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Identification and investigation of new low-dimensional quantum spin systems

by

Joseph M. Law

Doctoral Thesis

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

September 27, 2011

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Hwæt!

Beowulf - Unknown author

circa 8th-11th century
Abstract

This thesis focuses on one area of modern condensed matter physics, namely low-dimensional magnetism, and more specifically one-dimensional linear chains. The work herein can be split into three parts. The first part provides a tool for the greater community. I herein propose a Padé approximation for the temperature dependent magnetic susceptibility of a $S = 3/2$ spin chain, that is more accurate than those already known. The approximation allows one to fit experimentally measured magnetic susceptibilities and ascertain values such as the near-neighbour spin exchange interaction and the $g$-factor. The second and third parts of this thesis are both concerned with experimentally and theoretically characterizing two isostructural linear $S = 1/2$ chain compounds on opposite ends of the 3$d$ transition metal series. The compounds, CuCrO$_4$ ($3d^9$) and TiPO$_4$ ($3d^1$), are shown to have completely different ground states despite both being largely isostructural and $S = 1/2$ quantum spin systems. In this work and the resulting publications it is shown that CuCrO$_4$ is a one-dimensional $S = 1/2$ spin chain with anti-ferromagnetic nearest- and next nearest-neighbour spin exchange interactions. The ratio of these spin exchange interactions is shown experimentally and theoretically to be approximately 2, putting CuCrO$_4$ in the vicinity of the Majumdar-Ghosh point, for which the magnetic ground-state can
be solved analytically. Small ferromagnetic inter-chain coupling leads to long-range ferromagnetic ordering between anti-ferromagnetic chains at 8.2(2) K. At this temperature a spontaneous electrical polarization is observed. This classifies CuCrO$_4$ as a type-II multiferroic. Contrary to CuCrO$_4$, TiPO$_4$ has a non-magnetic ground state. At 111 and 74 K TiPO$_4$ undergoes a two stage phase transition, which is interpreted as a spin-Peierls transition. There is evidence that below 74 K TiPO$_4$ has a new crystal structure, in which there are alternating dimerised chains and two different PO$_4$ tetrahedral units. Currently the new structure has not been identified and no super-structure reflections have been confirmed in either low-temperature neutron or x-ray diffraction.

In summary this thesis presents some experimental and theoretical contributions to the field of low-dimensional magnetism.
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Introduction

The study of solid materials, their properties and their phases is known as condensed matter physics. It is a very wide, varied, research field, ranging from the study of single atoms on a substrate to the phase transitions of bulk samples and beyond.

A subsection of these studies focusses on magnetic phenomena. Magnetism is a integral part of condensed matter physics and consists of many sub-fields. Initially the only known (ferro) magnetic materials were the three ferrous transition metals, iron, cobalt and nickel and a few naturally occurring, more complex, minerals. Later new compounds were synthesized/discovered that had new and interesting characteristics.

Magnetic materials are normally discussed as either itinerant or non-itinerant. Itinerant magnets are systems where the magnetic moments are non-localized. This is generally realized in metals where there is a spin polarization of the electrons at the Fermi surface. Non-itinerant magnets, which are the subject of this PhD thesis, have a well defined magnetic moment and are typically insulating materials. Here I concentrate on 3d transition metal oxides where the interplay of spin, charge and orbital degrees of freedom can result in a plethora of magnetic prop-
For $3d$ ions with open shells magnetism and hence the magnetic moment can be rather well understood within the Russel-Saunders coupling scheme. Here $S$ is the spin, an intrinsic property of a particle (1/2 for an electron), and $L$ is the angular momentum. Both are good quantum numbers. For $f$ electrons, namely the $4f$ Lanthanoids and to some extent also the $5f$ Actinoids series, the magnetic properties are best described by the quantum number $J$ which is the total angular momentum. The total angular momentum of the ground-state is, for the less than half full occupation of the $f$-levels, the absolute value of the difference between $L$ and $S$, $|L - S|$, and the sum of $L$ and $S$ for the more than half full situation, i.e. $|L + S|$. However, for the transition metals, the $3d$, $4d$ and $5d$ series, the magnetic properties can often be well described by using spin only because of the quenching of the orbital angular momentum. This PhD thesis will only concern itself with the magnetism of $3d$ transition metals, hence only the quantum number $S$ is of relevance.

The work that follows concentrates on non-itinerant transition metal compounds that exhibit characteristics of one-dimensional magnetism. The first chapter will concentrate on characteristics of one-dimensional magnetism, some phenomena of one-dimensional magnets and some known compounds. The second chapter will describe the experimental and com-
putational methodology used for the investigations reported here. The third and fourth chapters focus on the presentation of two new magnetically one-dimensional systems, CuCrO$_4$ and TiPO$_4$. Despite both being essentially isostructural and $S = 1/2$ systems they exhibit very different magnetic properties.
Chapter 1

Magnetism

In this chapter I will discuss some elementary concepts of magnetism and then focus in more detail on low dimensional magnetism. In particular aspects of multiferroicity and other systems, that are pertinent to my PhD work, will be reviewed.

1.1 Magnetism

Magnetism is a wide and vivid research area. This thesis will concentrate on a small subsection of the vast field of physics, namely on $3d$ non-itinerant, one-dimensional magnetism. Here $3d$ refers to the electrons that contribute to the magnetism of transition metals. Non-itinerant means that the magnetic moment is confined to an atom or atoms. This
is the case for non-conducting materials. More information can be found in many condensed matter text books [1, 2, 3].

1.1.1 The magnetic moment

For many transition metals the magnetic moment is best described by the spin quantum number $S$. Scaling linearly with the $g$-factor the effective magnetic moment, which enters into the Curie law is given as

$$\mu_{\text{eff}} = g\sqrt{S(S+1)}.$$ 

The magnetic susceptibility $\chi(T)$ of a set of free uncoupled spin entities is given by the Curie-law:

$$\chi(T) = \frac{C}{T},$$

with

$$C = \frac{N_A \mu_{\text{eff}}^2}{3k_B}.$$ 

In the case of exchange interaction between the magnetic centers the magnetic susceptibility is given by the Curie-Weiss law

$$\chi(T) = \frac{C}{T - \theta}.$$ 

Provided that the thermal energy $k_B T$ is significantly larger than the exchange interaction energy. The Curie-Weiss temperature $\theta$ is given by

$$\theta = \frac{1}{3} \sum_i z_i J_i S_i (S_i + 1).$$
where $z_i$ is the number of neighbours with which a single atom interacts via the spin exchange $J_i$.

It the temperature becomes comparable with the typical spin exchange interaction energy one generally encounters magnetic ordering phenomena. These depend on many details of the lattice arrangement, crystal anisotropies. Magnetic ordering phenomena on highly anisotropic lattices, i.e. lattices in which spin exchange interactions along a special direction are predominant, are the subject of this thesis. Generally, one encounters regimes of extended short-range correlations before at sufficiently low-temperatures long-range magnetic ordering appears.

The electronic $g$-factor is 2, but values slightly greater or smaller than 2 are seen for real systems since spin-orbital coupling perturbs the system in such a way that;

$$g_{\text{eff}} = g - f(\lambda \ldots)$$

here $f(\lambda \ldots)$ scales linearly with $\lambda$, the spin-orbital coupling constant. The absolute value of $\lambda$ generally increases as one progresses through the transition metal series, with the exception of $S = 5/2$ ($\text{Mn}^{2+}$ or $\text{Fe}^{3+}$) where it is effectively zero. The sign of the spin-orbital coupling also changes as on progresses through the transition metal series. For transition metals with less than half filled shells, e.g. $\text{Ti}^{3+}$, $\lambda$ is positive, but for the more than half filled shells, when one is dealing with quasi-
particles (holes), $\lambda$ is negative. As such one expects a $g$-factor of slightly less than 2 for Ti$^{3+}$ and more than 2 for Cu$^{2+}$.

1.1.2 Crystal electric field

For a free 3$d$ transition metal atom one finds a surrounding spherical electron cloud with all 5 3$d$ states degenerate in energy. But when that atom is put into a material the 3$d$ electron clouds distort and the energy levels are no longer degenerate. This is the effect of the crystal electric field of the other surrounding ions. It originates from an electrostatic interaction. When a transition metal is in an oxygen octahedral environment the 5 3$d$ states are split into a doublet, $e_g$, higher in energy and a triplet $t_{2g}$ that is lower in energy, the former can be filled by 4 and the latter by 6 electrons. An elongation or compression of the octahedra results in a further splitting of the energy levels. The 3$d$ orbitals and the orbital energy landscape are shown in figure 1.1.
Figure 1.1: Taken from magnetism and magnetic materials by J. M. D. Coey [1].

(a): The five orbitals of the 3\textit{d} transition metals. 

(b): The energy splitting of the 3\textit{d} orbitals (from left to right); a free atom, an atom in a triangular based pyramid environment, an atom in a non-distorted octahedral environment and an atom in a cubic environment.

(c): The energy landscape of the 3\textit{d} orbitals in an elongated (left) and a compressed (right) octahedral environment.

The Pauli exclusion principle states that electrons with the same quantum numbers can not occupy the same space. Hence, each orbital can
accommodate two electrons one with spin up and one with spin down. The electrons fill the orbitals starting with the lowest one in energy. It is not always energetically advantageous (due to Coulomb repulsion) for two electrons to occupy the same orbital. In some cases the electrons half fill the lowest energy orbitals and then continue to half fill the higher energy orbitals. This is known as the high-spin configuration and it is common for some magnetic atoms e.g. Fe$^{3+}$ and Mn$^{2+}$. When the electrons totally fill the lower energy orbitals first the arrangement is known as the low-spin configuration. This is shown in figure 1.2. More information can be found in most magnetism text books [4].

![Figure 1.2: A pictorial representation of the high- and low-spin configurations for Fe$^{3+}$.](image)

### 1.1.3 Interactions

Exchange interactions are integral to long-range magnetic ordering. They can take many forms: Ruderman-Kittel-Kasuya-Yosida (RKKY) inter-
action, direct exchange, double exchange and superexchange to name a few. Here I will introduce the three forms of exchange that are pivotal to non-itinerant magnetism and this PhD work.

**Direct exchange**

When neighbouring magnetic atoms interact with each other directly it is known as direct exchange. This is not normally the case since direct exchange requires a strong overlap of electron wave functions. Direct exchange can be described for two Hydrogen atoms. Each atom has one electron. When these atoms are in close proximity to one another they find it energetically favorable to bond and this form a singlet ground state. This is shown pictorially in figure 1.3.

![Figure 1.3: A graphical representation of the radial wave functions of the free, bonded and anti-bonded states of the H₂ molecule. Taken from Magnetism in Condensed Matter Physics by S. Blundell [2].](image-url)
Mediated exchange

Mediated exchange, sometimes also known as superexchange, indirect exchange or Kramers-Anderson superexchange, is exchange between two magnetic atoms mediated through a diamagnetic only atom such as O$_2^-$ or F$^-$. It acts over a longer distance than direct exchange and it is integral to most non-itinerant magnets. It arises from the hybridization of the transition metal’s $d$ electrons and the mediator’s $p$ electrons. A $p$ electron hops from the O$_2^-$ or F$^-$ to the transition metal in the same manner as for the direct exchange mechanism. A $d$ electron from the other transition metal atom the hops into the empty $p$ hole. This creates an excited state, which relaxes when the $p$ electrons return to the O$_2^-$ or F$^-$ orbitals. The sign of the exchange is governed by the orbitals involved and their arrangement with regards to one another. This can be seen as two direct exchange pathways. The exchange pathways can become very large, sometimes including an additional direct O$_2^-$···O$_2^-$ or F$^-···F^-$ exchange.

Anisotropic exchange terms

The interaction between two spins can generally be given by

$$H = S_i \cdot J_{i,j} \cdot S_j,$$
where $J_{i,j}$ is a $3 \times 3$ tensor that contains all information pertaining to the spin exchange interaction. The tensor can take the decomposed form,

$$J_{i,j} = T_{i,j} + A_{i,j}.$$ 

Here $T_{i,j}$ is the symmetric component of $J_{i,j}$ and $A_{i,j}$ is the antisymmetric component. This is an important relativistic spin exchange interaction known as the Dzyaloshinski-Moriya (DM) interaction. It takes the form of an extra term in the exchange Hamiltonian given by

$$H_{DM} = -\frac{1}{2} \sum_{ij} D_{ij} \cdot S_i \times S_j,$$

here the DM interaction is represented by the DM vector, $D_{ij}$. A non-zero DM vector generally requires a low-symmetry environment with the absence of an inversion center. DM interactions are reported to play a major role in one-dimensional chain compounds and other transition metal oxides and could possibly give rise to multiferroicity [5, 6].

### 1.1.4 Spin models

In a simple interpretation, spin models can be classed by the dimensionality of the spin. The simplest one-dimensional spin model is known as the Ising model. This is where an infinite easy axis anisotropy confines the magnetic moments to $\pm \mathbf{z}$ direction. The two-dimensional model, called the XY model, occurs when an easy plane anisotropy confines the
magnetic moments to the $xy$-plane. In this case there is no $z$-axis component of the magnetic moment entering into the exchange Hamiltonian. The final, three-dimension model, the Heisenberg model, is isotropic and has components of the magnetic moment in all three cartesian coordinates.

In a formal sense spin models are better described by the spin Hamiltonian:

$$
\mathcal{H} = \sum_{i,j} J_{ij}^{xx} S_i^{xx} \cdot S_j^{xx} + J_{ij}^{yy} S_i^{yy} \cdot S_j^{yy} + J_{ij}^{zz} S_i^{zz} \cdot S_j^{zz}.
$$

The Ising system is the special case for which one spin exchange term is finite and the other two are zero. The XY model is obtained when two spin exchange terms are finite, but not necessarily the same, and the third is zero. The three-dimensional case is encountered when all three terms are finite. For the isotropic Heisenberg model they are restricted to be the same.

### 1.2 One-dimensional magnetism

A system is considered to be a one-dimensional magnet when it has an infinite chain of interacting magnetic atoms running through crystal structure. Each magnetic atom interacts with nearest-neighbours along the chain via an inter-chain spin exchange.
It is a common occurrence that within the chain the nearest-neighbour (nn) atoms generally interact strongly. However, the next nearest-neighbour (nnn) atoms can, in some cases (that will be discussed later), also interact via a strong, if not stronger, spin exchange interaction. The nn, nnn spin exchange interactions are indicated pictorially in figure 1.4.

