theta = 90^\circ) \) and \( S = 1/2 \).

\[ M_{2}^{DD}[A^{2}/m^{2}] = \frac{3 \times 2.235^{2}\mu_{B}^{2}}{2} \left( \frac{1}{(3.3\text{Å})^{3}} \right)^{2} \frac{3}{4} \]  
\eqref{eq:4.8.17}

\[ = 3.692 \times 10^{12} [A^{2}/m^{2}] = 3.7 \times 10^{6} [\text{Oe}^{2}] \]  
\eqref{eq:4.8.18}

**Anisotropic exchange perturbation**

The anisotropic exchange is calculated from eqn 4.8.15. The exchange integral \( J_{nn} \) is taken from the analysis of the susceptibility data assuming a \( S = 1/2 \) antiferromagnet Heisenberg chain with uniform nearest neighbour interaction \( J_{nn}/k_{B} = 110 \) K. The anisotropic exchange second moment is then

\[ M_{2}^{AE}[A/m] = \frac{3}{2 \times 2.235^{2}\mu_{B}^{2}} \left( \frac{[2.235 - 2]}{2.235} \right)^{2} \frac{110 \times k_{B}}{2} \times \frac{3}{4} \]  
\eqref{eq:4.8.19}

\[ = 0.65028 [A/m] = 6.5 \times 10^{7} [\text{Oe}^{2}] \]  
\eqref{eq:4.8.20}
Antisymmetric exchange perturbation

The same parameters are used as before, yielding for the *antisymmetric* exchange perturbation

\[ M_{2}^{DM} [\text{A/m}] = \frac{1}{3 \times 2.235^2 \mu_B^2} \left( \frac{2.235 - 2}{2.235} \right)^2 \times 3/4 \]

\[ = 14.715 \ [\text{A/m}] = 1.5 \times 10^9 \ [\text{Oe}^2] \]  

4.8.6 Major perturbation in CuCl₂

It follows from these calculations that along the \( b \) axis in CuCl₂

\[ M_{2}^{DM} \gg M_{2}^{AE} > M_{2}^{DD} \]  

According to ref [109], the linewidth is given by,

\[ \Delta H = \frac{h^2 M_2}{g \mu_B |J_{m}|} \]

Using our values as calculated above, we can use this relation to calculate the effect of line broadening on the ESR line for each perturbation. The value of \( J_{m} \) is the same as used above. The values calculated are given below

\[ \Delta H_{DD} \simeq (3 - 10) \ \text{Oe} \]

\[ \Delta H_{AE} \simeq (50 - 200) \ \text{Oe} \]

\[ \Delta H_{DM} \simeq (1000 - 2000) \ \text{Oe} \]
Theoretically, this would give the major line broadening at room temperature coming from the D-M interaction: all other interactions are small compared to this one. Experimentally, by looking at the magnitude of the linewidth as a function of rotation and also of temperature reveal that the major contribution from perturbation effects actually comes from the anisotropic exchange contribution. Indeed, the antisymmetric exchange is zero, by symmetry in the space group of CuCl$_2$ (see e.g. [24] page 33). Therefore, this does not contribute to the broadening of the linewidth. It would predict that the linewidth at room temperature should be of the order of kOe. This is not observed experimentally. The plot of the angular dependence of the different interactions is shown in fig 4.41. The closed circles are that from the ac rotation with the large crystal. It should be noted that the only extra parameter used to compare the theory with the experimental data is an offset angle corresponding to misalignments of the crystal, so that the minima lie at the same
4.8.7 Temperature dependance of the ESR linewidth and intensity along the principle crystallographic directions

In this chapter, the temperature dependance of the linewidth, resonance position and intensity will be shown for the three principle crystallographic directions. As we always have three lines in the spectra, they merge to give one broad line at higher temperatures \((T \geq 100\, \text{K})\). Consequently, at higher temperature it is very difficult to resolve each line as we have to fit nine parameters to an observation that is eventually one line (in which 3 parameters would be sufficient). Depending on which signal we are interested in, depends how far in temperature we can fit without making large errors. In general, we could fit the data until \(T \sim 250\, \text{K}\). Starting with the resonance position as a function of temperature, the insert of figure 4.42 shows the temperature dependance along \(a^*, b\) and \(c\). The standard behaviour is seen for the \(a\) and \(c\) axes, with the resonance position varying very little across the whole range. However, along the \(b\) axis this behaviour is observed up to 160 K and then due to the broadening of the line and losses in intensity large errors are introduced.

Fig 4.42 shows the temperature dependance of the linewidth along the \(a\), \(b\) and \(c\) directions. To a good approximation all directions produce a linear dependance with temperature above \(\approx 50\, \text{K}\). The discontinuities that are seen at certain temperatures, are ascribed to systematic errors coming from the fits of the spectra, as increasing the temperature broadens the three signals into one.

Lastly, the temperature dependance of intensities can be compared with the SQUID
Figure 4.42: Linewidth as a function of temperature along the three principle directions. Insert: Resonance position as a function of temperature along the three principle directions. Note that the discontinuities at higher temperatures arise from the fitting procedure.

Figure 4.43: Intensity as a function of temperature along the three main directions. Insert: comparison with the SQUID susceptibility.
signal. In Fig 4.43 the intensity for each direction is shown as a function of temperature. All the intensities fall off quickly as a function of increasing temperature (note that the \( b \) axis intensity is smaller than the other axes due to the the smaller crystal used so cannot be compared). As the ESR intensity follows the SQUID measurements, there should be some correspondence. At approximately 70 K, there is a maximum in the susceptibility due to one dimensional short range antiferromagnetic correlations. Interestingly this is not observed in the ESR signal, rather a somewhat sharper maximum appears at 40 K. This is seen in all three directions, but more so in the \( a' \) direction because of the clearer signal. The insert of Fig 4.43 shows a direct comparison with the ESR signal from the \( a' \) direction with the susceptibility also along this direction. In the case of the susceptibility, we have an averaged effect, due to the twin and polycrystalline pieces. However, for the ESR signal we are following one contribution only, so are separating out the response from the non-crystalline pieces. This could affect the comparison.

4.9 Discussion

In this chapter I have shown that CuCl\(_2\) and CuBr\(_2\) can be modelled as one dimensional magnets with competing interactions. By fitting the magnetic susceptibility and also the magnetic specific heat, it is shown that they can be explained by a model assuming a smaller antiferromagnetic nearest neighbour interaction and a larger antiferromagnetic next nearest neighbour interaction. High field measurements on CuCl\(_2\) single crystals have shown an interesting phase diagram in which there is a spin flop transition at \( \approx 4 \) T. The magnetic structure at zero field is shown to be incommensurate along the chain direction and results in a magnetic cell which is approximately four times larger than the crystallographic unit cell. The refined magnetic structure gives an \( ab \) plane helix and a moment of \( \approx 0.6 \mu_B \). ESR measurements on single crystals revealed the inherent twinning of all investigated
crystals and gave an anisotropic $g$ factor. From a detailed comparison of possible linewidth broadening effects I conclude the broadening of the signal is due to the anisotropic exchange perturbation. A summary of the magnetic properties of CuCl$_2$ and CuBr$_2$ is given in chapter 6.
Chapter 5

LiCuVO$_4$: An Ideal 1D frustrated magnet?

