Magnetic Ground State of the 2D $S=1/2$ Square Antiferromagnet
Copper Formate Tetrahydrate

by

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ABSTRACT

I performed a series of NMR experiments to investigate the magnetic ground state properties of the 2D S=1/2 square antiferromagnet copper formate tetrahydrate. This material contains planes of copper atoms which are linked by formate groups and are arranged in a square lattice. I measured the NMR frequency shifts for the deuterium nuclei in the formate groups as a function of field orientation. At 10 K, the shifts depend on the orientation of the local spins at the Cu sites. The orientation of these spins is governed by the magnetic free energy which contains the anisotropic Heisenberg exchange, the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling to the external field. I created a $T = 0$ classical model of the free energy and determined the orientation of the sublattice magnetizations for different strengths of the various interactions. By calculating the resulting NMR shifts and comparing them to the experimental data, I showed that both the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling need to be included in the free energy in order to model the data successfully. This point has not been appreciated in the literature to date. Furthermore, I determined the various parameters needed to describe the magnetic behavior of copper formate tetrahydrate. The Heisenberg exchange coupling $J$ is $4.0 \pm 0.4$ meV or $47 \pm 4$ K and the anisotropies in this were found to be negligible. The average moment of the antiferromagnetically ordered spins is $0.571 \pm 0.004 \mu_B$ and the two Dzyaloshinskii-Moriya vectors are $D^+ = (-0.03 \pm 0.01, 0.0, -0.18 \pm 0.02)$ meV and $D^- = (0.0, 0.00 \pm 0.06, 0.0)$ meV.
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Chapter 1

Introduction

Since loadstone was first found millennia ago, magnetism has been a fascinating phenomenon. Long before they were understood, magnetic materials were used in navigation as well as in other less scientifically sound endeavors such as fortune telling. The modern science of magnetism dates back to 1600, when Gilbert wrote *De Magnete* in which he described magnetic fields and made the observation that the Earth is in fact a giant magnet. However, his microscopic theory was based on the belief that loadstone had a soul. By the early 19th century, scientists Oersted and Faraday had discovered that magnetism and electricity were somehow connected and in the late 19th century, Maxwell outlined the relationship between them with his famous equations and classical electromagnetism was complete. However, permanent magnets were still a mystery. In 1907, Weiss proposed the molecular field theory to explain ferromagnetism but the microscopic basis for the large internal fields present in these materials was still not clear. It was not until the development of quantum mechanics that magnetism was finally understood. Dirac and Heisenberg showed that the Weiss fields are a result of the Pauli exclusion principle. When combined with the Coulomb interaction, the magnetic Hamiltonian for the ferromagnetic interaction between two spins $S_1$ and $S_2$ could be written as

$$\mathcal{H} = JS_1 \cdot S_2$$

(1.1)
where \( J \) was negative. Then in 1936, Néel proposed that antiferromagnetism would result if \( J \) was positive and this was very successful in explaining the behavior of many novel materials at that time. The Néel ground state for antiferromagnets is found by minimizing the energy of classical spins but an important correction to this was made by including quantum fluctuations which modified the ground state.

With the discovery of high temperature superconductors, there has been a renewed interest in antiferromagnetism. The undoped cuprates are \( S = 1/2 \) 2D square lattice antiferromagnets and although there is no static magnetism in the superconducting cuprates, antiferromagnetic correlations are still present and may be involved in superconductivity. This renewed interest has stimulated much theoretical work on the subject and considerable progress has been made recently using numerical techniques which are only now feasible. The many theoretical predictions for ideal antiferromagnets have been studied in materials like copper formate tetrahydrate (CFTH) which are also \( S = 1/2 \) 2D square lattice antiferromagnets. In recent years, there has also been a lot of interest in the magnetic anisotropies in these kinds of materials. Not only are antiferromagnetic interactions present, but there is a cornucopia of other exchange mechanisms that govern the behavior of real magnetic materials. Magnetism is still far from trivial and the study of magnetic materials remains challenging.

When this work began, the hope was to model CFTH as an ideal antiferromagnet but during the course of the experiments, I discovered that CFTH was far from being ideal. I decided to focus instead on this non-ideal behavior in an effort to understanding real 2D antiferromagnets. Since NMR is a good local probe, I was able to do a thorough study of the static low-temperature magnetism by measuring the NMR frequency shifts as a function of crystal orientation in a magnetic field. I also created a \( T = 0 \) classical model of CFTH's magnetic free energy. By comparing the model results to the experimental data, I gained understanding of the magnetic anisotropies in CFTH and determined the coupling parameters for the interactions between the spins.

The rest of this thesis is structured as follows. This chapter contains an introduc-
tion to copper formate tetrahydrate followed by a description of the samples and the magnetic susceptibility measurements. NMR fundamentals, the experimental details and the frequency shift data are described in Chapter 2. In Chapter 3, I discuss the interactions between the nuclear quadrupole moment and the local electric field gradient. I then fit the theory to the data to obtain the electric field gradient parameters and the alignment of the sample. All of the magnetic interactions present in CFTH are described in Chapter 4, as is the $T = 0$ free energy I used to numerically model the data. In Chapter 5, I explain how I used the free energy model and the interactions between the electrons and the nuclei to calculate the frequency shifts. I then fit the numerical results to the 10 K data to determine all of the free energy parameters. I also discuss briefly some results at higher temperatures. Finally, the conclusions are given in Chapter 6.