![Figure 1.4: A simplified one-dimensional chain of atoms, with the nn and nnn spin exchange interactions indicated.](image)

In the situation of nn, nnn anti-ferromagnetic spin exchange interactions the system becomes frustrated and not all spin exchange interactions can be satisfied simultaneously. This is demonstrated in figure 1.5. Frustration can also result from nn ferromagnetic and nnn anti-ferromagnetic spin exchange interactions.
One-dimensional magnetism shows itself in many different ways, some of which will be discussed below. A characteristic is a broad hump in the magnetic susceptibility as shown for a uniform non-alternating Heisenberg spin chain in figure 1.6. The hump is due to short-range magnetic correlation. It has been rigorously proven by Mermin-Wagner that for truly one-dimensional systems and two-dimensional Heisenberg magnets there is no long-range ordering at finite temperature [7]. This is why there is no sudden drop in the magnetic susceptibility in figure 1.6. For real systems there is generally a drop or kink in the magnetic susceptibility due to long-range magnetic ordering. This will be discussed later.
Figure 1.6: The magnetic susceptibility of a uniform nn Heisenberg spin chain with $J_{nn} = 1$ and a $g$-factor = 2, calculated using the Padé approximation put forth by Johnston et al. [8].

1.2.1 Multiferroicity

A multiferroic is a material that exhibits more than one form of order, e.g. anti-/ferromagnetic, anti-/ferroelectric and or anti-/ferroelastic ordering [9]. Multiferroics can be split into two groups, type-I and type-II. Type-I, or proper multiferroics, are systems which have two or more independent ‘ferroic’ subsystems. These materials have two or more order parameters that are not coupled with one another and appear at dif-
ferent temperatures. Well known examples include BiMnO$_3$ or PbVO$_3$ [10, 11]. More pertinent to this work are type-II multiferroics, traditionally referred to as improper multiferroics. Within these systems, ferroelectricity does not exist independently of magnetic order [12, 13]. For spin 1/2 systems ferroelectricity can be the result of a helicoidal spin density wave, for which inversion symmetry is broken upon entering the long-range ordered states [5]. At the phase transition, long-range ordering, the sample goes from paramagnetic and dielectric to a magnetically ordered ferroelectric. It has been formulated by Katsura, Nagaosa and Balatsky and Mostovoy [14, 5] that for such a case a relationship exists between the electrical polarization $P$, the vector $e_{12}$ connecting the two spins $S_1$ and $S_1$ and the cross product of the magnetic moments of neighbouring spins $[S_1 \times S_2]$, as given by:

$$P \propto e_{12} \times [S_1 \times S_2].$$

1.2.2 Some known low-dimensional $S = 1/2$ quantum spin chains

Helicoidal magnetic ordering can be realized in one-dimensional systems which have competing nn and nnn spin exchange interactions. Figure 1.7 demonstrates the phase diagram of nn, nnn spin exchange interactions on a one-dimensional lattice. The phase diagram is split into
three sections. An anti-ferromagnetic phase exists between $J_{nnn} = 0$ with $J_{nn}$ anti-ferromagnetic and approximate values corresponding to the Majumdar-Ghosh line (MG). The Majumdar-Ghosh line \cite{15, 16} is when the nn and nnn spin exchange interactions are anti-ferromagnetic and $J_{nn} = 2 \times J_{nnn}$. At this special line the spin Hamiltonian;

$$E = J_{nn} \sum_{i=1}^{\infty} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \frac{J_{nnn}}{2} \sum_{i=1}^{\infty} \mathbf{S}_i \cdot \mathbf{S}_{i+2},$$

can be solved exactly. This point is generally accepted as the boundary between the anti-ferromagnetic and the frustrated phases. The second phase, where a helicoidal spin structure and hence multiferroicity should exist, continues from the Majumdar-Ghosh line to approximately $J_{nnn}/J_{nn} = 0.25$ whereupon there is a first order transition into a ferromagnetic state, the FF point \cite{17, 18}. The remaining segment is taken up by the ferromagnetic phase.

To date a number of nn nnn spin chains are known. A few pertinent systems that have attracted a lot of attention in recent years are included in figure 1.7. Except for the one inelastic neutron scattering result for LiCuVO$_4$, which is indicated by LiCuVO$_4$ INS, all other spin exchange parameters are based on density functional theory calculations taken from various sources, as indicated in the figure caption. Hence the results are displayed as sections rather than points, since the spin exchange interactions have been calculated for multiple values of the
on-site repulsion, $U$.

Figure 1.7: The nn nnn spin exchange phase diagram for $S = 1/2$ one-dimensional system, adapted from Bursill et al. [17]. The coloured sections/lines are density functional theory calculations for real systems, except the line labeled LiCuVO$_4$ INS which is based on an inelastic neutron scattering results [19, 20, 21, 22, 23, 24].

Some examples of multiferroic systems are described in more detail below.
LiCuVO$_4$

LiCuVO$_4$ is a well known intrinsically low-dimensional type-II multiferroic [19, 23, 25, 26]. At $\approx 2.4$ K LiCuVO$_4$ undergoes long-range ordering and becomes multiferroic. It has been reported to have a helicoidal spin spiral structure with ferromagnetic nn and anti-ferromagnetic nnn spin exchange interaction [25]. The multiferroicity is evidenced by an anomaly in the dielectric properties and a spontaneous electrical polarization, as shown in figure 1.8.

![Figure 1.8](image)

**Figure 1.8**: Main (o): The relative dielectric constant of LiCuVO$_4$ versus temperature. Inset (o): The electrical polarization of LiCuVO$_4$, calculated from the pyroelectric current, versus temperature. Taken from Schrettle et al. [26].
CuCl$_2$ was the subject of many investigations which probed its multiferroic behaviour at low-temperature [20, 27]. CuCl$_2$ undergoes long-range ordering at 23.9(1) K as evidenced by specific heat, magnetic susceptibility and elastic neutron scattering experiments, see figure 1.9 and the citation(s) therein. At long-range ordering a sharp spike is seen in the dielectric constant below which there is a spontaneous electrical polarization. At lower temperatures, immediately below the long-range ordering anomaly, the relative dielectric constant starts to grow. With decreasing temperature it levels off and then starts to decrease. This has the appearance of a broad asymmetric hump. With the application of a magnetic field the spike does not change but the hump decreases in size and moves to higher temperatures. The dielectric constant and spontaneous polarization are displayed in figure 1.10.
Figure 1.9: Main (o): The molar magnetic susceptibility of CuCl$_2$ measured in a magnetic field of 1 T versus temperature. Inset (o): A log-log plot of the specific heat of CuCl$_2$ versus temperature. All results taken from Banks et al. [20].
Figure 1.10: Main (o): The relative dielectric constant of CuCl$_2$ versus temperature, for various magnetic fields. Inset (o): The electrical polarization of CuCl$_2$, calculated from the pyroelectric current, versus temperature. Taken from Seki et al. [27].

TiOX (X=Cl or Br)

The compounds with composition TiOX (X=Cl or Br) have drawn much attention recently, since both compounds have a two-step spin-Peierls transition [28, 29, 30, 31, 32, 33]. The magnetic susceptibilities of both materials are dominated by a broad hump at high temperatures indicative of one-dimensional short range anti-ferromagnetic correlations. At lower temperatures there are two subsequent sharp decreases of the mag-
netic susceptibility, leaving only a finite van Vleck plus diamagnetic contribution and a small paramagnetic impurity. The spin-Peierls transition in both compounds happens in two steps: The first transition (drop in magnetic susceptibility at 92 and 47 K for the Cl and Br compounds, respectively) is a second order or continuous transition from a paramagnetic phase into a structurally incommensurate phase. At the second transition at 67 and 28 K for Cl and Br, respectively, a drop in magnetic susceptibility is observed. At lowest temperature both samples become fully dimerised. This transition is first order and hysteretic in nature. A new crystal structure has been reported for TiOCl below 28 K [34]. For more information see the cited articles.

1.2.3 Inter-chain couplings and long-range ordering

Generally, weak inter-chain spin exchange interactions, $J_\perp$, lead to long-range magnetic ordering at sufficiently low-temperatures. One can estimate the inter-chain coupling from the long-range ordering temperature. Yasuda et al. calculated the Néel temperature ($T_N$) of a quasi one-dimension Heisenberg anti-ferromagnet on a cubic lattice with the isotropic inter-chain coupling $J_\perp$, inducing three-dimensional long-range magnetic ordering at $T_N$ [35]. By scaling their quantum Monte Carlo simulations they extrapolate for infinite system size, a relationship be-
tween inter- and intra-chain coupling, given by;

\[ T_N/|J_\perp| = 0.932 \sqrt{\ln(A) + \frac{1}{2} \ln(\ln(A))}, \quad (1.1) \]

where \( A = 2.6 J_\parallel/T_N \) and \( J_\parallel \) is the intrachain spin exchange constant.

### 1.2.4 Electron paramagnetic resonance theory

Oshikawa and Affleck [36, 37] developed a theory for the electron paramagnetic resonance of \( S = 1/2 \) quasi-one-dimensional chain compounds at low-temperatures which have anisotropic or antisymmetric exchange terms i.e. \( J^{xx} \neq J^{yy} \neq J^{zz} \). At low-temperatures near long-range ordering they found that there is a positive linear slope of the linewidth with increasing temperature. The proportionality constant depends upon many aspects and as such no quantitative results can be obtained easily. But there is a system independent factor of 2 between the proportionality pre-factors parallel and perpendicular to the easy axis. Such as;

\[ \frac{\delta w_{\perp \text{easy axis}}}{\delta w_{\parallel \text{easy axis}}} = 2, \]

where,

\[ \delta w = \frac{\partial (\text{HWHM})}{\partial T}. \]
They went on to demonstrate this for some known chain compounds. Their published comparisons are displayed here in figure 1.11. The reported temperature dependencies are tabulated in table 1.1.

Prior to the work by Oshikawa and Affleck, Kubo and Tomita reported that for $S = 1/2$ anti-ferromagnetic nn chain systems the saturation of linewidth at high-temperatures could be due to the anisotropic or anti-symmetric spin exchange interactions [38]. Defining $\delta$ as the deviation from the isotropic exchange such as,

$$J_{zz} = J_{xx} \times (1 - \delta),$$

they put forth the relationship in equation 1.2, where $J_{nn}$ is the nn spin
<table>
<thead>
<tr>
<th>$\delta w$ (T/K)</th>
<th>Compound</th>
<th>Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4.2 \times 10^{-4}$</td>
<td>CuGeO$_3$</td>
<td>B∥c</td>
</tr>
<tr>
<td>$4.7 \times 10^{-4}$</td>
<td>CuGeO$_3$</td>
<td>B∥a</td>
</tr>
<tr>
<td>$17 \times 10^{-4}$</td>
<td>KCuF$_3$</td>
<td>B∥c</td>
</tr>
<tr>
<td>$22 \times 10^{-4}$</td>
<td>KCuF$_3$</td>
<td>B∥a</td>
</tr>
<tr>
<td>$1.3 \times 10^{-4}$</td>
<td>NaV$_2$O$_5$</td>
<td>B∥c</td>
</tr>
<tr>
<td>$0.65 \times 10^{-4}$</td>
<td>NaV$_2$O$_5$</td>
<td>B∥b</td>
</tr>
</tbody>
</table>

Table 1.1: The half width at half maximum for known low-dimensional chain compounds as shown in figure 1.11, taken from the work by Oshikawa and Affleck [37].

exchange, and $\Delta H$ is half line-width at half maximum of the electron paramagnetic resonance absorption line.

$$\Delta H(T \to \infty) \approx \frac{\delta^2}{g\mu_B J_{nn}}$$ (1.2)

Now that I have given an introduction to one-dimensional magnetism I will discuss as a first result a Padé approximation for the temperature dependence magnetic susceptibility of a $S = \frac{3}{2}$ Heisenberg quantum antiferromagnetic spin chain.
1.2.5 Padé approximation for the molar magnetic susceptibility of a $S = \frac{3}{2}$ Heisenberg quantum anti-ferromagnetic spin chain

One-dimensional magnetic systems can be characterized by magnetic susceptibility, see section 1.2. Being able to model the temperature dependent magnetic susceptibility of a one-dimensional system is very helpful since values such as the nn spin exchange interaction and the $g$-factor can be ascertained.

A Padé approximation is a useful tool in mathematics to approximate a given function. Padé approximations have been widely used in modern condensed matter physics for fitting observables, e.g. the molar magnetic susceptibility or specific heat. A well known and highly cited example is the Padé approximation for the molar magnetic susceptibility and the specific heat of a $S = 1/2$ Heisenberg alternating chain, as put forth by D. C. Johnston et al. [8]. Within the paper Johnston et al. discussed a non-alternating $S = 1/2$ Heisenberg chain. In the spirit of Johnston’s work, the Padé approximation for the magnetic susceptibility of a $S = \frac{3}{2}$ Heisenberg quantum anti-ferromagnetic spin chain was formulated from results obtained by quantum Monte Carlo simulations for a $S = 3/2$ Heisenberg chain.
A Padé approximation is given by:

\[
f(x) = \frac{1 + \sum_{i=1}^{m} A_i \cdot x^i}{1 + \sum_{j=1}^{n} B_j \cdot x^j}.
\]

Here both summations include sufficient terms to approximate the function to the desired accuracy such that the difference between the Padé approximation and the calculation is similar if not smaller than the error resulting from the quantum Monte Carlo simulations.

For the Padé approximation already discussed and the new approximation put forth here, \( f(x) \) is the spin susceptibility multiplied by \( S(S+1) \) and \( x \) is \( J_{nn}/T \) or the reciprocal reduced temperature. Hence the approximation now takes the form of:

\[
\chi^*(J_{nn}/T) = \frac{1 + \sum_{i=1}^{m} A_i \cdot (J_{nn}/T)^i}{1 + \sum_{j=1}^{n} B_j \cdot (J_{nn}/T)^j}.
\] (1.3)

Here

\[
\chi_{\text{mol}}(J_{nn}, g, T) = \chi^*(J_{nn}/T) \times \frac{N_A \mu_B^2 g^2}{k_B \times J_{nn}}.
\]

Previous to this work, Padé approximations for all possible spins of the transition metal series, i.e. \( S = 1/2 \cdots 5/2 \), were put forth in the PhD thesis of S. N. Grossjohann [39]. However, the system size chosen was
rather small, 512 spins and as such the results severely suffered from finite size effects at relatively high temperatures. Previous to the work by Grossjohann a trivial approximation was put forth by Hiller et al. [40].