5.1 Previous work

First specific heat and susceptibility measurements on a powder sample of LiCuVO$_4$ found a short range ordering maximum at 20 K and the characteristic long range magnetic order transition at 2.5 K [111]. It was first argued that LiCuVO$_4$ can be described by a nearest neighbour exchange model only with an exchange integral $J \approx 44$K [111, 112, 113, 110]. However, the magnetic structure was determined by single crystal neutron diffraction [72] to be an incommensurate helix polarized along the chain direction similar to that of CuCl$_2$ and CuBr$_2$ as discussed before. The incommensurability was proposed to be caused by a scenario of frustration involving a nearest and next nearest interaction along the chain rather than a single $J$ model as described before e.g. eqn 4.3.1. Subsequent inelastic neutron scattering [21] found the nearest neighbour exchange being ferromagnetic ($J_1 \approx -12$ K), and the next nearest neighbour exchange being larger and antiferromagnetic ($J_2 \approx 41$ K), thus unquestionably confirming this scenario of frustration. Due to the low long
range ordering temperature and frustration in this compound, without crystal twining and moisture sensitivity, makes it an ideal system to study the effects of nearest neighbour and next nearest neighbour competing interaction. In the next few sections, I describe further work on LiCuVO₄ in an applied magnetic field, including the investigation of the phase diagram and the first observation of a two peak specific heat in zero field.

5.2 Crystal structure

LiCuVO₄ crystallizes in the inverse spinel structure, with an orthorhombic distortion due to a cooperative Jahn-Teller effect induced by the Cu²⁺ ions. LiCuVO₄ crystallizes with the space group *Imma* with lattice constants \( a = 5.6599 \) Å, \( b = 5.8108 \) Å, and \( c = 8.7595 \) Å [20]. Fig 5.1 shows the crystal structure, with the Cu²⁺ ions forming chains along the crystallographic \( b \) direction. Single crystals of LiCuVO₄, of dimension up to 12 x 4 x 4 mm³, were grown from solutions of LiCuVO₄ in a LiVO₃ or LiVO₃-LiCl melt according to the procedures described elsewhere [114]. Composition and homogeneity was checked using electron microprobe energy dispersive X-ray analysis (EDX). Elemental analysis, performed on several crystallites, revealed a slight homogeneity range on the Li, Cu, and V sites of approximate composition, \( \text{Li}_{0.99(1)}\text{Cu}_{1.02(1)}\text{V}_{1.00(1)}\text{O}_4 \).

5.3 High field magnetisation

Fig 5.2 and 5.3 shows the derivative of the magnetisation with respect to the magnetic field, up to 55 T for \( H \parallel c \) and \( H \parallel a \) respectively. For \( H \parallel c \) there exist two features, one of them at 40.7 T which marks the saturation field. This value is in good agreement with the field strength required to break the exchange interaction as deduced by inelastic neutron diffraction [21]. A second peak is seen when the field is applied along all crystallographic directions at 7.5 T. In addition, for \( H \parallel a \), a third peak is seen at 3.5 T. From the magnetic
Figure 5.1: Crystal structure of LiCuVO$_4$ according to [20]. Spatially separated Cu$^{2+}$ chains can be seen along the crystallographic $b$ axis. The grey tetrahedra are VO$_4$ tetrahedra.
structure [72], one could expect a spin-flop phase transition for $H \parallel a$, as the spins lie in the $ab$ plane, similar to what happens for CuCl$_2$ as seen for $H \parallel b$ in the previous chapter. However, for a field applied parallel to $c$ one gets a singularity in the magnetisation at 8.5 T. One would not expect such a spin-flop like transition to occur for $H \parallel c$ because the helix lies in the $ab$ plane. In addition, an anisotropic field of 9 T is quite large. Therefore, we interpret this extra transition at low field not to be due to a local anisotropy field resulting in a spin flop like phase. Following on from the high field data, I discuss next the investigation of the nature of the 9 T transition.

The magnetization ($M - H$ curve) of an antiferromagnetic chain with nearest and next nearest neighbour interaction at zero [115] and finite temperatures [116] was calculated
using DMRG$^1$ in the thermodynamic limit for various ratios of $J_2/J_1$ of the frustration parameter, $\alpha$. At zero temperature, a so-called “middle field cusp singularity” (MFCS) was seen in the $M - H$ curve for $\alpha > 0.25$. The responsible mechanism for this cusp singularity was the difference in the dispersion curve as the parameter $\alpha$ is changed. For $\alpha \leq 0.25$, the dispersion of a “one down spin” has one minimum. For $\alpha > 0.25$, at $k = \pi$ a local maximum and two minima appear at either side of the maximum. These maxima lead to a van Hove type singularity in the magnon density of states leading to the cusp in the magnetization. To reveal such effects in real materials a finite temperature calculation was calculated showing that increasing the temperature decreases the effect of the MFCS.

Using DMRG calculations the magnetisation was calculated using the parameters from inelastic neutron scattering, to see if there is any middle field cusp singularity in this parameter regime. In this case from neutron measurements, we have $\alpha (=J_2/J_1) = -3.5$. The

$^1$These calculations have been preformed for this work by F. Heidrich-Meisner and A. Honecker.
results of the calculations are shown in fig 5.4. They have been obtained for system sizes, $N = 48, 72, 120$ and $156$. In all cases we see no magnetisation change by a jump or a singularity. Therefore in this parameter range of LiCuVO$_4$ we have no evidence of a middle field cusp singularity.

The next section will show the phase diagram constructed from three different experimental techniques, and a discussion of the possible phase transition at 9 T.

### 5.4 Low temperature phase diagram

The low temperature phase diagram has not been investigated in detail until now. It offers the possibility as with CuCl$_2$ to see other phases in an applied field. In this section, I show
the phase diagram along all crystallographic directions by three different experimental techniques, high field magnetisation, specific heat and magnetic susceptibility measurements.

5.4.1 $H \parallel c$

The phase diagram $H \parallel c$ is shown in fig 5.5. The application of a magnetic field along $c$, therefore perpendicular to the spin plane, produces two phases. Due to the low temperature of the long range order, it makes it difficult using only commercial equipment to determine an accurate phase diagram at very low temperatures, i.e. below 1.5 K. However, we have detected two low temperature phases, one is the helical phase as solved by neutron scattering. The second phase, at $\sim 8$ T ($T = 0$), is currently unknown and is not a MFCS as discussed above. It is most likely not due to local anisotropies, resulting in a spin flop field, due to the large magnetic field required to induce it. Rather it may represents a complete reorientation in magnetic structure, i.e. the spins are not only in the $ab$ plane but have a component perpendicular, or more exotically, a field induced spin liquid phase. Further studies are necessary to reveal the nature of this phase.

5.4.2 $H \parallel b$ and $H \parallel a$

With the magnetic field applied in the plane of the helix, i.e. in the $ab$ plane, offers a rich phase diagram. In this case, we reveal 3 distinct phases. Like in the case of CuCl$_2$, above a field of approx 3.5 T there exists a phase in which the spin structure changes in the plane, this is likely to be a spin flop phase. In addition, there is also another phase, like for the case of $H \parallel c$, which is still not understood. In fig 5.7 the dashed line represents a tentative phase boundary which was difficult to follow with our experimental equipment ($T_{min} \approx 1.8$ K, $H_{max} \approx 9$ T).

As for the case of CuCl$_2$, there exists a spin flop phase with $H \parallel b$. However, due to the twinning of the CuCl$_2$ single crystals, it may not be possible to detect a spin flop in the $a$
Figure 5.5: Phase diagram of LiCuVO₄ with $H \parallel c$. Closed circles: specific heat measurements, closed triangles: susceptibility, closed squares: high field measurements. Dashed lines represent tentative phase boundaries.

Figure 5.6: Phase diagram of LiCuVO₄ with $H \parallel b$. Closed circles from specific heat measurements, closed triangles from susceptibility, closed squares from high field measurements. Dashed lines represent tentative phase boundaries.
directions, although it is argued that it probably may exists. The interesting difference is at high fields, where CuCl₂ only has one phase in an applied field when the field is applied in the spin plane. Further neutron scattering measurements are required to understand the interesting phases of LiCuVO₄ in an applied field.

5.5 Two peak specific heat

In addition to the interesting low temperature phase diagram, and to the low ordering temperature, an investigation of the specific heat of LiCuVO₄ at $T \geq T_N$ is of interest. In this section the two peak specific heat nature of LiCuVO₄ is shown. Theoretically, much work has been carried out on the two $J$ model for a one dimensional Heisenberg antiferromagnet ever since the discovery of non-classical ground states that can exist for a frustrated model [15, 70]. Calculation of the thermodynamic properties resulted in possible
novel excitations of a domain wall type [117]. However, due to finite size results, the low temperature behavior of the specific heat was considered not reliable. It was reported that two maxima were seen in the specific heat for a frustration parameter of $\alpha = J_1/J_2 = 0.2$ [118]. More recently, much theoretical work has been carried out using density-matrix renormalization group (DMRG) technique [119] which does not suffer from the sign problem as in the case of Monte Carlo simulations, and also not from finite size effects as with full diagonalization techniques. A recent study showed two peaks in the low temperature specific heat using transfer-matrix renormalization group method (TMRG) in the parameter range $\alpha = -0.3$ [120].

There is no diamagnetic compound isostructural to LiCuVO$_4$ which could serve as an adequate reference for the phonon contribution to the heat capacity and a phonon spectra is not available at present. We therefore constructed the lattice contribution to the heat

Figure 5.8: Specific heat of LiCuVO$_4$. Closed black circles: raw specific heat data including the magnetic and lattice contribution, dashed black line: lattice estimation. Red open circles: magnetic contribution to the specific heat. Blue solid line: Full diagonalization calculation for 20 sites with $J_1 = -12$ K and $J_2 = 41$ K.
capacity at intermediate temperatures using an extended Debye approach. The lattice contribution was estimated from

$$C_{lat}(T) = \beta_1 T^3 - \beta_2 T^5 + \beta_3 T^7 - \beta_4 T^9 + \ldots \quad (5.5.1)$$

For $T \leq 100$ K, we found the best description using $\beta_1 = 0.17$ mJ/molK$^4$, $\beta_2 = 2.65 \times 10^{-8}$ J/molK$^5$, $\beta_3 = 2.06 \times 10^{-12}$ J/molK$^8$ and $\beta_4 = 6.27 \times 10^{-17}$ J/molK$^{10}$. Using $\beta_1$ and seven atoms per formula unit, we arrive at a Debye temperature $\Theta_D(T = 0) \approx 400$ K. Similar values have been reported for other copper based edge sharing compounds [121].

The solid blue line in fig 5.8 is the full diagonalization of the following Hamiltonian up to chain fragments with 20 members

$$H = J_1 \sum_i S_i S_{i+1} + J_2 \sum_i S_i S_{i+2} \quad (5.5.2)$$

with $J_1 = -12$ K and $J_2 = 41$ K as deduced from INS measurements. Using the ALPS libraries [84] we then diagonalized the Hamiltonian for a $N = 20$ ring. The measured raw data in fig 5.8 clearly shows the peak at 12 K. It should be noted that the first peak at 12 K does not come from short range order, using the exchange parameters from INS gives a broad short range order maximum at 32 K which is also seen in the magnetic heat capacity. Therefore we must conclude that another mechanism is responsible for it. The reason why the peak at 12 K is seen better than the peak at 32 K is due to the plot of $C_p / T$ which magnifies the low temperature region, so that the low temperature peak at 12 K can be clearly seen. Fig 5.9 shows a log-log plot of the magnetic heat capacity of LiCuVO$_4$ showing the clear two peak nature. The arrow shows the position of the second low temperature peak. Also plotted is the result of the full diagonalization calculation with $J_1 = -12$ K and $J_2 = 41$ K, this shows that the second peak can be fitted using these exchange integrals from INS experiments. Using a nearest neighbour only model does not show a second feature in the low temperature region.
Fig 5.9: Specific heat of LiCuVO$_4$. Open black circles: magnetic specific heat. Red solid line: Two $J$ model with $J_1 = -12$ K and $J_2 = 41$ K. Blue dashed line: nearest neighbour only exchange $J_{nn} = 44$ K.

Fig 5.10 shows a plot of the heat capacity as a function of temperature and the effect of a magnetic field on the heat capacity of single crystals of LiCuVO$_4$ with $H \parallel c$. At 9 T the transition broadens. The broad peak at 12 K still remains, but the maximum shifts to lower temperatures.