Previous to all of these works, Fischer put forth a classical approximation for any spin system [41]. A comparison of the three previous works pertaining to the temperature dependent magnetic susceptibility of a $S = 3/2$ spin chain and our quantum Monte Carlo calculations are shown in figure 1.12. The previous non-classical work suffers from finite size effects and the quantum Monte Carlo results being reported here are more accurate and closer to the true temperature dependent magnetic susceptibility of such a chain. A $S = 3/2$ system is best described as being a quantum spin system and as such the classical approach does not describe the system adequately.
Figure 1.12: (o): Our quantum Monte Carlo results, see text for more information. Solid blue line: The Padé approximation by Grossjohann [39]. Solid green line: The classical approximation put forth by Fischer [41]. Solid black line: The approximation by Hiller et al [40].

The modified spin susceptibility for a $S = 3/2$ anti-ferromagnetic Heisenberg spin chain was calculated using the looper algorithm on a cluster within the ALPS suite. For more details see section 2.6.1. Initially the magnetic susceptibility was calculated at sufficiently low values of $T/J_{nn}$ for different system sizes, so as to ascertain a system size that would be acceptable to reproduce what would be observed for a real system ($N \gg N_A$), the results are shown in figure 1.14 insets b. A system size
of $N = 2000$ was chosen, since for systems sizes $N \geq 2000$ converging values of the spin susceptibility were obtained within error bars, see figure 1.14 (b). Bigger systems could have been chosen but this would have drastically increased computation times for little gain. The scaling of computation time with both system size and spin can be seen in figure 1.13. A clear non-linear scaling can be seen for both variables, the system size scaling is exponential as one would expect.
Figure 1.14: (a): The temperature dependent modified spin susceptibility for a $S = 3/2$ spin chain with nn spin exchange interactions, calculated by quantum Monte Carlo using the ALPS suite, versus reduced temperature. Solid red line: A fit to a Padé approximation as discussed in the text. (a): (o): The difference between the modified spin susceptibility as calculated by quantum Monte Carlo and the Padé approximation fitted to the simulation. The solid red lines denote the boundaries of the error bars given for the quantum Monte Carlo calculation. (b) The modified spin susceptibility for different systems sizes at a fixed reduced temperature of 0.05. $N$ denotes the number of spins.
Table 1.2: The refined coefficients of the Padé approximation in equation 1.3, as shown in figure 1.14.

<table>
<thead>
<tr>
<th>i/j</th>
<th>A_i</th>
<th>B_j</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-68.72481</td>
<td>489583.7</td>
</tr>
<tr>
<td>2</td>
<td>613928.0</td>
<td>1.89146E6</td>
</tr>
<tr>
<td>3</td>
<td>805554.35929</td>
<td>3.86820E6</td>
</tr>
<tr>
<td>4</td>
<td>703853.6</td>
<td>6.07049E6</td>
</tr>
<tr>
<td>5</td>
<td>394585.7</td>
<td>2.81538E6</td>
</tr>
<tr>
<td>6</td>
<td>21142.94</td>
<td>645334.4</td>
</tr>
<tr>
<td>7</td>
<td>-872.0836</td>
<td>-23234.23</td>
</tr>
<tr>
<td>8</td>
<td>-78.03424</td>
<td>-431.4632</td>
</tr>
<tr>
<td>9</td>
<td>4.440790</td>
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</tr>
<tr>
<td>10</td>
<td>-0.067570</td>
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<td>2.24279E-5</td>
</tr>
<tr>
<td>12</td>
<td>2.742790E-4</td>
<td>-1.75778E-4</td>
</tr>
</tbody>
</table>

The modified spin susceptibility was fitted to the aforementioned approximation with reduced $\chi^2$ values of 1.21 and an adjusted $R^2$ of 1.00. The fit can be seen in figure 1.14 with the difference between calculated and fitted values shown in inset (a). The temperature dependent error of the quantum Monte Carlo results are indicated by the two red lines. The terms of the Padé approximation up to the 12th order are tabulated in table 1.2.
1.3 Summary

In this chapter I discussed multiferroicity and low-dimensional magnetism with an emphasis on what is relevant for this PhD thesis. I also discussed relevant materials that will be commented on in the following chapters.

The next chapter will give a brief overview of experimental methodology and computation that will be used to characterize CuCrO$_4$ and TiPO$_4$ in the latter chapters.
Chapter 2

Experimental methodology and computation

In this chapter I will discuss and explain the experimental methodology and computations that were used to characterize the systems reported on in the following chapters. This chapter is meant to be a concise experimental overview. More information can be found in the pertinent manuals and the published papers.
2.1 X-ray and neutron diffraction

2.1.1 Single crystal diffraction

CAD4 diffractometer

CAD4 is a four circle diffractometer manufactured by Enraf Nonius, that allows data acquisition from $0 \leq \theta \leq 2\pi$ and $0 \leq \phi \leq \pi$. It employs non-monochromated Ag radiation (0.5608 Å). The machine was primarily used for orientating single crystals.

STOE IPDS diffractometer

The STOE IPDS diffractometer is a two circle diffractometer. It uses an imaging plate detector which allows data acquisition from $0 \leq \theta \leq 2\pi$. It uses non-monochromated Ag radiation (0.5608 Å). The machine was primarily employed for crystal structure determination.

2.1.2 Powder diffraction

Lab-based x-ray diffractometers

Two x-ray powder diffractometers were used, both STOE Stadi P machines. One machine produced monochromated Cu x-ray radiation (Cu-
$K_{\alpha 1}$ 1.54056 Å) and the other used monochromated Mo x-ray radiation (Mo-$K_{\alpha 1}$ 0.70930 Å). Both are equipped with Germanium(111) monochromators, and as such both select fully monochromated $K_{\alpha 1}$ radiation. The advantage of having access to Mo$K_{\alpha 1}$ is such that it allows one to measure elements that would absorb the frequently used Cu radiation, e.g. Cr. The samples were mounted in thin walled quartz capillaries ($\varnothing = 0.3$ or 0.1mm). This technique allows for preparation in a glove box and hence patterns of air sensitive samples could be easily collected [42].

**High resolution powder diffractometer for thermal neutrons - HRPT**

HRPT is a high resolution thermal neutron powder diffractometer. It was designed for small samples and has a resolution comparable to those of synchrotron x-ray powder diffraction studies, with a possible resolution of $\leq 0.05^\circ$. The machine is located at SINQ in the Paul Scherrer Institute, Switzerland. A schematic can be seen in figure 2.1.
2.2 Magnetisation

2.2.1 SQUID magnetometry

Magnetisation was measured using a Quantum Design Magnetic Property Measurement System, or MPMS for short. The machine allows the measurement of magnetisation in the range of $\pm 7$ T in the temperature range 1.85 K to 400 K. An additional oven insert enables measurements
in the higher temperature range of 300 K to 800 K. The sample, whether it is a powder or crystal, was generally mounted in the sample holder by two different methods. The simplest and fastest method has the sample contained within a diamagnetic only gelatine capsule, which weighs approximately 40 mg. The raw magnetisation could then be later corrected for the magnetisation of the sample holder. A gelatine capsule is shown in figure 2.2. The second, more time consuming method, was mounting the sample in a suprasil\textsuperscript{©} quartz tube. The tube is thin walled, so as to add the smallest background signal possible. It is sealed half way up its length, in a manner that deforms the longitudinal distribution of weight as little as possible, i.e. the longitudinal mass distribution (mg/cm) remains relatively constant. This could never be fully guaranteed, but measurements of the magnetisation of such a sealing yielded a magnetic susceptibility of $\approx 10^{-9}$ emu/Oe for which the raw data could be corrected. Once the sample was mounted, the tube was evacuated and flushed with helium gas a few times. This ensured that there was no O\textsubscript{2} gas that would give an additional signal at low-temperature and provide a good thermal contact to the cryostat. The tube was finally sealed. A sealed tube and the seal half way up the tube are displayed in figure 2.3.
Figure 2.2: Left: A filled gelatine capsule as used for measuring the magnetization. Right: A disassembled, empty, gelatine capsule, prior to use for measuring magnetization.

Figure 2.3: Left: A filled and sealed quartz tube ready for magnetization measurements. Right: A closer view of the seal half way up the tube.
The molar magnetic susceptibility could be calculated from the raw magnetisation by

\[ \chi_{\text{mol}}[\text{cm}^3/\text{mol}] = \frac{M(T, H)[\text{emu}] \times m[\text{g}]}{M_m[\text{g/mol}] \times H[\text{Oe}]} \]

where \( M(T,H)[\text{emu}] \) is the measured magnetisation, \( m[\text{g}] \) is the mass of the sample, \( M_m[\text{g/mol}] \) is the molar mass of the sample and \( H[\text{Oe}] \) is the applied magnetic field.

The magnetic susceptibility also required correcting for the diamagnetic contribution resulting from the closed shells of the atoms contained within the sample. The values are well known and tabulated by Selwood [44]. An example which is relevant to this work would be \( \text{Cu}^{2+} \) which has a diamagnetic contribution of \(-11 \times 10^{-6}\) cm\(^3\)/mol.

In addition to the diamagnetic signal of the samples, an additional positive temperature independent van Vleck contribution also needed to be subtracted from the magnetic susceptibility. The van Vleck contribution, sometimes referred to as the van Vleck temperature independent paramagnetism, arises from the population of the magnetic states that are higher in energy than the magnetic ground state. As such, it is system specific quantity. For \( \text{Cu}^{2+} \) it typically amounts to values between \(20 \times 10^{-6}\) cm\(^3\)/mol and \(120 \times 10^{-6}\) cm\(^3\)/mol depending on the direction...
of the applied magnetic field with respect to the crystal axes.

2.3 Specific heat

2.3.1 Relaxation calorimetry

Specific heat was measured using a Quantum Design Physical Property Measurement System (PPMS), via the relaxation technique. The machine allows the measurement of multiple physical properties, but for this work only the specific heat option was used. The specific heat was measured in the magnetic field range of ± 9 T and in the temperature range of 1.85 K to 350 K. An additional 3He insert allows one to measure down to ≈ 400 mK. Crystals were mounted to a thermally decoupled sample holder by Apiezon© vacuum grease. A pre-measurement, an ”addenda” measurement, was done before mounting the sample so that the specific heats of the sample holder and the Apiezon© vacuum grease could be subtracted from the total specific heat, yielding the specific heat of the sample.

Powders could also be measured on a PPMS sample holder, either by pelletizing and mounting it in the same way as crystals or by slightly melting the Apiezon© grease, once the addenda has been measured, and adding the powder. The slightly molten Apiezon© vacuum grease would
allow the powder to sink into it and thermally anchor the sample. A
typical sample investigated by this method weighed approximately 2 mg.

2.3.2 Adiabatic Nernst calorimeter

A home built quasi-adiabatic Nernst-type calorimeter was also used. It
allowed one to measure specific heat in the temperature range 2.0 K to
300 K. The machine’s construction and testing has been the subject of M.
Banks’ PhD thesis [45]. The calorimeter can accommodate single crystal
and powder samples. The powder samples were first housed in a flat
bottom high purity glass bell jar filled with helium gas. The mass of the
glass must be known so it can be subtracted later from the total specific
heat. An empty and full glass bell jars are shown in figure 2.4. This is
discussed in depth in M. Banks’ thesis. The sample, be it a powder or
a single crystal, is then attached to a thermally isolated sapphire plate,
which has a heater and a calibrated thermometer, via Apiezon® vacuum
grease. See the aforementioned thesis for more details.
2.4 Electron Paramagnetic Resonance spectroscopy

The electron paramagnetic resonance spectra were collected on a home-built microwave spectrometer. The spectrometer operates at $\sim 9.5$ GHz (X-band). The required field was created by an iron core Bruker BE25 magnet equipped with a BH15 field controller. The cryostat is a continuous flow system and can operate in the range of 3 K to 295 K. There are two sample mounts. The first is an electron paramagnetic resonance neutral low-background suprasil® quartz tube. The second is an elec-
tron paramagnetic resonance neutral mount with an attached calibrated temperature sensor (Cernox CX 1050) next to the sample. The sensor is shielded by a gold foil so as not to create an additional electron paramagnetic resonance signal. This sample holder allows for a very precise temperature measurement next to the sample. Both samples holders are shown in figure 2.5.

![Figure 2.5: Left: The electron paramagnetic resonance sample holder with a mounted temperature sensor. Right: The electron paramagnetic resonance neutral low-background suprasil® quartz tube with a sample mounted.](image)

Typically an electron paramagnetic resonance signal is the differential of a single, or a convolution of many, lorentzian resonance peaks. The spectrum could be fitted to the equation;
\[ EPR_{signal} = \sum_{i=1}^{N} \frac{d(L_i(H))}{dH} + y_0 + y_1 \times H + y_2 \times H^2, \]  

(2.1)

where \( y_0, y_1 \) and \( y_2 \) are variable background terms, \( N \) represents the total number of peaks and \( L(H) \) is given as:

\[ L(H) = \frac{I}{\pi} \times \frac{\Delta w + \alpha \times (H - H_{res})}{(H - H_{res})^2 + (\Delta w)^2}. \]  

(2.2)

Where \( I \) is the intensity, \( \Delta w \) is the half width at half maximum, \( H_{res} \) is the resonance position and \( \alpha \) is the dispersion. When an electron paramagnetic resonance signal is very broad, the negative field resonance should also be included.

The \( g \)-factor can be ascertained from the resonance field \( H_{res} \) by

\[ g \mu_B H_{res} = h \nu. \]  

(2.3)

Hence,

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

where \( \nu \) is the applied microwave frequency.
2.5 Dielectric capacitance

Dielectric capacitances were measured with either an Andeen-Hagerling AH2500A or an AH2700 capacitance bridge. Both are high precision variable AC-voltage bridges. The latter has a variable frequency option, 50 to 20000 Hz in discrete steps, whereas the former operates at a fixed 1000 Hz frequency. Samples were mounted via two methods. The first method, used for single crystals or pelletized powders, involved creating contacts on either side, with silver paint/paste or by depositing gold on the surface. Gold wires where then connected to the contacts which in turn where soldered to co-axial copper wire that led to the bridge. The second method applicable for powder samples only, had the powder compacted and sandwiched between two copper pistons in a vespel® tube. The copper pins were then in turn connected to co-axial copper wire which led to the bridge. All measurements where done in an Oxford helium cryostat equipped with a variable temperature insert allowing temperatures between 1.2 K and 300 K using a 12 T superconducting magnet.
2.6 Computation

2.6.1 Algorithms and Libraries for Physics Simulations - ALPS

"The ALPS project (Algorithms and Libraries for Physics Simulations) is an open source effort aiming at providing high-end simulation codes for strongly correlated quantum mechanical systems as well as C++ libraries for simplifying the development of such code. ALPS strives to increase software reuse in the physics community." [46]

The ALPS v1.3.5 project incorporates many programs. The two most pertinent programmes to this work are the looper code for quantum Monte Carlo simulations [47] and the Full Diagonalization Package for exact solutions of finite systems. The looper code allows the calculation of observables such as spin magnetisation, spin susceptibility, specific heat and staggered magnetisation for large \((N \geq 1000)\) finite systems. For such large systems the observables can be assumed to be those of an infinite system, with only very low-temperature observables \((T/J < 0.01)\) showing a deviation from an infinite system, i.e. an \(N\) dependence for large \(N \geq 1000\). This makes quantum Monte Carlo a very powerful tool for simulating different systems. However, the quantum Monte Carlo approach has a problem. When it comes to frustrated systems it encounters the sign problem [48] and the solution does not
converge. This is where the second package, Full Diagonalization, comes into play. Full Diagonalization allows one to exactly solve the hamiltonian for a finite system and as such calculate observables. But the system size is heavily limited by computing power and more importantly by RAM memory capacity. As such modern computers can only solve $S = 1/2$ systems for approximately 24 atoms. With larger spins the system size has to be significantly reduced. This results in deviations (finite size effects) at relatively large temperatures, $T/J < 0.3$. However, with these limitations in mind Full Diagonalization can be used to obtain observed behaviour in many systems.

2.7 Summary

In this chapter I briefly described the experimental method used for characterization of the systems discussed in the other chapters.

In the next chapter I will be discussing our investigation of CuCrO$_4$. This is a chemically well-known compound but its magnetic properties have never been studied until now. We reported in our publication, that CuCrO$_4$ is a previously unknown type-II multiferroic [24].
Chapter 3

CuCrO$_4$ - A new multiferroic material

In this chapter I will discuss the magnetic properties of CuCrO$_4$, a $S = 1/2$ 3$d^9$ spin chain. Here I am reporting a detailed experimental and theoretical investigation characterizing the magnetic properties of CuCrO$_4$ for the first time.
3.1 Crystal structure

Figure 3.1: The crystal structure of CuCrO$_4$, projected slightly off of the $c$-axis. The unit cell is doubled along the $c$-axis. Blue octahedra: CuO$_6$ units. Green tetrahedra: CrO$_4$ units.

CuCrO$_4$ crystallizes with the CrVO$_4$ structure-type (space group $Cmcm$), with Cu and Cr in the oxidation state 2$^+$ and 6$^+$, respectively [49, 50]. Cu$^{2+}$ has the electronic configuration $3d^9$ with one hole in the $3d$ shell, hence $S=1/2$, while Cr$^{6+}$ has an empty $d$-shell. Consistent with the other compounds which belong to the CrVO$_4$ structure-type, the pertinent structural feature is the corrugated CuO$_2$ ribbon chains running along the $c$-axis. The ribbon chains are made up from planar CuO$_4$
plaquettes which are connected via trans-edges, as shown in figure 3.1. The CuO₄ plaquettes form the basis of elongated (Jahn-Teller distorted) CuO₆ octahedra. The ribbon chains are interconnected by slightly distorted CrO₄ tetrahedra, which inhabit interstitial voids. At room temperature the Cu²⁺⋯Cu²⁺ distance is reported to be 2.945(2) Å with a Cu²⁺⋯O²⁻⋯Cu²⁺ angle of 97.067(7)° [50].

3.2 Sample preparation

The preparation of CuCrO₄ is rather intriguing, mainly due to the instability of the copper-chromate 1:1:4 stoichiometry. According to Hanic et al. at rather low-temperatures CuCrO₄ decomposes into the spinel-type CuCr₂O₄ and CuO [51]:

\[
4 \text{CuCrO}_4 \xrightarrow{687 \text{K} - 773 \text{K}} 2 \text{CuO} + 2 \text{CuCr}_2\text{O}_4 + 3 \text{O}_2.
\]

So-far this seriously hampered the growth of crystals, suitable for bulk characterization, as well as the preparation of highly homogenous samples.

The second problem associated with sample preparation is a health and safety concern, Cr⁶⁺ is considered a genotoxic carcinogen [52]. As such all samples must be handled with care.
Multiple methods can be employed to prepare polycrystalline sample of CuCrO$_4$. All measurements reported here were undertaken on a single powder sample ($\approx 160$ mg total available sample) that was prepared by separately dissolving equimolar amounts Copper(II) hydroxide and Chromium(VI) oxide in distilled water*. The two solutions were mixed and boiled to dryness. The resulting powder was heat treated in air at a temperature of 150$^\circ$C for 2 days. This method was first described by Arsene et al. [53]. The phase purity of the sample was checked by x-ray powder diffraction measurements using a STOE STADI-P diffractometer with monochromated Mo-$K\alpha_1$ radiation. The powder pattern was fitted using the Rietveld profile refinement method employed within the Fullprof Suite [54]. No other reflections besides those of CuCrO$_4$ were observed. The pattern and the resultant fit can be seen in figure 3.2. The structural parameters of this fit are tabulated in table 3.1. Later, larger samples intended for powder neutron diffraction were prepared along a similar route replacing Copper(II) hydroxide by anhydrous Copper(II) acetate. It should be noted that the sample is reported and was found to be brick red in colour. But black samples, initially believed to be decomposed samples, can also be obtained. According to x-ray powder diffraction are isostructural to their red counterparts. The only difference in their preparation was a longer or higher annealing temperature.

---

*The sample was prepared by Prof. R. Glaum and his group at Bonn University, Bonn.
3.3 Magnetic susceptibility

The molar magnetic susceptibility of a powder sample of CuCrO$_4$, contained within a gelatin capsule was measured in the temperature range of 2 K to 350 K in an applied dc magnetic field of 1, 3, 5 and 7 T. Above $\approx 20$ K no field dependence was observed, suggesting minimal ferromagnetic impurities. However, upon cooling a noticeable field dependence became apparent. At lowest temperatures an almost asymptotic be-
Table 3.1: Atomic positional parameters of CuCrO$_4$ (space group $Cmcm$) as obtained from a profile refinement of the x-ray powder diffraction pattern collected at room temperature. The lattice parameters amount to $a = 5.43877(50)$ Å, $b = 8.97225(83)$ Å and $c = 5.89044(55)$ Å.

<table>
<thead>
<tr>
<th>oxidation atom</th>
<th>state</th>
<th>Wyckoff position and letter</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>$+2$</td>
<td>4a</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>0.0000(0)</td>
<td>0.089(8)</td>
</tr>
<tr>
<td>Cr</td>
<td>$+6$</td>
<td>4c</td>
<td>0.0000(0)</td>
<td>0.3700(3)</td>
<td>0.2500(0)</td>
<td>0.904(7)</td>
</tr>
<tr>
<td>O1</td>
<td>$-2$</td>
<td>8f</td>
<td>0.0000(0)</td>
<td>0.2652(5)</td>
<td>0.0312(9)</td>
<td>0.800(12)</td>
</tr>
<tr>
<td>O2</td>
<td>$-2$</td>
<td>8g</td>
<td>0.2326(7)</td>
<td>-0.0198(6)</td>
<td>0.2500(0)</td>
<td>0.800(12)</td>
</tr>
</tbody>
</table>

Behaviour was observed for small fields, with a kink at $\approx 8$ K and an ill-defined shoulder ranging from $\approx 11$ to $20$ K. In small magnetic fields a thermal hysteretic behaviour was seen below the ill-defined shoulder. Upon application of a larger magnetic field the molar magnetic susceptibility decreased and the asymptotic and hysteretic behaviour died away. The kink became more pronounced and it is interpreted as evidence of long-range magnetic order. The ill-defined shoulder gradually faded away and was replaced by a well-defined hump, which is indicative of one-dimensional short range correlations, with a maximum centered at $\approx 15$ K.
Figure 3.3: The molar magnetic susceptibility of CuCrO$_4$, in the low-temperature regime, versus temperature for various magnetic fields. Red symbols: Heating data. Blue symbols: Cooling data.

At high temperature, $\approx 100$ K, the molar magnetic susceptibility followed the modified Curie-Weiss law:

$$\chi_{\text{mol}}(T) = \frac{C}{T - \Theta} + \chi_{\text{dia}} + \chi_{vV}, \quad (3.1)$$
where $C$ is the Curie constant pertaining to the spin susceptibility of the Cu$^{2+}$ entities. The Curie constant is given as $C = N_A g^2 \mu_B^2 S(S + 1)/3k_B$. 

$\chi_{\text{dia}}$ refers to the diamagnetic susceptibilities of the electrons in the closed shells which could be estimated from the tabulated increments given by Selwood as $-62 \times 10^{-6}$ cm$^3$/mol [44]. The $\chi_{\nu\nu}$ contribution cannot be tabulated and cannot be calculated precisely, but values are known for similar compounds and comparisons can be made (see above).
Figure 3.4: (o): The inverse molar magnetic susceptibility versus temperature of CuCrO$_4$, measured in a field of 7 T. Red solid line: Fit to the modified Curie-Weiss law as given in equation 3.1.

Best agreement was found with a $g$-factor of 2.17(2), a $\Theta$ of -56(1) K and $\chi_{\text{dia}} + \chi_{\text{VV}} \approx +20 \times 10^{-6}$ cm$^3$/mol. This implies a $\chi_{\text{VV}}$ of $\approx +80 \times 10^{-6}$ cm$^3$/mol which is a reasonable value for Cu$^{2+}$ in this environment [20].
Below 100 K the magnetic susceptibility deviated from a Curie-Weiss law due to short-range correlations. The temperature dependence of the lower-temperature range can be approximated theoretically by full diagonalization calculations of a finite system (N=20). Such results for $\chi_{\text{chain}}^*(\alpha,T)$ were available from Heidrich-Meissner et al. [55] for $\alpha$ from
+4 to -4, where $\alpha = J_{nn}/J_{nnn}$. Guided by density functional theory calculations (see sections 3.7) values of $\alpha$ ranging from 1.5 to 2.5 were compared to the experimental data along with the molar magnetic susceptibility of a uniform nn anti-ferromagnetic chain [8]. Inter-chain spin exchange interactions could be approximated with a mean-field correction, such as

$$\chi_{\text{mol}}(T) = \frac{\chi_{\text{chain}}(T)}{1 - \lambda \times \chi_{\text{chain}}(T)} + \chi_0,$$

where $\lambda$ is given by

$$\lambda = \frac{1}{N_A g^2 \mu_B^2} \sum_i z_i J_i S_i (S_i + 1).$$

Here $J_i$ is an inter-chain spin exchange interaction constant that occurs $z_i$ times for a given atom with spin $S_i$. $\chi_0$ can be taken from above, $\approx +20 \times 10^{-6}$ cm$^3$/mol. A $g$-factor of 2.125 was used, which is consistent with electron paramagnetic resonance measurements, see section 3.5. $J_{nnn}$ was scaled so as to reproduce the hump at the correct temperature. The results are shown in figure 3.5. It is apparent from the graph that best agreement is obtained for an $\alpha \approx 2$, $J_{nnn} = -27$ K and a $\lambda$ of $7(1)$ mol/cm$^3$. $z_1 = 4$, $z_2 = 2$ was assumed for the density functional theory calculations. As shown by the density functional theory calculations
with a $\lambda$ of 7(1) mol/cm$^3$ and $J_1 \approx -1/4 \times J_2$ one finds $J_2 = 12(2)$ K. This is in very good agreement with the experimental results (see section 3.7 and table 3.2).

A future high magnetic field experiment has been scheduled. A pulsed magnetic field of $\approx 70$ T will be applied and the magnetisation versus field will be measured. In order to predict the results full diagonalization of a finite ($N=18$) system was performed using the ALPS package (see section 2.6.1 for details relating to the ALPS package). The system of 18 spins on a one-dimensional lattice with periodic boundary conditions was solved with nn and nnn spin exchange interactions set to the values ascertained from magnetic susceptibility measurements ($-27$ K and $-54$ K, respectively). The results, with a $g$-factor of 2.125 at 1.4 K, can be seen in figure 3.6.
Figure 3.6: Full diagonalization results. Solid red and black lines are the magnetisation $M$ and $\frac{d(M)}{d(H)}$ versus applied magnetic field, respectively.

3.4 Specific heat

The specific heat versus temperature of CuCrO$_4$ was measured on a powder sample of 2.43 mg (see figure 3.7 and for experimental details see section 2.3). A broad, smeared, $\lambda$-type anomaly centered at 8.2(2) K can be clearly seen. This is indicative of long-range magnetic ordering.
Within figure 3.7 there is also presented the specific heat measured with an applied magnetic field of 9 T. The data is offset so as to be clearly distinguishable from the 0 T data. Within error bars the data for the two different fields are identical. This implies that the long-range ordering anomaly does not shift as a function of applied magnetic field. The intra-chain is \( \approx -27 \) K, this is substantially larger in energy than 9 T and as such one would not expect a significant change of the spin arrangement. Specific heat divided by temperature is plotted versus temperature and it is shown in figure 3.8. This plot allows an estimation to be made of the entropy contained within the long-range ordering anomaly. \( \Delta S \approx 0.6 \) J/mol.K was found to be contained within the anomaly. This is \( \approx 10\% \) of the expected total magnetic entropy for a \( S = 1/2 \) system, \( S = R \ln(2S+1) \). For \( S = 1/2 \) we obtain \( R \ln(2) \), where \( R \) is the molar gas constant. The other 90\% of the entropy has been removed by short-range correlations at higher temperatures. At long-range ordering the single ribbon chains are high correlated and most of the entropy left pertains to the ordering of the chains with respect to each other.
Figure 3.7: The specific heat versus temperature for CuCrO$_4$. (o): 0 T data. (△): 9 T data, offset by +0.5 J/molK.
Figure 3.8: (o): The specific heat divided by temperature versus temperature for CuCrO$_4$, in the temperature range of the anomaly.