Our calculations for the specific heat for a range of the frustration parameter $\alpha$ shows a two peak feature in the specific heat originating from frustration. For large $\alpha$, i.e. for large $J_1$, the effect of the two peaks in the specific heat is clear (see figure 5.11), this results from a large nearest neighbour and smaller next nearest neighbour interaction. As $\alpha$ is reduced the effect of the second peak becomes smaller, until at $\alpha = -0.3$ it is barely visible. This effect is in agreement with our specific heat measurements which shows a very small peak, almost as a shoulder to the main short range order peak, as a result of a more dominant next nearest neighbour interaction. However, the effect is still visible even at this reduced $\alpha$. 
Figure 5.10: Low temperature second peak as a function of magnetic field. Néel temperature is shown at $\sim 2.5$ K.

Figure 5.11: Specific heat per site against reduced temperature for $N = 20$ sites. The effect of the second low temperature peak on increasing the frustration ratio, $\alpha$, is shown by the arrows.
5.6 Discussion

The title of this chapter poses a question regarding whether or not LiCuVO$_4$ can be described as an ideal one dimensional frustrated compound. In this chapter I have shown that there are many properties that this compound exhibits which shows it to close to an ideal case. First of all, the low long range ordering temperature at 2.5 K, gives us an idea that the interchain coupling is sufficiently weak compared to the intrachain coupling. This has been further substantiated by inelastic neutron scattering, which also shows that this compound has a weaker nearest neighbour coupling and a stronger next nearest neighbour coupling, giving rise to frustration along a chain. Furthermore, we have found a two peak feature in the specific heat which originates from the frustrated nature of the exchange integrals, and gives a ferromagnetic and antiferromagnetic component to the magnetic specific heat. Although the zero field properties of the one dimensional compound LiCuVO$_4$ are largely understood, the field dependance has not been investigated until now. It has been shown that with applied field there exists more than one phase. When the field is applied in the spin plane i.e. along $a$ or $b$ axes we encounter 3 phases. The first is the helical phase which extends up to $\sim 3$ T. Then another phase occurs which is assigned to a spin flop phase due to local anisotropy. Possibly the most interesting phase transition occurs at $\sim 8$ T when the field is applied along any axes. We investigated this in terms of a middle field cusp singularity. However, with a frustration parameter of $\alpha = -0.3$, a middle field cusp singularity should not be expected. Therefore, this phase transition is either due to an essential change of the magnetic structure, or more exotically to a transition to a spin liquid phase. Additional neutron scattering experiments are required to understand the magnetic structure in these new phases with experimental facilities which are equipped with high magnetic fields (currently up to 15 T) in order to do a full investigation.

In summary, this section has shown that LiCuVO$_4$ represents an ideal one dimensional
frustrated system, by its fortunate relation of intra to inter-chain exchange. The simple crystal structure and the availability of large single crystals make LiCuVO$_4$ an ideal system for further investigations.
Chapter 6

Common physics and outlook in 1D frustrated chains

The common properties of edge sharing cuprates offer surprising and intriguing results. In this chapter I will briefly summarize known compounds which share common physics due to the edge sharing nature of their geometry. As shown in chapter 3 on the properties of magnetism in edge and corner sharing cuprates, due to the nature of the Cu 3d and O 2p orbitals the difference in the edge and corner sharing cuprate is profound and in both cases very interesting. As seen in fig 3.7, there exist different ground states for a one dimensional chain with competing nearest and next nearest neighbour interactions depending on the sign and magnitude of the exchange interactions. I will summarize in this section properties of other compounds which lie in the frustrated helical part of this phase diagram. So far there have been 5 compounds (two of which are introduced in this thesis, CuCl₂ and CuBr₂) identified which have a Cu-X-Cu bond angle close to 90 degrees (see table 6.1), with strong one dimensional correlations and with incommensurate helical ground states.

6.1 Magnetic structures

The most common properties that are shown by these compounds with frustration in one dimension is the occurrence of an incommensurate magnetic structure in the long range
Table 6.1: Crystallographic properties of one dimensional frustrated compounds. The configuration for LiCu$_2$O$_2$ and NaCu$_2$O$_2$ are shown in detail in fig 6.1.

<table>
<thead>
<tr>
<th>Compound name</th>
<th>space group</th>
<th>Cu-Cu distance (Å)</th>
<th>Cu - X - Cu angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCuVO$_4$ [20]</td>
<td>Imma</td>
<td>2.905</td>
<td>94.96</td>
</tr>
<tr>
<td>LiCu$_2$O$_2$ [22]</td>
<td>Pnma</td>
<td>2.861</td>
<td>89.52 / 89.70</td>
</tr>
<tr>
<td>NaCu$_2$O$_2$ [23]</td>
<td>Pnma</td>
<td>2.933</td>
<td>94.81 / 95.87</td>
</tr>
<tr>
<td>CuCl$_2$ [82]</td>
<td>C 2/m</td>
<td>3.000</td>
<td>93.644</td>
</tr>
<tr>
<td>CuBr$_2$ [83]</td>
<td>C 2/m</td>
<td>3.474</td>
<td>92.028</td>
</tr>
</tbody>
</table>

Figure 6.1: Different Cu-O-Cu bond angles in a CuO plaquette for a) LiCu$_2$O$_2$ [22] and b) NaCu$_2$O$_2$ [23].
ordered phase. This incommensurate magnetic structure is the key indication that frustration plays a large role in these compounds by providing a spin structure that is not commensurate with the lattice. Furthermore, in all cases, the propagation vector roughly quadruples the magnetic unit cell in regard to the nuclear unit cell. The magnetic structure is characterized by a polarized helix along the chain. Table 6.2 summarizes the magnetic properties for the five compounds. The first two columns list the exchange integrals, \( J_1 \) being the nearest neighbour exchange and \( J_2 \) the next nearest neighbour exchange along the chain. In this case the values are taken from susceptibility fits and magnetic specific heat, if available. In the case of the magnetic susceptibility, there will be three parameters, \( J_1 \) and \( J_2 \) and also a \( g \) factor. Usually the \( g \) factor has been measured \textit{a priori} by ESR. The third column is \( \alpha \), which is the ratio of \( J_2 \) to \( J_1 \). The fourth column is the long range ordering temperature. The fifth to seventh columns are required to describe the magnetic structure, in terms of the propagation vector \( \xi \), the Cu-Cu spin angle and the ordered moment. The last few columns give the maximum temperatures of the broad short range ordering anomalies from the specific heat and the susceptibility, if known. The common magnetic structure then gives the possibility of a common phase diagram as discussed in the next section.