The low-temperature specific heat, below the long-range ordering temperature, consists of both phonon and magnon contributions. The temperature dependence of the phonon contribution could be assumed to follow a Debye $\propto T^3$ power law, whereas the magnon contribution varies in a manner depending upon the spin wave dispersion relation. For three-dimensionally ordered samples one expects, for anti-ferromagnetically
long-range ordered materials, a contribution to the specific heat with a temperature dependence similarly to that of the phonon contribution \( \propto T^3 \). When the sample is ferromagnetic magnons provide a \( \propto T^{3/2} \) contribution [56]. Figure 3.9 displays a plot of \( C_p/T^{3/2} \) versus \( T^{3/2} \). Since the data shows a non-zero intercept one can infer that the specific heat comprises of a \( \propto T^{3/2} \) contribution indicative of a contribution of ferromagnetic magnons. This is consistent with the density functional theory calculations. The linear behaviour in figure 3.9 could be explained by equation 3.2. \( \beta \) is related to the 0 K Debye temperature, \( \theta_D(T \to 0) \), by equation 3.3. In the case of CuCrO\(_4\) where \( N = 6 \) one finds \( \theta(T \to 0) = 138(1) \) K. Within ferromagnetic spin-wave theory the non-zero intercept, is given by equation 3.4 [57]. Here \( J_{\text{inter}} \) is the nn inter-chain coupling and \( q \) is a constant pertaining to the number of nearest-neighbours. If we assume a simple cubic arrangement of nearest-neighbours situation, which is not unreasonable for CuCrO\(_4\), then \( q = 0.113 \). With an intercept of 0.0109(1) J/molK\(^{5/2}\) we find \( J_{\text{inter}} \) to be \( \approx 19.5 \) K. Consistent with what was found from \textit{ab initio} calculations, see section 3.7.

\[
C_p/T^{3/2} = \beta T^{3/2} + \gamma \tag{3.2}
\]
\[ \beta = NR \frac{12 \pi^4}{5} \left( \frac{1}{\theta_D} \right)^3 \]  \hspace{1cm} (3.3)

\[ \gamma = \frac{qR}{J_{\text{inter}}^{3/2}} \]  \hspace{1cm} (3.4)

Figure 3.9: The specific heat divided by \( T^{3/2} \) versus \( T^{3/2} \). (o): Measured data. Solid red line: linear fit, with a slope of \( 4.31(1) \times 10^{-3} \) J/molK\(^4\) and an intercept of \( 0.0109(1) \) J/molK\(^{5/2}\).

As discussed in section 1.2.3 the inter-chain spin exchange that led to long-range ordering could be estimated from \( T_N \). Using the formulism
put forth by Yasuda et al. and assuming $J_{\parallel}$ to be the $J_{nn}$ as found from magnetic susceptibility, $|J_{\perp}|$ was found to be $\approx 5$ K. This is of the same order of magnitude as the value obtained from density functional theory calculations, as well as the experimentally ascertained value from the mean field correction term $\lambda$. The difference between the inter-chain coupling calculated from Yasuda’s formalism and the other values may arise since CuCrO$_4$ has two different inter-chain coupling constants, $J_1$ and $J_2$, and a nnn spin exchange interaction $J_{nnn}$, that was not included in Yasuda’s model. For CuCrO$_4$ these values are significant and need to be incorporated.

3.5 Electron paramagnetic resonance

The temperature dependent electron paramagnetic resonance was measured on a $\approx 5$ mg sample mounted in an electron paramagnetic resonance neutral low-background suprasil® quartz tube, see section 2.4. A single symmetric, broad Lorentzian line was observed centered at $\approx 3.4$ kOe with a temperature dependent peak-to-peak linewidth of 0.8 - 1 kOe. The line could be nicely fitted to the derivative of a single Lorentzian absorption line with a small dispersion contribution $|\alpha| \leq 0.04$. Since the half width at half maximum was so large, of the
same order of magnitude as the resonance position, both circular components of the exciting linearly polarized microwave field were taken into account, i.e. the negative magnetic field resonance centered at \(-H_{\text{res}}\), see section 2.4. The room-temperature spectrum can be seen in figure 3.10. The dispersion term fitted to the electron paramagnetic resonance signal was negligible over the whole temperature range and as such was ignored.

Figure 3.10: (o): Electron paramagnetic resonance signal for CuCrO$_4$ taken at 297(1) K. Solid red line: Fit to equation 2.1.
Figure 3.11 shows the temperature dependent fitted parameters of CuCrO$_4$. The intensity, which is proportional to the spin susceptibility, increased with decreasing temperature until $\approx 15$ K whereupon there is a cusp and from then on it decreased with decreasing temperature. This is very similar to what was seen for the magnetic susceptibility, see section 3.3. A Curie-Weiss behaviour is observed at high temperatures for the electron paramagnetic resonance signal. Above $\approx 100$ K the reciprocal intensity was seen to behave in a linear fashion with temperature, as shown in figure 3.12. It can be fitted to a Curie-Weiss equation according to:

$$I_{EPR} \propto \frac{1}{T - \theta_{EPR}}$$

The best fit was found for a $\theta_{EPR}$ of -60(5) K which is in very good agreement with what was found from the magnetic susceptibility measurements, see section 3.3. The fit is shown in figure 3.12.

The $g$-factor increased with decreasing temperature until approximately 150 K whereupon it saturated at a value of 2.125(2). This value is somewhat lower than would be expected for Cu$^{2+}$ powder electron paramagnetic resonance spectra and it is lower than the values ascertained from the molar magnetic susceptibility, see section 3.3, and an angular overlap model calculation compared to optical spectroscopy results reported by Law et al. [24]. A temperature dependent $g$-factor can be at-
tributed to slight changes of the ligand environment as the temperature decreases. The saturation of the \( g \)-factor at low-temperatures supports this, since the rate of change of the ligand environment would decrease with decreasing temperature.
Figure 3.11: Fitted parameters of the electron paramagnetic resonance signal of CuCrO$_4$ versus temperature. (a): Intensity of the electron paramagnetic resonance signal. (b): $g$-factor. (c): The half width at half maximum and the solid red line is a fit to a linear slope, with a gradient of 2.75(2) T/K and an intercept of -220(5) K.
The half width at half maximum was seen to decrease with decreasing temperature until $\approx 15$ K where it starts to rapidly increase down to lowest-temperatures. This is indicative of the onset of long-range ordering. Within the temperature range of $\approx 25$ K to $\approx 100$ K the half width at half maximum increased linearly with increasing temperature,
in accordance with results reported by Oshikawa and Affleck (see section 1.2.4). The slope was found to be $\approx 2.5 \times 10^{-4}$ T/K similar to that found for the spin-Peierls compound CuGeO$_3$ [58]. Deviation away from the Oshikawa and Affleck behaviour is seen at higher temperatures. The half width at half maximum then starts to show a concave dependence with increasing temperature. This is a cross over from the Oshikawa and Affleck to Kubo and Tomita regime, wherein there is a temperature independent linewidth. The half width at half maximum is seen to tend towards a constant temperature independent value, with an extrapolated saturation value of 0.14 T. Using the formalism put forth by Kubo and Tomita (see section 1.2.4) this implies a deviation from the symmetric Heisenberg spin exchange of $\delta \approx 3$ K or 5% of the nn spin exchange [38].

3.6 *ab initio* calculations

To understand the magnetic properties of CuCrO$_4$ first principles total energy calculations were performed\(^\dagger\). To examine the magnetic properties of CuCrO$_4$, the four spin exchange paths shown in figure 3.13 were considered. Then the spin configuration energies obtained by *ab initio* density functional theory calculations were mapped onto a Heisenberg

\(^\dagger\)The first principle density functional theory calculations were done by Prof. M. Whangbo and his group at North Carolina State University, Raleigh, N. C., USA.
spin exchange Hamiltonian

\[ H = - \sum J_{ij} \vec{S}_i \cdot \vec{S}_j, \]

where \( J_{ij} \) was the spin exchange for the interaction between spins located at lattice sites \( i \) and \( j \). The relative energies of the five ordered spin states of CuCrO\(_4\) were determined by density functional calculations with the Vienna \textit{ab initio} simulation package, employing the projected augmented-wave method [59, 60, 61], the generalized gradient approximation (GGA) for the exchange and correlation functional [62], with the plane-wave cut-off energy set to 400 eV and a set of 64 \( \mathbf{k} \)-points for the irreducible Brillouin zone. To account for the electron correlation associated with the Cu 3\( d \) state, GGA plus on-site repulsion (GGA+\( U \)) calculations were performed with \( U_{\text{eff}} = 4 \) and 6 eV for Cu [63].

The relative energies of the five ordered spin states obtained from our GGA+\( U \) calculations are summarized in figure 3.13. By mapping these relative energies onto the corresponding relative energies from the total spin exchange energies [64, 65, 66, 67, 68], the values of the spin exchange parameters, \( J_{nn}, J_{nnn}, J_1, \) and \( J_2 \) could be ascertained as summarized in table 3.2.
Figure 3.13: (a): Spin exchange pathways used for the mapping for the density functional theory results. (b): The five spin configurations for which the total energy has been calculated by GGA+$U$ calculations. Shown are the equations used from mapping the energies onto the aforementioned spin exchange pathways. Shown below in parentheses are the relative energies given in meV, first for $U = 4$ eV and then for $U = 6$ eV.
\[
\begin{array}{|c|c|c|c|c|}
\hline
J_i & U_{\text{eff}} = 4 \text{ eV} & (\text{K}) & U_{\text{eff}} = 6 \text{ eV} & (\text{K}) & \text{experiment (K)} \\
\hline
J_{\text{nn}} & -199.7(1.0) & -63.8 & -115.9(1.0) & -55.4 & -54 \\
J_{\text{nnn}} & -85.8(0.43) & -27 & -56.5(0.49) & -27 & -27 \\
J_1 & -8.6(0.04) & -2.7 & -6.00(0.05) & -2.9 & -4 \\
J_2 & +31.1(0.16) & +9.8 & +22.3(0.19) & +10.7 & +12 \\
\theta_{\text{CW}} & -43.2 & -38.8 & -38.8 & \approx -58 \\
\hline
\end{array}
\]

Table 3.2: The spin exchange parameters of CuCrO\textsubscript{4} as found by GGA+U calculations with the two different on-site repulsions \(U_{\text{eff}} = 4\) and 6 eV. The left column for each \(U_{\text{eff}}\) contains the direct theoretical results, while the values in the right column are the scaled theoretical results such that \(J_{\text{nnn}}\) equals the experimental finding of \(-27\) K. The rightmost column summarizes the experimentally found spin exchange values. The final row shows the Curie-Weiss temperatures of the scaled GGA+U spin exchange parameters, calculated using the mean field expression; \(\theta_{\text{CW}} = \frac{1}{\sum_i z_i} \sum_i z_i J_i S(S + 1)\) [69], where \(z_i\) is the number of neighbour with which a single atom interacts via the spin exchange \(J_i\), and the experimentally found values from electron paramagnetic resonance and magnetic susceptibility measurements.

Based upon the spin exchange interactions calculated by \textit{ab initio} methods, one can predict a magnetic structure. If one assumes the nn spin exchange interaction to be twice as large as the nnn spin exchange interaction and both to be anti-ferromagnetic. Treating only the intra-chain coupling and assuming the magnetic moment to be a classical vector one
can write the energy as

\[ E = \sum_i -JS_i \cdot S_{i+1} - \sum_i J S_i \cdot S_{i+2}. \]

Which can be rewritten as

\[ E = -J|S^2|\cos\theta - \frac{J|S^2|}{2}\cos2\theta, \]

where \( \theta \) is the pitch angle between two nn spins. The ground-state is given as \( \frac{dE}{d\theta} = 0 \). This is the case when \( \theta = \pm 60^\circ \), where the negative and positive results are the two different chiralities (handednesses). This gives a magnetic unit cell 3 times larger along the \( c \)-axis than the chemical unit cell. The inter-chain spin exchanges would result in a ferromagnetic arrangements of chains in the \( a \)-axis and an anti-ferromagnetic arrangement in the \( b \) direction. A pictorial representation of this is shown in figure 3.14. This would imply a magnetic propagation vector of \([0,0,\frac{1}{3}]\).
Figure 3.14: The predicted magnetic structure of CuCrO$_4$, the chemical unit cell is denoted by the dashed box. (a) The magnetic structure in the $a$-$b$ plane, white and black circles represent different magnetic moment directions. (b) The magnetic structure within the $a$-$c$-plane, with the magnetic moments represented by an arrow.

### 3.7 Dielectric capacitance

The dielectric constant, $\epsilon_r$, versus temperature of CuCrO$_4$ was measured on a non-pelletized compact powder, see section 2.5, using a AH2700 capacitance bridge with a constant frequency and excitation voltage of
1000 Hz and 15 V, respectively. At room-temperature the value $\varepsilon_r \approx 48$ was observed. Between room-temperature and $\approx 35$ K, $\varepsilon_r$ was seen to decrease in a smooth fashion. Between 35 and 15 K $\varepsilon_r$ passed through a shallow double maximum, possibly induced by some magnetostriction driven by short-range ordering effects above long-range ordering, see figure 3.15 (b). No reasonable assumptions can be made about the nature of the shallow double maximum, future neutron scattering experiments will be needed to probe that is the cause of these features. Just prior to long-range ordering at 10 K a value of $\approx 4.35$ was measured for $\varepsilon_r$.

In zero field, at long-range ordering, $\approx 8.5$ K, $\varepsilon_r$ started to rapidly increase with decreasing temperature until levelling off and falling once again, resulting in a rather broad asymmetric hump centered at $\sim 5.35$ K. There was no indication for a sharp spike near long-range ordering transition temperature. This behaviour is frequently found in multiferroic systems [27, 70]. Similar broad symmetric humps, centered at $T_N$, have been seen in CuCl$_2$ and CuBr$_2$ [27, 71]. The overall increase of $\varepsilon_r$ amounts to a $\approx 6\%$ effect when compared to the paramagnetic value prior to long-range ordering. With the application of a magnetic field the maximum of the magnetoelectric anomaly in $\varepsilon_r$ decreases and the maximum of the broad asymmetric hump moves to higher temperatures. Consistent with specific heat measurements the onset of the magnetoelectric anomaly,
long-range ordering, was not seen to move with an applied field. The shift of the hump is an artifact from the changing field dependent of $\epsilon_r$ at different temperatures. The temperature dependence of $\epsilon_r$ under various magnetic fields is displayed in figure 3.15 within the main panel. The decrease of $\epsilon_r$ with a magnetic field started above $\approx 1$ T and tended to saturation to the paramagnetic only value at sufficiently high fields. An isotherm is shown in figure 3.15 (a).
Figure 3.15: Main: The temperature dependence of the relative dielectric constant for \( \text{CuCrO}_4 \) at low-temperatures under various magnetic fields, refer to legend. (a): A magnetic isotherm of the relative dielectric constant at 5.2(1) K. (b): The relative dielectric constant of \( \text{CuCrO}_4 \) at higher temperatures in zero magnetic field.
3.8 Discussion and conclusion

It was shown in this chapter that at high temperatures CuCrO$_4$ can be explained as a paramagnet with a Curie-Weiss temperature of approximately -60 K. This was shown by both magnetic susceptibility and electron paramagnetic resonance measurements. At lower temperatures there are short-range one-dimensional correlations which manifests themselves as a broad hump in the magnetic susceptibility, similar to what has been seen for LiCuVO$_4$, CuCl$_2$ and CuBr$_2$ [25, 20, 71]. The electron paramagnetic resonance line width shows a linear behaviour with temperature at low-temperatures which is indicative of a one-dimensional magnet with anisotropic or antisymmetric exchange terms. This has also been seen for LiCuVO$_4$ by Schrettle et al. [70].

The low-temperature magnetic susceptibility was modelled against the exact diagonalization results for a nn and nnn one-dimensional $S = 1/2$ spin chain, with a small inter-chain coupling. Agreement was found for a ratio of $J_{nn}/J_{nnn} \approx 2$. The position of the broad hump in the magnetic susceptibility was best replicated with a $J_{nnn}$ of -27 K.

Long-range ordering was evidenced by a anomaly in the specific heat and the magnetic susceptibility at $\approx 8.2$ K. The dielectric constant exhibits clear evidence for a magnetoelectric effect at the long-range ordering
transition temperature, as seen in other type-II multiferroics. The long-range ordering anomaly is not seen to move with the application of a magnetic field. This is indicative of ferromagnetic ordering between the anti-ferromagnetically ordered chains.

The experimental results were complemented by theoretical *ab initio* calculations. These confirm a $J_{nn}/J_{nnn}$ ratio of approximately 2. However, density functional theory tends to overestimate spin exchange interactions, typically by a factor of 2-5 [72]. By renormalizing the density functional theory results to the experimentally observed $J_{nnn}$ of -27 K, agreement was found for the inter-chain couplings which were taken from the correction to the magnetic susceptibility.

However, the renormalized density functional theory results would suggest a Curie-Weiss temperature larger than what has been experimentally observed. This could be due to an insufficient correction of the van Vleck contribution to the magnetic susceptibility. But the electron paramagnetic resonance signal is not subject to a van Vleck correction and as such this argument does not hold for this case. Here the inconsistency could be due to poor fitting for the electron paramagnetic resonance absorption line. The counter argument, assuming the experimental results are correct, could be that there are additional spin exchange interactions that were not included and have not been taken into account in the mean
field approximation of the Curie-Weiss temperature.

On the basis of *ab — initio* density functional calculations a predictive magnetic structure could be formulated, which has a spin spiral structure and a commensurate magnetic propagation vector of $[0,0,\frac{1}{3}]$.

In conclusion, CuCrO$_4$ constitutes a new one-dimensional quantum antiferromagnet, which has a pronounced magnetoelectric anomaly originating at long-range ordering. Density functional calculations indicate that CuCrO$_4$ is a one-dimensional anti-ferromagnetic Heisenberg chain system, where both nn and nnn spin exchange interactions are antiferromagnetic. The ratio $J_{nn}/J_{nnn}$ was found to be close to 2, the Majumdar-Ghosh point [15, 16]. CuCrO$_4$ undergoes long-range ferromagnetic ordering due to a sizeable ferromagnetic inter-chain spin exchange interaction. The rather large magnetoelectric anomaly below the Néel temperature provides evidence for non-collinear, possibly helicoidal, spin ordering in the one-dimensional chains. CuCrO$_4$ is therefore a new system which exhibits type-II multiferroicity.

### 3.9 Summary

In the preceding chapter I have shown that CuCrO$_4$ is a quantum spin chain with type-II multiferroicity. There is still more work to be done
on this compound. Especially, elastic and inelastic neutron diffraction which will given an insight into the magnetic structure. High magnetic field magnetisation measurements are scheduled to confirm the plateaus seen in simulations.

A consistent set of spin exchange values has been obtained. Magnetic and dielectric properties have been measured as a function of temperature and applied magnetic field. *Ab initio* calculations support the experimental findings and allow a more informed modelling of the low-temperature characteristics to be carried out. Further measurements are needed to support some tentative interpretations of experimental results. This includes a detailed neutron scattering investigation of the structure of CuCrO$_4$ at low-temperature.

In the next chapter I will discuss my investigation of the 3$d^1$ system, TiPO$_4$. TiPO$_4$ is largely isostructural to CuCrO$_4$ and has been the subject of several, however inconclusive studies of its magnetic properties. I intend to show that new results which classify TiPO$_4$ as undergoing a spin-Peierls transition at low-temperature.
Chapter 4

TiPO$_4$ - A new spin-Peierls system?

In the following chapter I will report on our investigation into the magnetic properties of TiPO$_4$. Unlike the isostructural $3d^9$ compound CuCrO$_4$, that was reported on in the previous chapter, TiPO$_4$ undergoes a spin-Peierls transition and has a non-magnetic ground-state.

4.1 Introduction and crystal structure

TiPO$_4$ is a chemically well known material, but its physical, especially its magnetic, properties have never been subject to a detailed investigation. As such no conclusive results have been obtained and no clear understanding has been gained as of yet. TiPO$_4$ crystallizes in the CrVO$_4$ structure-type (space group $Cmcm$) with Ti$^{+3}$ ($3d^1 S = 1/2$)
housed in tetragonally compressed octahedron. The TiO$_6$ octahedra are edge sharing and arrange themselves in a one-dimensional configuration, see figure 4.1, forming corrugated ribbon chains running along the $c$-axis. The ribbon chains are buckled in the $ac$-plane with a buckling angle of $156.927(4)^\circ$. The Ti$^{3+}$···Ti$^{3+}$ distance at room-temperature is 3.1745(10) Å with a Ti$^{3+}$···O$^{2-}$···Ti$^{3+}$ angle of $95.484(5)^\circ$ [73]. The interstitial voids between the ribbon chains are partially filled by distorted PO$_4$ tetrahedra.

![Figure 4.1: The crystal structure of TiPO$_4$, projected slightly off the c-axis. The unit cell is doubled along the c-axis. Yellow octahedra: TiO$_6$ units. Purple tetrahedra: PO$_4$ units.](image)

Previous to this investigation [74] three papers reported the magnetic
properties of TiPO₄, one by Kinomura et al. [75], a second by Glaum et al. [76] and a third by Yamauchi and Ueda [77]. The first paper reported the magnetic susceptibility from 2 K to 600 K and described it as being “almost temperature independent above 150 K”. The second paper showed only the reciprocal magnetic susceptibility and simply compares it to earlier work by Kinomura et al. However, in this work the authors also probe the low-temperature (2 K) magnetic structure by neutron powder diffraction. The authors report no additional reflections due to coherent magnetic scattering and confirm the low-temperature chemical structure to remain isostructural to that of the room-temperature structure, except for a lattice contraction. The authors go on to comment on their null result, ascribing the absence of magnetic Bragg reflections as being due to the true one-dimensional linear anti-ferromagnetic nature of TiPO₄, wherein no long-range magnetic order would occur at finite-temperature. The authors of the third paper infer that TiPO₄ should have the characteristics of a $S = 1/2$ Heisenberg antiferromagnetic chain, quoting ”[A] broad maximum characteristic of a Heisenberg antiferromagnetic linear chain seems to be above room-temperature”.

The first crystal growth of this compound was reported by Glaum et al. [78]. They grew single crystals by vapor transport using iodine as a transport agent.
4.2 Sample preparation

![Figure 4.2: A single crystal of TiPO$_4$. The orientation and size are indicated.](image)

Single crystals as large as $5 \times 5 \times 2$ mm and powder samples of TiPO$_4$ were prepared via chemical vapor transport*. An example of a single crystal can been seen in figure 4.2. The preparation has been the subject of a previous publication [78], where it was reported that an initial reaction of

$$4 \text{TiP}_2\text{O}_7 + 4 \text{TiO}_2 + \text{TiP} \rightarrow 9 \text{TiPO}_4$$

in an inert atmosphere at $900^\circ$ for 12 hrs, resulted in a pure powder sample. Going on to chemically vapour transport the powder in an enclosed quartz ampoule with the temperature gradient $900^\circ \rightarrow 1000^\circ$.

---

*The sample was prepared by Prof. R. Glaum and his group at Bonn University, Bonn.
(source and sink, respectively), using I₂ as a transporting agent (approximately 200 mg of I₂ was used per 15 cm³), resulted in the very high quality single crystals.

4.3 Magnetic susceptibility

The molar magnetic susceptibility of a collection of many small randomly oriented crystals, contained within a suprasil® quartz tube, as discussed in detail already in section 2.2.1, was measured in the temperature range of 2 to 400 K in an applied dc magnetic field of 0.1, 1, 3, 5 and 7 T and in the temperature range from 300 to 800 K in a magnetic field of 1 T. No field dependence of the magnetic susceptibility was observed (not-shown here). As a result only the 1 T data is displayed.

The high-temperature molar magnetic susceptibility is characterized by a broad anomaly centered at ≈ 625 K, indicating short-range one-dimensional anti-ferromagnetic correlations. After correcting the data for the temperature independent diamagnetic contributions of the closed shells and the sample holder the high-temperature magnetic susceptibility (450 K ≤ T) can be explained by a S = 1/2 Heisenberg anti-ferromagnetic chain, with a uniform nn spin exchange interaction of -972(3) K, a g-factor of 1.93(3) and a temperature independent contri-
bution to the magnetic susceptibility of $\approx 109(10) \times 10^{-6}$ emu/mol [8]. The results of the fit can be seen in figure 4.3.

![Graph showing molar magnetic susceptibility versus temperature for TiPO$_4$](image)

Figure 4.3: (o): The molar magnetic susceptibility versus temperature for a powder sample of TiPO$_4$ measured in a field of 1 T. Red solid line: Fit to a $S = 1/2$ Heisenberg antiferromagnetic chain with a uniform nearest-neighbour spin exchange interaction model, as given by Johnston et al. [8].
Below $\approx 120$ K, two magnetic phase transitions are indicated by two rapid drops in the molar magnetic susceptibility at $111(1)$ and $74(0.5)$ K, respectively, as shown in figure 4.4. The transition at $111(1)$ K has no thermal hysteresis. The heating and cooling curves are identical within experimental error. However, the transition at $74(0.5)$ K does exhibit a thermal hysteresis of $50(10)$ mK. This can be clearly seen in figure 4.4.
The molar magnetic susceptibility between $\approx 105$ and $\approx 80$ K and below $\approx 70$ K can be modelled assuming a non-magnetic ground state (which is the case once a system undergoes a spin-Peierls transition) with a magnetic state higher in energy. Due to thermal excitation the higher in energy state will be slightly occupied. This assumption can be fitted to the measured magnetic susceptibility by equation 4.1, which consists of a $S = 1/2$ paramagnetic impurity, a constant temperature independent molar magnetic susceptibility and a thermal population of a magnetic state, $\Delta E$ above the non-magnetic ground-state.

$$\chi_{\text{mol}}\left[\frac{\text{cm}^3}{\text{mol}}\right] = y \times \frac{0.375\left[\frac{\text{cm}^3}{\text{mol}}\right]}{T[\text{K}]} + \chi_0\left[\frac{\text{cm}^3}{\text{mol}}\right] + (1 - y) \times A\left[\frac{\text{cm}^3}{\text{mol}}\right] \times e^{-\frac{\Delta E[\text{K}]}{T[\text{K}]}} \quad (4.1)$$

where $y$ is the fraction of a $S = 1/2$ entity, $\chi_0$ is the temperature independent magnetic susceptibility, $A$ is a prefactor, $\Delta E$ is the energy gap between the non-magnetic ground-state and the first magnetic excited state and $k_B$ is the Boltzmann constant. The fitted data can be seen in figure 4.5, with the tabulated values given in table 4.1.

It is apparent from the results listed in table 4.1 and displayed in figure 4.5, that within the two temperature ranges $T \leq \approx 70$ K and $\approx 80 \leq T \leq \approx 105$ K, the molar magnetic susceptibility conforms to the aforementioned model, but in a rather different manner. Most no-
Table 4.1: The values for the fits to the molar magnetic susceptibility displayed in figure 4.5, the errors are given in parentheses. (v) and (f) denote a varied or fixed quantity, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$T \leq \approx 70$ K</th>
<th>$\approx 80$ K $\leq T \leq \approx 105$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$y$</td>
<td>$8.00(1) \times 10^{-4}$ (v)</td>
<td>$8.00 \times 10^{-4}$ (f)</td>
</tr>
<tr>
<td>$\chi_0$ (cm$^3$/mol)</td>
<td>$5.68(3) \times 10^{-5}$ (v)</td>
<td>$8.2(1) \times 10^{-5}$ (v)</td>
</tr>
<tr>
<td>$A$ (cm$^3$/mol)</td>
<td>1 (f)</td>
<td>$0.0052(6)$ (v)</td>
</tr>
<tr>
<td>$\Delta E$ (K)</td>
<td>830(10) (v)</td>
<td>425(15) (v)</td>
</tr>
</tbody>
</table>

The table are the different values for the excitation $\Delta E$ values which imply an energy gap of $\approx 425$ K in the high-temperature regime, but a larger gap of $\approx 830$ K after the second transition, below $\approx 70$ K. The prefactor, $A$, is not the same for both temperature ranges. Within the low-temperature range the prefactor is 1 cm$^3$/mol, but in the higher temperature range the value was refined to $\approx 0.005$ cm$^3$/mol. One can clearly see that the two different regimes can be explained assuming a non-magnetic ground-state and a magnetic state higher in energy. However, the higher temperature regime has a much larger van Vleck contribution than the low-temperature regime, this implies two different energy landscapes. This is consistent with the change in $\Delta E$, since the van Vleck contribution is inversely proportional to the energy gap between the ground-state and the first excited state [4]. The change in energy landscape could be
due to the deformation of the ligand field at \( \approx 73 \) K. The transition at \( \approx 73 \) K was found to be a first order phase transition and hence includes a structural transition. The difference in the prefactors could be tentatively explained by describing the low-temperature regime as a static energy landscape (non-dynamic), while the higher temperature regime is highly dynamic and fluctuating. Due to the timescale of the magnetic susceptibility measurements one sees an average excitation and an average population of the excited state. This could possible explain the very small prefactor seen for the high-temperature regime. This is consistent with the nuclear magnetic resonance results which show the high-temperature regime to be non-static, see section 4.7. However this is not definitive and further experiments such as muon spin rotation will be needed to clarify the nature of the intermediate regime further.
Figure 4.5: (o): The low-temperature molar magnetic susceptibility versus temperature for TiPO$_4$. The red and blue solid lines are fits of the data using equation 4.1 and the values tabulated in table 4.1.

4.4 Specific heat

The specific heat of an orientated single crystal weighing 27.8 mg was determined in the temperature range 2 K to 220 K. The specific heat exhibits two $\lambda$-type anomalies at 110.9(0.6) and 74.1(0.3) K, see figure
4.6. The results are consistent with the molar magnetic susceptibility, see section 4.3. The anomaly at low-temperature was found to exhibit a thermal hysteresis of approximately $40(20)$ mK. Again no hysteresis was seen for the high temperature anomaly, see figure 4.7.