### 6.2 \( H - T \) phase diagrams

The properties of a common magnetic structure gives the possibility of a common phase diagram, once the magnetic properties are determined by interaction along the chain. Indeed, if we construct a temperature-field phase diagram, then we can see common properties. At low fields, due to local anisotropy, these compounds undergo a spin flop phase when the field is applied along the chain and also perpendicular to it (but still in the helix plane, i.e. along \( a \) in LiCuVO\(_4\)). However, in most of the compounds, twinning is present in single crystals.
Table 6.2: Magnetic properties of one dimensional frustrated compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( J_1 ) (K)</th>
<th>( J_2 ) (K)</th>
<th>( \alpha )</th>
<th>( T_N ) (K)</th>
<th>( \xi )</th>
<th>Cu-Cu spin angle, ( \phi ) (°)</th>
<th>( \mu_{Cu} ) (( \mu_B ))</th>
<th>( T_{\text{max}}^{\parallel} ) (K)</th>
<th>( T_{\text{max}}^{\perp} ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCuVO(_4)</td>
<td>-12</td>
<td>40</td>
<td>-3.3</td>
<td>2.5</td>
<td>0.532</td>
<td>83.6</td>
<td>0.31</td>
<td>32</td>
<td>28</td>
</tr>
<tr>
<td>LiCu(_2)O(_2) [73, 122]</td>
<td>-95</td>
<td>95</td>
<td>-1</td>
<td>22</td>
<td>0.174</td>
<td>62.6</td>
<td>?</td>
<td>?</td>
<td>37</td>
</tr>
<tr>
<td>NaCu(_2)O(_2) [74]</td>
<td>-47</td>
<td>90</td>
<td>-2</td>
<td>13</td>
<td>0.227</td>
<td>81.7</td>
<td>0.56</td>
<td>38</td>
<td>52</td>
</tr>
<tr>
<td>CuCl(_2)</td>
<td>30</td>
<td>120</td>
<td>4</td>
<td>23.9</td>
<td>0.224</td>
<td>80.6</td>
<td>0.63</td>
<td>56</td>
<td>71</td>
</tr>
<tr>
<td>CuBr(_2)</td>
<td>85</td>
<td>340</td>
<td>4</td>
<td>74</td>
<td>0.245</td>
<td>88.6</td>
<td>?</td>
<td>?</td>
<td>220</td>
</tr>
</tbody>
</table>

Therefore it may not be possible to see the effect in which direction the spins point from susceptibility measurements. Three to four of the five compounds in table 6.1 are thought to be twinned, and only single crystals of LiCuVO\(_4\) are free from twinning. In LiCuVO\(_4\), as shown in the previous chapter, at \( \sim 9 \) T another phase appears when the field is applied along all crystallographic directions. This has not been seen in any other compound so far. The magnetic structure in the applied field phases has not been investigated yet for any of the compounds.

### 6.3 Effect of the Cu-X-Cu angle

The properties with regard to the magnitude and sign of the dominating exchange integral in these compounds are expected to depend strongly on the Cu-X-Cu angle.

Fig 6.2 shows the nearest neighbour exchange integral, tabulated in table 6.1, as a function of the Cu-X-Cu angle, as tabulated in table 6.2. The striking feature is that they fit on a straight line, only LiCu\(_2\)O\(_2\) differs. However, first inelastic neutron diffraction on twinned single crystals of LiCu\(_2\)O\(_2\) proposed that there exists three exchange integrals of equal strength [123]. In addition to the nearest and next nearest neighbour exchange along the chain the authors conclude a longer exchange over 4 nearest neighbours which is of
equal magnitude to the next nearest neighbour interaction. Therefore, only two exchange integrals as shown in table 6.2 may not be sufficient to explain the magnetic susceptibility. However, the four other compounds seem to fit nicely on a straight line from susceptibility fits using a two $J$ model. The crossover from a ferromagnetic to an antiferromagnetic nearest neighbour coupling occurs at $94.3 \pm 0.3^\circ$. A similar behaviour has also been seen in di-$\mu$-hydroxo bridges copper complexes [24]. It has been shown that the singlet-triplet separation is linearly dependant on the Cu-O-Cu angle. A plot of this behaviour is shown in fig 6.3. Therefore, for an angle less than $\approx 97^\circ$, the spin triplet lies lowest, while for greater than $\approx 97^\circ$ the spin singlet is the ground state.

Fig 6.4 shows the frustration parameter $\alpha$ as a function of the Cu-X-Cu angle. Once again the values follow an approximate straight line, only LiCu$_2$O$_2$ differs due to the different nature of the coupling as discussed above. This shows that the bond angle represents a guide
Figure 6.3: Angular dependance of the $J$ coupling in di-$\mu$-hydroxo bridge copper complexes. Data taken from [24].

to obtain an estimate of the sign and magnitude of the exchange integrals.

### 6.4 Phase diagram of a $J_1$-$J_2$ chain

Using DMRG calculations, Bursill et al. [15] formed the phase diagram of a $J_1$-$J_2$ chain as previously discussed in section 3.1.3. In this section, I show the location on the phase diagram of the compounds in table 6.2. The position (angle) of the compounds can be calculated from the frustration parameter $\alpha$ ($=J_2/J_1$) using the following relation given by Bursill

$$\omega = \tan^{-1}(\alpha)$$  \hspace{1cm} (6.4.1)

Using the values of $\alpha$ from table 6.2, the position of the compounds has been determined and are plotted in fig 6.5. The compounds introduced in this thesis, CuCl$_2$ and CuBr$_2$, are
on the phase diagram most nearest to the Majumdar-Ghosh point ($\omega_{MG}$), and represents one of the first experimental cases of a compound with an antiferromagnetic $J_1$ and $J_2$ exchange path. The other compounds lie on the negative $J_1$ (ferromagnetic) side of the phase diagram and LiCu$_2$O$_2$ is the nearest to the purely ferromagnetic ground state ($\omega_{FF}$). However, all compounds lie firmly in the frustrated regime of the phase diagram agreeing well between theory and experiment.

Using the information from $\alpha$ we can calculate, the classical pitch angle from the following formula given by Bursill for classical spin systems

$$\cos \phi = \frac{1}{-4\alpha} \quad (6.4.2)$$

For this we arrive at the following angles, LiCuVO$_4$ (85°), LiCu$_2$O$_2$ (75°), NaCu$_2$O$_2$
Figure 6.5: Phase diagram for a $J_1-J_2 S = 1/2$ chain taken from Bursill et al. [15]. On the phase diagrams are the compounds as presented in table 6.2 (compare with fig 3.7).
(82°) and 93° for both CuCl₂ and CuBr₂. The experimental pitch angles from the incommensurate wave vector are shown in table 6.2. It seems difficult to compare if the predictions from theory are experimentally realized, for example the comparison for LiCuVO₄ and NaCu₂O₂ seem to match the theoretical prediction, but for the other compounds the prediction is significantly different from the measured values.