Figure 4.6: Main (o): The specific heat versus temperature for TiPO$_4$. Insert (o): The specific heat divided by temperature versus temperature.
Figure 4.7: The specific heat of TiPO$_4$ (o): Cooling data. (o): Heating data. Left: The specific heat versus temperature in the region on the 74 K transition. Right: The specific heat versus temperature in the region of the 111 K transition.

4.5 Electron paramagnetic resonance

The temperature and angular dependent electron paramagnetic resonance signal was measured on an oriented 1.72 mg single crystal mounted on a samples holder with a calibrated temperature sensor next to the sample, see section 2.4. A single Lorentzian absorption line was ob-
served. It could be fitted by equation 2.1. An example of a spectrum can be seen in figure 4.8. The resonance was narrow enough to resolve angular dependent intensity, half width at half maximum and the $g$-factor very precisely.

![Graph showing EPR signal](image)

Figure 4.8: (o): The electron paramagnetic resonance signal of TiPO$_4$ versus applied magnetic field taken at 200(1) K with $H \perp c$. Solid red line: Fit to equation 2.1.

The room-temperature angular dependent half width at half maximum and $g$-factor are shown in figure 4.9. The change of the half width at half maximum or $g$-factor with angle can be modelled by
\[ \text{obs}(\theta) = y_0 + A \times \sin^2(\theta - \theta_0). \]

Here \( \text{obs}(\theta) \) is the said observable, be it either intensity, \( g \)-factor or half width at half maximum, \( y_0 \) is a constant background term, \( A \) is the prefactor and \( \theta_0 \) corrects for angular offset. The latter is needed when maximum or minimum values of the observable do not occur at \( \theta = 0 \).

The temperature dependence was measured in two perpendicular orientations \( H \parallel [1,2,0] \) and \( H \parallel c \), consistently coloured red and black in all pertaining figures. The intensity of the absorption line versus temperature (shown in figure 4.10) in two different crystallographic orientations, mimics the temperature dependent magnetic susceptibility and exhibits two transitions at 112(3) and 74(2) K below which the intensity drops to zero. Below approximately 74 K, a new significantly weaker, multi-line spectrum evolves. The multi-line spectrum grows in amplitude with decreasing temperature and can be confidently ascribed to paramagnetic impurities and/or structural defects.
Figure 4.9: Fitting parameters for the electron paramagnetic resonance signal of TiPO$_4$ at 306(1) K, versus angle of the applied magnetic field with regards to the [1,2,0]c-plane. Solid red line: Fit to a $\sin^2(\theta)$ dependence. Main: The half width at half maximum. Insert: $g$-factor.

As shown in figure 4.10 above 74 K the $g$-factor for the two selected orientations ($H \parallel c$ and $H \parallel [1,2,0]$) shows a mild, almost linear decrease with increasing temperature. On closer inspection, however, an anomaly is observed in both orientations at $\approx 110$ K, consistent with other exper-
iments. A $\approx 0.01\%$ decrease is apparent in the $H \parallel [1,2,0]$, with a slight change in temperature dependence observed for $H \parallel c$. Above 120 K the half width at half maximum for both orientations are seen to increase in a linear fashion with increasing temperature. This is in agreement with theoretical work by Oshikawa and Affleck and similar to values found for CuGeO$_3$ (see section 1.2.4) [36, 37]. A linear behaviour of the half width at half maximum at low-temperatures can be ascribed to anisotropic anti-ferromagnetic one-dimensional spin exchange interactions. A linear dependence of $8.48(3) \times 10^{-4} \text{ T/K}$ and $5.79(2) \times 10^{-4} \text{ T/K}$ was found for $H \perp$ chain and $H \parallel$ chain, respectively. Their ratio

$$\frac{d(\Delta w(H \perp \text{chain}))}{dT} \frac{dT}{d(\Delta w(H \parallel \text{chain}))} \approx 1.5,$$

differs from the suggested ratio of 2 [36, 37]. The deviation could be due to $H \perp c$ and $H \parallel c$ not being parallel to $H \perp ac_e$ and $H \parallel ac_e$, respectively, where $ac_e$ is the easy plane. Due in part to the canting of the easy axes with regards to each other i.e. there are two easy axes which are canted away from the the crystallographic $b$ axis slightly into the $c$-axis. The ratio does, however, confirm that the easy axis is rather more parallel to $b$ than to $c$.

With decreasing temperature, below $\approx 110$ K, the half width at half
maximums start to increase until at $\approx 100$ K where they once again start to decrease, see figure 4.10. The half width at half maximums continue to decrease from then on, until the signal intensity drops to zero at $\approx 74$ K.
Figure 4.10: (o): $H \parallel [1,2,0]$. (o): $H \parallel c$. Fitted electron paramagnetic resonance parameters of TiPO$_4$ versus temperature (a): The intensity. (b): The $g$-factor. (c): The half width at half maximum, the solid black (gradient 0.058(1) mT/K and intercept 58.2(1) K) and red (gradient 0.085(1) mT/K and intercept 59.0(1) K) lines are linear fits to the $H \parallel c$ and $H \parallel [1,2,0]$ data, respectively.
4.6 *ab initio* calculations

To probe the magnetic properties of TiPO$_4$ first principles total energy calculations were performed\(^1\). To examine the magnetic properties of TiPO$_4$, the three spin exchange paths shown in figure 4.11 were considered. Subsequently the spin configuration energies were mapped onto a Heisenberg spin exchange Hamiltonian (the same procedure described in detail for CuCrO$_4$, in the previous chapter);

\[
H = - \sum_{ij} J_{ij} \vec{S}_i \vec{S}_j.
\]

Here, $J_{ij}$ is the spin exchange for the spin exchange interaction between the spins at sites $i$ and $j$, while $\vec{S}_i$ and $\vec{S}_j$ are the spin angular momentum operators. The Hamiltonian includes nn and nnn intra-chain spin exchange interactions $J_1$ and $J_2$. Additionally, the inter-chain spin exchange coupling, $J_3$, was allowed. $J_3$ connects Ti atoms with identical $y$ and $z$ coordinates, i.e. along the crystallographic $a$ direction, see figure 4.11. The calculations of the total energies of the four ordered spin states of TiPO$_4$, FM, AF1, AF2, and AF3, were done on the basis of density functional theory electronic band structure calculations. The density

\(^1\)The first principle density functional theory calculations were done by Prof. M. Whangbo and his group at North Carolina State University, Raleigh, N. C., USA.
functional theory calculations employed the Vienna \textit{ab initio} simulation package [59, 61, 60] with the projected augmented-wave method, the generalized gradient approximation (GGA) for the exchange and correlation functional [62]. A plane-wave cut-off energy of 400 eV was used with a set of 56 \textit{k}-points in the irreducible Brillouin zone and a threshold of $10^{-5}$ eV for the self-consistent-field convergence of the total electronic energy. More details can be found in Law \textit{et al.} [74].

To account for electron correlations associated with the Ti 3\textit{d} state, GGA plus onsite repulsion (GGA+\textit{U}) calculations were performed with $U = 2$ and 3 eV for Ti [63]. The relative energies of the four ordered spin states obtained from our GGA+\textit{U} calculations are summarized in table 4.2. By mapping the relative energies of the four ordered spin states given in terms of the spin exchange parameters, see figure 4.11, onto the corresponding relative energies obtained from the GGA+\textit{U} calculations the spin exchange parameters $J_1 - J_3$ were found. They are summarized in table 4.2.
Figure 4.11: The spin exchange pathways and the four spin configurations for which the total energy has been calculated by GGA+U calculations. Relative energies in parentheses given in meV, first for $U = 2$ eV and then for $U = 3$ eV. Below the figures are the equations for mapping the energies onto the aforementioned spin exchange pathways.

Since there is a first order transition at $\approx 74$ K, any group subgroup relations do not apply. Hence, one can not predict the new low-temperature structure by systematically lowering the symmetry. So in order to probe
Table 4.2: Values of the spin exchange parameters $J_1 - J_3$ (in K) for TiPO$_4$ obtained by mapping the GGA+$U$ total energies of the four spin configurations, see figure. 4.11, onto the Hamiltonian details are given in the text.

<table>
<thead>
<tr>
<th>$J_i$</th>
<th>$U = 2$ eV</th>
<th>$U = 3$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>-988</td>
<td>-751</td>
</tr>
<tr>
<td>$J_2$</td>
<td>-1.4</td>
<td>+0.7</td>
</tr>
<tr>
<td>$J_3$</td>
<td>-20</td>
<td>-15</td>
</tr>
</tbody>
</table>

the low-temperature structure, structure optimization based on first principles density functional theory calculations were carried out. They started from crystal structure configurations which were slightly distorted modifications of the room-temperature structure. Within the calculations the atom positions were allowed to relax, only retaining $P1$ (translation) symmetry for a supercell $2\times2\times2$ times the $Cmcm$ unit cell. A dimerisation of the Ti chains with a sizeable bond alternation, Ti···Ti = 3.1737 Å $\pm$ $\Delta$ ($\Delta = 0.2760$ Å) and two different phosphorus environments, were observed. The resulting lowest energy structure consisted of 48 atoms in $P1$ symmetry. By employing the ADDSYM routine [79, 80] within the PLATON[81] program, hidden symmetry elements could be found and the structure reclassified. Employing this, the lowest energy structure was found to best conform to the space group $Pmmm$ with $a = 5.29(1)$ Å, $b = 6.34(1)$ Å and $c = 7.91(1)$ Å. The
resulting atomic parameters are given in table 4.3.

The total energy of the Pmmn structure was found to be $\approx 48.26$ meV per formula unit lower than the non-relaxed room-temperature structure.

Figure 4.12 displays the interatomic distances for the TiO$_6$ octahedron and the PO$_4$ tetrahedra with the Ti···Ti distances, for the predicted low-temperature structure of TiPO$_4$.

<table>
<thead>
<tr>
<th>atom</th>
<th>oxidation state</th>
<th>Wyckoff position and letter</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>+3</td>
<td>4e</td>
<td>0.7500</td>
<td>0.0216</td>
<td>0.2437</td>
</tr>
<tr>
<td>P1</td>
<td>+5</td>
<td>2b</td>
<td>0.7500</td>
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<td>0.8909</td>
</tr>
<tr>
<td>P2</td>
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<td>4e</td>
<td>0.2500</td>
<td>-0.0488</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

Table 4.3: The predicted atomic parameters for TiPO$_4$, in the space group Pmmn.
4.7 Magic angle spinning $^{31}$P nuclear magnetic resonance and Raman spectroscopy measurements

Magic angle spinning $^{31}$P nuclear magnetic resonance (resonance frequency 80.98 MHz) spectroscopy was undertaken on a powder TiPO$_4$ sample‡, using a center field of $\approx 8.5$ T and a spinning frequency of $\approx 25$ kHz. The spectra were collected between $\approx 35$ K and room-temperature, in a continuous flow cryostat using a cryoMAS probe. The temperature was measured with a calibrated Cernox Resistor placed a

‡The magic angle spinning nuclear magnetic resonance was done by Prof. I. Heinmaa and Dr. R. Stern at the National Institute of Chemical Physics and Biophysics, Estonia.
fixed distance away from the sample. The distance resulted in the sample temperature being approximately 5\% higher than the measured temperature, which was later corrected for. Above \(\approx 140 \text{ K}\) a single \(^{31}\text{P}\) symmetric nuclear magnetic resonance line accompanied by two sets of very weak symmetrically placed spinning sidebands was observed. The spectra are displayed in descending temperature in figure 4.13. Near 112 K the line becomes distorted and broadens into a highly asymmetric continuum limited by two boundary peaks. With decreasing temperature the continuum continues to expands, until it finally washes out at \(\approx 76 \text{ K}\), whereupon the lower boundary grows and finally consists of two symmetric equally intense lines. Each line is accompanied by two sets of symmetric spinning sidebands. The peak positions and/or the boundary edges are displayed versus temperature in figure 4.14. The onset of the two \(^{31}\text{P}\) lines, at \(\approx 76 \text{ K}\) is in good agreement with the transition temperatures found by specific heat and molar magnetic susceptibility measurements. The occurrence of two \(^{31}\text{P}\) lines results from two different \(\text{PO}_4\) tetrahedra. This is consistent with the predicted new low-temperature structure from density functional theory calculations. The structural distortion that would result in two different \(\text{PO}_4\) tetrahedra would also distort the \(\text{TiO}_6\) octahedra, resulting in two different \(\text{TiO}_6\) environments and possible two different \(\text{Ti}^{3+}\cdots\text{Ti}^{3+}\) bond lengths.
Figure 4.13: Magic angle spinning $^{31}$P nuclear magnetic resonance spectra for TiPO$_4$ shown as parts per million (ppm) versus intensity (temperatures indicated on each spectrum). The orange hashed area highlights the incommensurate continuum.
Figure 4.14: The magic angle spinning $^{31}$P nuclear magnetic resonance peak shifts given as parts per million (ppm) and/or the boundary edges versus temperature. Inset: The 41.1 K spectrum.

In an attempt of an exploratory preliminary Raman scattering investigation, Raman spectra were collected from an unorientated xenomorphic single crystal fragment, in a randomly chosen but consistent direction. Spectra were measured between 15 and 300 K. The spectra are shown in figure 4.15 with indicated descending temperatures. All spectra
shown here were measured with a green laser ($\lambda = 532$ nm). The room-
temperature spectrum consists of 13 modes. The CrVO$_4$ structure-type
should exhibit as many as 15 Raman active modes according to sym-
metry analysis, 5 $A_g$ modes, 4 $B_{1g}$ modes, 2 $B_{2g}$ and 4 $B_{3g}$ [82]. The 2
missing modes could be due to a combination of several of the following
reasons:

Accidental degeneracy where they occur at the same wave number as
other peaks and therefore they can not be seen.

Zero intensity of the two missing peaks due to a small, effectively zero,
coupling constant.

Lastly their absence could be explained because they may have low in-
tensity in the direction of observation. This would imply that in another
orientation they would be visible.

Between 300 and 125 K the spectra are practically identical, with only
a small shift of position ($\approx 0.2\%$) and narrowing ($\approx 30\%$) of the peaks.
Figure 4.15: Raman spectra of a TiPO₄ crystal collected in an arbitrary and constant orientation. The data are displayed in descending temperature as indicated. The x-axis is broken between 700 and 900 cm⁻¹.
Figure 4.16: The room-temperature and the (offset) 15 K Raman spectra, red and black, respectively. In the 15 K spectrum new peaks are indicated by asterisks.
Figure 4.17: (o) and (o): Two new low-temperature regime Raman modes, centered at \( \approx 231 \text{ cm}^{-1} \) and \( \approx 400 \text{ cm}^{-1} \), respectively. Upper: The development of the full width at half maximum for both modes versus temperature. Lower: The integrated intensity of the two modes versus temperature. Blue solid line: Fit to both data sets, with \( T_c = 125(1) \text{ K} \) and \( \beta = 0.28(3) \). Inset: A different representation of the lower figure on a log-log plot, with \( 1-T/T_c \) as the \( x \)-axis rather than temperature. The solid blue line is the fitted line from the lower figure.

Below \( \approx 125 \text{ K} \), 12 new peaks start to grow out of the background. They continue to increase in intensity with descending temperature until \( \approx 75 \text{ K} \), whereupon their intensity stays relatively constant with descending
temperature. It should be noted that the predicted low-temperature structure is expected to exhibit a maximum of 36 Raman active modes. The 300 and 15 K spectra are illustrated in figure 4.16 for comparison. The development of two new low-temperature modes with descending temperature is shown in figure 4.17, the integrated intensity, $I$, was fitted to a critical power law such as, $I(T) \propto (1 - \left(\frac{T}{T_c}\right))^2$, yielding a critical exponent of 0.28(3) and a transition temperature, $T_c$, of 125(1) K. All modes display a relatively constant width and intensity below $\approx 75$ K, but a slight shift ($\approx 0.05\%$) of position to smaller wavenumbers is resolved between $\approx 125$ K and the lowest-temperature. A more detailed Raman scattering investigation of TiPO$_4$ is underway.

### 4.8 Low-temperature diffraction

Single crystal x-ray diffraction patterns $^\S$ were collected between room-temperature and 93 K, using the STOE STADI-I, from a xenomorphic fragment of TiPO$_4$. After correction for absorption effects the integrated intensities were refined. Down to 93 K the crystal structure remained isostructural to that reported previously for the room-temperature structure [73]. The lattice constants and atomic positions were followed as a

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$^\S$The single crystal structure determination has been done in collaboration with Dr. C. Hoch, MPI-FKF Stuttgart, Germany.
function of temperature. The unit cell volume, $V$, and lattice constants $a$, $b$ and $c$ are displayed versus temperature in figure 4.18. Between room-temperature and $\approx 110$ K the $a$ and $b$ lattice constants increase with decreasing temperature by $\approx 0.15\%$ and $\approx 0.07\%$, respectively. The $c$ lattice constant decreases with temperature within the same range by $\approx 0.25\%$. As a result the volume is seen to stay relatively constant. The volume thermal expansion; $\alpha = \frac{1}{V_0} \frac{\partial V(T)}{\partial T}$ amounts to $\approx 2 \times 10^{-6}$ K$^{-1}$, comparable to that of low thermal expansion materials such as diamond, which has a coefficient of thermal expansion of $\approx 1 \times 10^{-6}$ K$^{-1}$ at room-temperature [83].
Figure 4.18: Results of the refinement of the single crystal diffraction patterns of TiPO$_4$, solid lines are a guide for the eye. (a) The $a$ lattice parameter versus temperature. (b) The $b$ lattice parameter versus temperature. (c) The $c$ lattice parameter versus temperature. (d) The volume of the unit cell versus temperature.
The quality of the investigated crystal proved to be exemplary. As such the residual electron density as a function of temperature could be followed. Comparing the calculated electron density, based upon a spherical model, with those ascertained from our single crystal diffraction patterns, considerable residual electron density was found located within the $ac$-plane adjacent to the Ti atom. The residual electron density was mainly confined to four pockets (two pairs). One such pair was situated on opposite sides of the Ti atom in an interstitial position in the ribbon chain. The second pair was again on opposite sides of the Ti atom but perpendicular to the ribbon chain. Due to the symmetry of the structure within the pairs, the pockets must have equal intensity. At room-temperature the residual electron density of the two pairs appears approximately equally occupied. Upon cooling there was a gradual migration of the density away from the perpendicular pair into the interstitial pair. This change is complemented by a reduction in the Ti···Ti distance by $\approx 0.5\%$ and a similar reduction in the angle of the nn superexchange pathway by $\approx 0.4\%$. The development of the residual electron density with decreasing temperature is displayed in figure 4.19.
Figure 4.19: The residual electron densities, obtained from single crystal structure refinements of TiPO$_4$, at different temperatures. The temperatures are indicated on the right hand side.

In order to probe the low-temperature structure, a neutron powder
diffraction pattern was collect at 1.5 K using the HRPT diffractometer at PSI, Switzerland ($\lambda_n = 1.8860 \, \text{Å}$). The diffraction pattern was collected for 4 hours. The pattern and the refinement of the pattern, using the Rietveld profile refinement method employed within the Fullprof Suite [54], are shown in figure 4.20 (a). No change to the structure, other than small changes of the lattice parameter and general positions, was found. All peaks, bar three, conformed to the $Cmcm$ structure. It is unclear as of yet whether the three peaks, marked by an asterisk in figure 4.20 (a), are due to a superstructure or impurity(ies). It is clear, however, that the structure proposed by the density functional theory calculations, see section 4.6, was not found. A comparison of the simulated diffraction patterns for the $Cmcm$ and $Pmmn$ structures are shown in figure 4.20 (b). Both simulations have the same lattice constants, general positions and the same wavelength of the aforementioned low-temperature neutron diffraction pattern. For the structure predicted by $ab$ initio calculations there are numerous new Bragg peaks. The density functional theory calculations would suggest there are four new relatively high intensity peaks, at 26.8°, 37.5°, 64.0° and 65.0°. There was also no evidence for a new structure in low-temperature powder and single crystal x-ray diffraction experiments, the results of which are not shown here.
Figure 4.20: (a): Measured 1.5 K neutron diffraction pattern of TiPO$_4$ ($\lambda_n = 1.8860$ Å). Solid red line: Calculated pattern ($R_p = 12\%$, reduced $\chi^2 = 12.1$). Solid blue line: The offset difference between measured and calculated patterns. The positions of the Bragg reflections used to calculate the pattern are marked by the green vertical bars in the lower part of the figure. Additional peaks are indicated by asterisks. (b): The simulated neutron diffraction patterns with the position of the Bragg reflections marked by vertical bars for the $Cmcm$ and $Pmmn$ structures, black and red, respectively.
4.9 Discussion and conclusion

In this chapter it was shown that at high-temperatures TiPO\textsubscript{4} is an exceptionally strongly coupled one-dimensional Heisenberg anti-ferromagnet. The magnetic susceptibility of TiPO\textsubscript{4} exhibits a broad hump in the magnetic susceptibility that could be fitted to a uniform non-alternating $S = 1/2$ chain, with $J_{nn} \approx -970$ K. The very large superexchange is confirmed by density functional theory calculations that show TiPO\textsubscript{4} to have a nn spin exchange interactions of $\approx -970$ K with a small effectively zero nnn spin exchange interaction. Laboratory based x-ray diffraction at room-temperature confirmed the crystal structure to be of the CrVO\textsubscript{4} structure-type. \textit{Ab initio} density functional calculations suggest that at lower temperatures TiPO\textsubscript{4} should undergo long-range ordering via inter-chain coupling.

At 111 K an anomaly is seen in specific heat, magnetic susceptibility and electron paramagnetic resonance measurements. The anomaly is second or high order (it exhibits no thermal hysteresis) and is reminiscent of those seen in TiOHal [28, 29, 30, 31, 32, 33]. Below 111 K the magnetic susceptibility can be explained by a thermal population of a magnetic state higher in energy than the non-magnetic ground state. Below 111 K new Raman peaks are visible, indicating a new crystal structure. Magic
angle spinning $^{31}\text{P}$ nuclear magnetic resonance confirms the transition at 111 K and shows a broad continuum of nuclear magnetic resonance intensity indicative of an incommensurate structure. However, at 90 K low-temperature x-ray diffraction does not show a new crystal structure.

At lower temperatures still, 74 K, a second anomaly is seen in the magnetic susceptibility, specific heat and electron paramagnetic resonance which is hysteretic, hence first order in nature. At this point the broad continuum seen in nuclear magnetic resonance washes out to leave two $^{31}\text{P}$ peaks of equal intensity, unequivocally showing that there is a new crystal structure. The magnetic susceptibility is still explainable by a thermal population of a magnetic state above a non-magnetic ground state but the gap is much larger. The electron paramagnetic resonance signal intensity falls fully to zero. This is clear evidence for a non-magnetic ground-state.

The observed phase transitions are interpreted as a two part spin-Peierls transition, where between 111 and 74 K TiPO$_4$ is in a dynamically fluctuating spin-Peierls state. Below 74 K the spin-Peierls phase becomes static and a new dimerised phase should exist. The new low-temperature structure has been predicted by \textit{ab initio} calculations, but neither this structure nor any other new structure have been observed in a 1.5 K high intensity powder neutron diffraction experiment. However, the new
structure predicted by ab initio calculations could quite possibly be incorrect, since the calculations could have converged to a local, rather than the global, energy minimum. Future experiments are planned to search for superstructure reflections. They will involve using high resolution powder neutron diffraction to search for peak splitting which might not have been seen in the 1.5 K experiment.

In conclusion, there is overwhelming evidence from molar magnetic susceptibility, electron paramagnetic resonance and magic angle spinning $^{31}\text{P}$ nuclear magnetic resonance measurements that TiPO$_4$ has a non-magnetic ground-state. There is a confirmed, unknown, new static low-temperature structure below $\approx 74$ K, as evidenced by specific heat and nuclear magnetic resonance measurements, Raman scattering and ab initio calculations. Within this new structure there is strong evidence that there are two different phosphorus environments and a bond-alternation within the Ti···Ti chains. However, no diffraction experiment has shown a new structure, as of yet. Within the temperature range of $110.9(0.6) \geq T \geq 74.1(0.3)$ K a non-magnetic possible dynamic state exists. At high-temperatures TiPO$_4$ can be described by a $S=1/2$ Heisenberg anti-ferromagnetic chain with a nn exchange of $\approx 970$ K.
4.10 Summary

In the preceding chapter it was shown that there is strong evidence from magnetic susceptibility, electron paramagnetic resonance, nuclear magnetic resonance and specific heat measurements that TiPO$_4$ might undergo a two-stage spin-Peierls transition. However, lab based x-ray diffraction at 90 K and powder neutron diffraction at 1.5 K do not show a new structure, in either the intermediate or low-temperature phase. TiPO$_4$ has the highest spin-Peierls transition temperature known to date. However, there still remain some unanswered questions. If there is a spin-Peierls transition what is the new structure at low-temperature and does the spin-Peierls transition move with the application of a magnetic field? In order to answer these questions and definitively prove that TiPO$_4$ undergoes a spin-Peierls transition further experiments should complement our exploratory investigation.

In the final chapter, I will summarize the work reported in this PhD thesis and address some outstanding questions.
Chapter 5

Conclusion

In my PhD thesis I report a theoretical effort of establishing a Padé approximation for the description of the temperature dependence of a $S = 3/2$ non-alternating spin chain. The approximation can be used as a handy tool for researchers and can be modelled against their data. However, this approximation is not yet tested against a real system. This work could be continued by extending the calculations to higher reduced temperature and modelling against known compounds. Expanding further, similar calculations could be done for other spin systems, such as $S = 1, 2$ and $5/2$. It could also be extended to include the larger magnetic moments of the rare earth atoms e.g. Gd$^{3+}$, Eu$^{2+}$ with $S = 7/2$. However, there would not be a significant improvement over the classical approximation.
In the first experimental chapter the preparation and characterization of CuCrO$_4$ was discussed, the results were supported by *ab initio* calculations. CuCrO$_4$ was characterized by molar magnetic susceptibility, electron paramagnetic resonance, specific heat and dielectric constant measurements. Experimental results show clear indication for one-dimensional magnetism with long-range ordering at $\approx 8.2$ K which is accompanied by a dielectric anomaly. The temperature dependent molar magnetic susceptibility could be modelled against a nearest-neighbour and next nearest-neighbour nnn $S = 1/2$ Heisenberg spin chain with $J_{nn}/J_{nnn} \approx 2$. Theoretical calculations support the ratio of $J_{nn}/J_{nnn}$ being close to 2, putting CuCrO$_4$ in the vicinity of the Majumdar-Ghosh point. CuCrO$_4$ was found to be a new type-II multiferroic system.

Future high magnetic field measurements are planned in order to confirm the prediction of magnetization plateaus at low-temperatures. Additionally, high intensity neutron diffraction experiments are scheduled to confirm long-range magnetic ordering, to establish the magnetic structure and to confirm the spin spiral structure. High resolution neutron diffraction experiments are planned to follow the structural parameters as a function of temperature and to probe the shallow double maximum seen in the dielectric constant measurements. Furthermore muon spin rotation experiments are planned to investigate the possibility of long-
range magnetic ordering, $^{53}$Cr nuclear magnetic resonance measurements are scheduled to probe the possible incommensurate magnetic structure. However, the most pressing concern is the growth of single crystals, since with them it would be possible to investigate in more detail ferroelectricity by measuring a ferroelectric polarization loop.

In the fourth chapter of my PhD thesis the experimental and theoretical characterization of TiPO$_4$ was reported. Single crystal of TiPO$_4$ were grown by chemical vapor transport, these were then characterized by molar magnetic susceptibility, electron paramagnetic resonance and specific heat measurements. Additionally low-temperature single crystal and powder diffraction was carried out, using x-ray and neutron radiation. TiPO$_4$ was found to have a two stage spin-Peierls transition with an exceptionally high transition temperature. At $\approx 111$ K TiPO$_4$ undergoes a transition into a dynamically dimerised phase. At lower temperatures still, $\approx 74$ K, TiPO$_4$ passes through a first order phase transition into a fully dimerised phase. There is overwhelming evidence for a new low-temperature structure, but as of yet this has not been confirmed. In the near future I am planning to measure low-temperature single crystal neutron diffraction patterns of TiPO$_4$ in order to investigate a new low-temperature structure. I plan to follow this up by collecting high resolution powder neutron diffraction patterns at 4.2 K. High magnetic field
measurements are also planned in order to; firstly search for a magnetic field induced magnetic state at low-temperatures, and secondly to probe whether the two phase transitions move with the application of a large magnetic field. Additionally I intend to determine the spin gap in TiPO$_4$ via muon spin rotation, which is expected to be more accurate than nuclear magnetic resonance or magnetic susceptibility measurements.
Bibliography


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