Bursill also calculated the pitch angle as a function of ω. This is shown in fig 6.6. One of the main conclusions of this investigation was the difference between the classical pitch angle and the quantum pitch angle as obtained from DMRG calculations. The quantum pitch angle stays much closer to π/2 for varying values of ω than the classical pitch angle, which immediately deviates from π/2, as ω itself deviates from π/2. In fig 6.6 the experimental values of φ and ω have been plotted, from the propagation vector and the ratio of J₁ and J₂ in the case of each of the five compounds. It is interesting to see that they lie close to the classical estimation than the quantum (DMRG) estimate. Only LiCu₂O₂ and CuCl₂ deviate significantly. Of course in the case of LiCu₂O₂, a two J model was found not to be sufficient to describe the inelastic neutron scattering study. Therefore a two J fit to the susceptibility is probably not accurate to describe the magnetism and hence affects the significance of the value of ω. The results of CuCl₂ is quite surprising and at the moment and not fully understood. However, it seems interesting that the classical approximation can account quite well for the pitch angle for a number of these compounds.

6.5 Discussion and further work in frustrated one dimensional compounds

Compounds that exhibit one dimensional magnetism with frustration have been shown to have interesting features. It seems now that they can be modelled correctly in zero field. The magnetic structures are known, and reproduced in five compounds. Also the exchange
Figure 6.6: Pitch angle as a function of $\omega$ taken from Bursill et al. [15]. Also shown on the plot are locations of the compounds listed in table 6.2 lie. 1) CuBr$_2$ 2) CuCl$_2$ 3) LiCuVO$_4$ 4) NaCu$_2$O$_2$ 5) LiCu$_2$O$_2$. 
integrals, even when fitting the susceptibility by a two $J$ model, are quite robust. Inelastic neutron diffraction has shown that the model of magnetism, with a weaker nearest neighbour and a stronger antiferromagnetic next nearest neighbour interaction, is correct. However, the field dependant properties have not been studied until now. With the solution in zero field comes the interest in the properties in an applied field. It has been shown in this thesis that a common magnetic structure and also a common phase diagram may exist. With an applied field, there appears more than one phase: a spin flop phase at low fields and in some cases another phase at higher fields. More work is needed, especially neutron studies in a magnetic field, to unravel the magnetic structure of these phases. Especially for LiCuVO$_4$ the structure at $H \geq 9$ T might be of particular interest to investigate. It either represents a major change in the magnetic structure or possibly a transition to a spin liquid state. In conclusion, a concise study has been done in these compounds in zero field. In my thesis I have introduced two new compounds to broaden the possible number of one dimensional frustrated compounds with helical magnetic structures to five in total. I have summarized and discussed their properties in terms of the Cu-X-Cu angle and their magnetic properties. As a result the complex phase diagram with applied field has been obtained for future investigations.
Appendix A

Program code for the heat capacity programs

A.1 Einstein model

C Program to calculate the Einstein Heat capacity
C CALLS FUNCTION func

REAL*8 T, FUNC, x, Te, CP, R
OPEN(10, FILE='Einstein.OUT')
R=8.314d0
DO 100 J=1,21,1
   Te=100.0D0+DFLOAT(J-1)*50.0D0
DO 200 I=1,300
   T=DFLOAT(I)*1.0D0
   x = Te/T
   f = dexp(x)/(dexp(x)-1)/(dexp(x)-1)
A.2 Debye model

C Program to calculate the Debye Law Heat capacity
C CALLS FUNCTION func

REAL*8 T,FUNC,A,B,Theta,CP,R,S
OPEN(10,FILE='DEBYE.OUT')
A=0.0d0
NIN=14
EXTERNAL FUNC
DO 100 J=1,21,1
   THETA=100.0d0+DFLOAT(J-1)*50.0d0
DO 200 I=1,300
   T=DFLOAT(I)*1.0d0
   B=Theta/T
   CALL TRAPZD(func,A,B,S,NIN)
   CP=9.0d0/B/B/B*S
   write(10,1300) Theta,T,CP
200 CONTINUE 100 CONTINUE
C FORMATSTATEMENTS
1300 FORMAT(3F20.8)
STOP
END

C FUNCTION to calculate the Integrand of a Debye function

Function func(x)
Real*8 func,x,x2,dx1,dx2
x2=x*x
dx1=dexp(x)
dx2=dx1-1.0D0
FUNCl=x2*x2*dx1/dx2/dx2
END

C External subroutine to calculate the integral by
C Trapezoidal rule

SUBROUTINE trapzd(func,a,b,s,n)
INTEGER n
REAL*8 a,b,s,func
EXTERNAL func
INTEGER it,j
REAL*8 del,sum,tnm,x
if (n.eq.1) then
   s=0.5d0*(b-a)*(func(a)+func(b))
else
   it=2**(n-2)
   tnm=it
   del=(b-a)/tnm
   x=a+0.5d0*del
   sum=0.
do 11 j=1,it
    sum=sum+func(x)
    x=x+del
11     continue

s=0.5d0*(s+(b-a)*sum/tnm)
endif
return
END

A.3 Calculating the Chebychev coefficients using a function minimization subroutine

Program chebyfit
C program to fit a set of data of Resistance and temperature values using the chebychev C polynomial to calibrate the temperature sensors on the cryostat. C program by Michael Banks, 3rd oct 2002. Subroutine NELMIN by Dr R Kremer.

real*8 xmin,start,step,ynewlo,reqmin,stes
real*8 res,t,ctemp,tdiff, chi, chisum
dimension res(84),t(84), ctemp(84),tdiff(84)
dimension xmin(8),start(8),step(8),ifrei(8),stes(8)
    common res, t, ctemp,tdiff
\[ m = 8 \]
\[ k = 84 \]
\[ knovge = 5 \]
\[ reqmin = 1.d-20 \]
\[ icount = 9999 \]

C opening files, first start.dat, where the starting values of the coefficients are C placed with the step values and ifrei.
lakeshore.txt is where the resistance and C temperature values are, area1,2,3 are the 3 defined areas for fitting in the total C range, diff is the output file of resistance, calculated temp by chebychev, measured C temp, and the diff of calculated temp to measures temp, coeff is the output coefficients

```plaintext
open(10,file='start.txt')
open(11,file='lakeshore.txt')
open(12,file='area1')
open(13,file='area2')
open(14,file='area3')
open(15,file='diff.o')
open(20,file='coeff.o')
do 3 is = 1, m ,1
  read(10,*) start(is), step(is), ifrei(is)
3  stes(is) = step(is)*dble(ifrei(is))
do 30 i = 1, k ,1
  read(11,*) t(i), res(i)
30  continue
```

C finished reading from files.
do 40 i = 1,29,1
write(12,*) t(i),res(i)
40    continue

do 50 i = 30,55,1
write(13,*) t(i),res(i)
50    continue

do 60 i = 56,84,1
write(14,*) t(i),res(i)
60    continue

call nelmin (m,start,ynewlo,reqmin,stes,konvge,icount)
do 210 i = 1,29,1
   tdiff(i) = (t(i) - ctemp(i))
write(15,*) i,res(i),t(i),ctemp(i),tdiff(i)
210    continue

do 220 is=1,m, 1
write (20,*) xmin(is)
220    continue

C finished writing to files.
C to calculate chi squared.

chisum = 0.0

do 240 i=1,29,1
   chisum = chisum + (tdiff(i))**2/t(i)
240 continue

chi = (chisum/21)
print*, chi
stop
C end of program
end

C function subroutine which contains the chebchev polynomial,
output is the C coefficients 'a'.

function fn(a)
real*8 fn,a
real*8 res,t,ctemp
real*8 uppres,lowres,zu,zl,z,x,ax,sum
dimension res(84),t(84),ctemp(84)
dimension a(8)
common res,t, ctemp
m = 8
k = 84
uppres = 41149.6752422178
lowres = 844.372266602526
ZU = dlog10(uppres)
ZL = dlog10(lowres)
fn = 0.0

C loop around the resistances.
do 100 i = 1,29,1
Z = dlog10(res(i))
x = ((Z-ZL)-(ZU-Z))/(ZU-ZL)
ax = dacos(x)
sum = 0.0

C loop around the order, m
do 200 is = 1,m,1
C chebychev formula
    sum = sum + a(is)*dcos(dfloat((is-1))*ax)
200 continue
ctemp(i) = sum
fn = fn + ((ctemp(i)/t(i))-1d0)*((ctemp(i)/t(i))-1d0)
100 continue
C normalise the function
    fn = 100.d0*dsqrt(fn/dfloat(k))
return
end
Appendix B

Example input and output file from *McPhase*

B.1 An example of the input file for *cfield*

Below shows an example input file for the program *Cfield* which calculates the eigenenergies and eigenvalues for a certain $x$ and $W$. The example is for the case of TmGa$_3$ with $x = -0.44$ and $W = -0.222$ K, calculated at 10 K in a cubic co-ordination.

```
| VERSION :  5.20 |
```

```
C F I E L D
A Crystal field program

Programmator:
Peter Hoffmann
Forschungszentrum Juelich
Institut fuer Festkoerperforschung
Tel.: 02461-616896
```

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Crystal Field parameter \( x, W \) (real) in Kelvin for cubic Symmetry

Starting with

\[
H = B + 0(J) + B + 0(J)
\]

\[
H_F = \begin{array}{ccc}
40 & 4 & 60 \\
60 & 6 & 64
\end{array}
\]

Where

\[
0(J) := STEV(J) + 5 \ast STEV(J)
\]

\[
4 \quad 40 \quad 44
\]

\[
0(J) := STEV(J) - 21 \ast STEV(J)
\]

\[
6 \quad 60 \quad 64
\]

Setting

\[
-1 \leq x \leq 1 \quad x \ast W = B \ast F(4)
\]

\[
40
\]

\[
(1 - |x|) \ast W = B \ast F(6)
\]

\[
60
\]

\[
F(k) := F(J) := GGT(\{<JM'|STEV'|JM>\})
\]

\[
x_0 \quad x_0 \quad M.M'=-J..J
\]

In the case of \( J=9/2 \) one puts \( F(4)=60 \) instead of \( 84 \)

\[
F(6)=2520 \text{ instead of } 5040
\]

In case of \( J=8 \) one puts \( F(4)=60 \) instead of \( 420 \)

Note: the \( <JM'|STEV'|JM> \) are integers.
- The $B$ parameters contain the quantisation parameters $\theta$ (L), therefore $\kappa J$

The $x, w$-Parameter and $B$-Parameter follow the same selection rules regarding the quantisation parameters.

Especially for the ground state

\[
\begin{align*}
2S+1 & \quad 04(5/2) \\
F & \text{ from Ce : } B = 0 \Rightarrow H = x*w*\\
\frac{5}{2} & \quad 60 \\
\end{align*}
\]

Energy Eigenvalues are in meV
Temperature of the probe : 10.00 Kelvin
Ion : Tm$^3^+$
Symmetry : Kubisch    Symmetry number : 8
Magnetic field : applied

The co-ordinates of the magnetic field are given in KARTESISCHEN co-ordinates.
B := Magnetic field in Tesla

Exemplar of an output file using `cfield`

The output file once the program `cfield` is run with the given input in B.1 is given below, showing the energy level scheme and the transition energies and intensities.

```plaintext
#--------------------------------------------------------------
#                         OUTPUT                               |
#--------------------------------------------------------------
# Temperature of the sample  :  10.00 Kelvin                |
# Ions                    :  Tm3+                             |
# Lande factor of the ion  :  1.166667                      |
# Total angular momentum J of the ion  :  1.166667          |
#--------------------------------------------------------------
```
Spin - orbit - level  : 6.0 | # |
# Electrons in 4f shell  : 12 | # |
#--------------------------------------------------------------| #
| # local point symmetry | #
| # of the ion  : kubisch | #
| # Symmetry number  : 8 | # |
#--------------------------------------------------------------#
Parameters | #
#--------------------------------------------------------------#
Parameter  : x, W in Kelvin | #
#--------------------------------------------------------------| #
| #  x  =  -0.440000 | #
|  W  =  -0.222000 | #
#--------------------------------------------------------------#
# Energy Eigenvalues are in meV . | #
#--------------------------------------------------------------| #
# Number of different energy levels  : 6 | #
| # Energy shift (Eshift)  :  -15.43 | #
#--------------------------------------------------------------#
# Because of the calibration freedom the smallest energy eigenvalue is shifted to zero. You can get the energy eigen-value of the applied eigen-value problem by shifting the energy by the added energy value above #
# E( 1) = 0.0000 Degeneracy : 1-fold | #
| E( 2) =  0.0979 Degeneracy : 1-fold | #
| E( 3) =  0.3953 Degeneracy : 3-fold | #
| E( 4) =  0.4362 Degeneracy : 3-fold | #
| E( 5) =  2.5037 Degeneracy : 2-fold | #
| E( 6) =  3.0297 Degeneracy : 3-fold | #
#--------------------------------------------------------------#
# Then with * marked Energy eigenvalues have a non-vanishing Matrix element of the Ground state E( 1). | #
# Matrix Elements for Single Crystal

Only the matrix elements that are non-zero are written.

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>2</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>a &lt;-&gt; b</td>
<td>&lt;a</td>
<td>J</td>
<td>b&gt;</td>
</tr>
<tr>
<td>x</td>
<td>y</td>
<td>z</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>#</th>
<th>3 &lt;-&gt; 1</th>
<th>11.793774</th>
<th>11.793774</th>
<th>11.793774</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>3 &lt;-&gt; 3</td>
<td>0.005316</td>
<td>0.005316</td>
<td>0.005316</td>
</tr>
<tr>
<td>#</td>
<td>4 &lt;-&gt; 2</td>
<td>14.000000</td>
<td>14.000000</td>
<td>14.000000</td>
</tr>
<tr>
<td>#</td>
<td>4 &lt;-&gt; 3</td>
<td>21.354046</td>
<td>21.354046</td>
<td>21.354046</td>
</tr>
<tr>
<td>#</td>
<td>4 &lt;-&gt; 4</td>
<td>0.500000</td>
<td>0.500000</td>
<td>0.500000</td>
</tr>
<tr>
<td>#</td>
<td>5 &lt;-&gt; 3</td>
<td>5.594397</td>
<td>5.594397</td>
<td>5.594397</td>
</tr>
<tr>
<td>#</td>
<td>5 &lt;-&gt; 4</td>
<td>2.000000</td>
<td>2.000000</td>
<td>2.000000</td>
</tr>
<tr>
<td>#</td>
<td>6 &lt;-&gt; 1</td>
<td>2.206226</td>
<td>2.206226</td>
<td>2.206226</td>
</tr>
<tr>
<td>#</td>
<td>6 &lt;-&gt; 3</td>
<td>3.252466</td>
<td>3.252466</td>
<td>3.252466</td>
</tr>
<tr>
<td>#</td>
<td>6 &lt;-&gt; 4</td>
<td>4.145954</td>
<td>4.145954</td>
<td>4.145954</td>
</tr>
<tr>
<td>#</td>
<td>6 &lt;-&gt; 5</td>
<td>20.405603</td>
<td>20.405603</td>
<td>20.405603</td>
</tr>
<tr>
<td>#</td>
<td>6 &lt;-&gt; 6</td>
<td>11.989751</td>
<td>11.989751</td>
<td>11.989751</td>
</tr>
</tbody>
</table>
# Matrix elements

# for the transition:  E -> E

# Sum rule:

# \[ \sum_{i, r, s} T_{i, k, r, s}^2 = 2 (J(J+1)) \]
Transition intensities in barn.

\[ E - i, r, s > n e i \]

with

\[ u = x, y, z \]
\begin{verbatim}
# und
#
# const = 4*pi*( --- r  g )
#    2 0 J
#
# -12
# r = -0.54 * 10 cm
#
#--------------------------------------------------------------1
#
# 1. Sum rule:
# - E / T
# ---- = 2
# i e n i
# > | == *** const * J(J+1) * -------------
# ---- = 3
# - E / T
# k E -> E
# > n e i
# i k
# ---- i
#
#--------------------------------------------------------------2
# 2. sum rule:
#
# ---- = 2
# > | == *** const * J(J+1)
# ---- = 3
# k E -> E
# i k
#
#--------------------------------------------------------------
# Temperature of the sample
# 10.00 Kelvin
#--------------------------------------------------------------
\end{verbatim}
# partition function = 5.76

# Total magnetic scattering intensity = 34.68 barn

# Total quasielastic intensity = 0.28 barn

# Neutron-Energy-loss
# middle position of the energy : 0.23 meV
# relative error in the middle position : 143.71 %
# intensity of the middle position : 6.66 barn

# Neutron-Energy-Gain
# middle position of the energy : -0.06 meV
# relative error in the middle position : 65.67 %
# Intensity of the middle position : 5.83 barn
#
Transition Energy (meV) vs Intensity (barn)
#
<table>
<thead>
<tr>
<th>Energy (meV)</th>
<th>Intensity (barn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>0.40</td>
<td>5.07</td>
</tr>
<tr>
<td>0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>2.80</td>
<td>0.00</td>
</tr>
<tr>
<td>3.03</td>
<td>0.95</td>
</tr>
<tr>
<td>-0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.32</td>
<td>0.00</td>
</tr>
<tr>
<td>0.34</td>
<td>5.37</td>
</tr>
<tr>
<td>2.71</td>
<td>0.00</td>
</tr>
<tr>
<td>2.93</td>
<td>0.00</td>
</tr>
<tr>
<td>-0.40</td>
<td>3.20</td>
</tr>
<tr>
<td>-0.30</td>
<td>0.00</td>
</tr>
<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.04</td>
<td>5.80</td>
</tr>
<tr>
<td>2.41</td>
<td>1.62</td>
</tr>
<tr>
<td>2.63</td>
<td>0.88</td>
</tr>
<tr>
<td>-0.44</td>
<td>0.00</td>
</tr>
<tr>
<td>-0.34</td>
<td>3.63</td>
</tr>
<tr>
<td>-0.04</td>
<td>5.53</td>
</tr>
<tr>
<td>0.00</td>
<td>0.13</td>
</tr>
<tr>
<td>2.37</td>
<td>0.52</td>
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<tr>
<td>2.59</td>
<td>1.07</td>
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<tr>
<td>-2.80</td>
<td>0.00</td>
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<td>-2.71</td>
<td>0.00</td>
</tr>
<tr>
<td>-2.41</td>
<td>0.09</td>
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<tr>
<td>-2.37</td>
<td>0.03</td>
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<tr>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.23</td>
<td>0.34</td>
</tr>
<tr>
<td>-3.03</td>
<td>0.03</td>
</tr>
<tr>
<td>-2.93</td>
<td>0.00</td>
</tr>
<tr>
<td>-2.63</td>
<td>0.04</td>
</tr>
<tr>
<td>-2.59</td>
<td>0.05</td>
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<tr>
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<td>0.26</td>
</tr>
<tr>
<td>0.00</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Appendix C

CuCl$_2$ single crystal refinement data

C.1 Room temperature structural refinement

The following table presents the refinement of twinned crystal structure of CuCl$_2$ at 300 K using the lattice parameters as defined in table 4.1 and to the twin matrix as defined by eqn 4.7.1. The data was collected on D10 at the ILL at a wavelength of $\lambda = 2.34$ Å.

Table C.1: Observed and calculated nuclear integrated intensities for CuCl$_2$ from single crystal neutron diffraction on D10 at 300 K.

<table>
<thead>
<tr>
<th>$F^2_{\text{obs}}$ (arb units)</th>
<th>$F^2_{\text{calc}}$ (arb units)</th>
<th>$hkl$</th>
</tr>
</thead>
<tbody>
<tr>
<td>376433.0000</td>
<td>361749.6250</td>
<td>(0 0 4)</td>
</tr>
<tr>
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### C.2 Magnetic structure refinement

The following table presents the refinement of the magnetic structure of CuCl$_2$ at 2 K. The data was collected on D10 at the ILL at a wavelength of $\lambda = 2.34$ Å.
Table C.2: Observed and calculated magnetic integrated intensities for CuCl₂ from single crystal neutron diffraction on D10 at 2 K. Note that the propagation vector, \( \tau \) should be added to each \((hkl)\) reflection. E.g. \((0 1 0) + \tau = (0.5 1.224 0)\).

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Bibliography


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