1.1 Copper Formate Tetrahydrate

Copper formate tetrahydrate (Cu(HCOO)$_2$·4H$_2$O or CFTH) is a good realization of an $S = 1/2$ 2D square lattice Heisenberg antiferromagnet. It has been studied since the 1950's [2] [3] but has seen its popularity increase with the discovery of the high temperature superconductors. Like the cuprates, CFTH contains planes of copper atoms arranged in a square lattice but instead of being linked by oxygen atoms they are linked by formate groups. These planes are separated by water molecules. CFTH's unit cell is monoclinic and below the antiferroelectric transition at 236 K [4] [5] its space group is $P2_1/n$ [6] [7]. The lattice parameters are $a = 8.113$ Å, $b = 8.119$ Å and $c = 12.45$ Å and monoclinic angle $\beta = 101.28^\circ$ [8]. The crystal structure is shown in Fig. 1.1 and a projection of the unit cell onto the $ab$ plane is shown in Fig. 1.2

CFTH's antiferromagnetic 2D nature was established early on [9] in susceptibility experiments: the broad maximum near 60 K (see Sec. 1.3) was seen as good evidence for short-range correlations in the planes. A change in the slope of the electron spin resonance (ESR) linewidth near 70 K was also interpreted to be due to these
Figure 1.1: The crystal structure of CFTH at low temperature. One unit cell is shown with D rather than H in the formate group (see Sec. 1.2). The monoclinic angle $\beta = 101.28^\circ$ is between the $a$ and $c$ axes.

correlations [10]. Estimates from the 60 K susceptibility bump gave an intraplanar coupling constant of $J = 71.5$ K [11]. Subsequent neutron scattering measurements on deuterated CFTH yielded $J = 108$ K [12] and more recently $J = 73$ K [13]. The coupling between the planes was estimated from magnetization experiments to be 4 to 5 orders of magnitude smaller than $J$ [14] meaning that the 2-dimensional copper lattices are well isolated. Nevertheless, this tiny interlayer coupling is what drives CFTH into a bulk 3D antiferromagnetic Néel state at $T_N \approx 16.5$ K [15]. The easy, intermediate and hard axes ($a''$, $b''$, $c''$) given by antiferromagnetic resonance [16] and the paramagnetic axes ($L_1$, $L_2$, $L_3$) given by ESR [3] [10] are shown in Fig. 1.3. Both
reflect the anisotropy in CFTH. At 4.2 K, the sublattice magnetization was found to be half of its classical value [15] presumably meaning that quantum fluctuations play an important role in this 2D antiferromagnet.

As well as the obvious antiferromagnetism exhibited by CFTH, weak ferromagnetism is also present. Evidence of this was first noted in the early susceptibility experiments. The maxima seen in $\chi$ at the Néel temperature were much too sharp to be due only to conventional Curie behavior and were also quite anisotropic [9] [17] [18]. Parasitic ferromagnetism was proposed to explain both phenomena. The rotation patterns obtained from low field proton NMR in the antiferromagnetic state [19] [20], the line broadening near $T_N$ seen in ESR experiments [10] and the jumps and slope changes in magnetization curves [9] [21] could also be understood qualitatively by including weak ferromagnetism. Neutron scattering eventually confirmed this and a moment of 0.05 $\mu_B$ in the $b$ direction was seen in a 1.2 T field [15].

Eventually, a magnetic structure for CFTH emerged. Below the Néel temperature and in zero external field, the spins are mainly anti-parallel and lie along the easy antiferromagnetic axis $a''$ with a small canting in the $b''$ direction. However, the
canting alternates from plane to plane and so the net ferromagnetic moment for the whole crystal is zero [21] [15]. This is described as a 4-sublattice structure as there are 4 inequivalent spins. At a field of 0.5 T, the magnetic structure undergoes a phase transition to a 2-sublattice structure [14] [22] where the spins are still anti-parallel and canted, but now the canting points in the same direction for all the planes and a net magnetic moment is seen. In other words, there is a phase transition where the canted components of the spins go from being antiferromagnetically ordered to being ferromagnetically ordered.

Two mechanisms for this CFTH's magnetic behavior have been proposed. The first is the Dzyaloshinskii-Moriya [23] [24] exchange $D \cdot (S_1 \times S_2)$ which is present in systems with low symmetry. This interaction was used to explain the temperature dependence of the ESR line width [10] [25] and the anisotropy of the antiferromagnetic resonance modes [16]. The second mechanism involves the Zeeman interaction. The spins are coupled to the external field $H_0$ through $S_1 \cdot g_1 \cdot H_0$ and $S_2 \cdot g_2 \cdot H_0$ and

Figure 1.3: The different sets of axes in CFTH. ($a$, $b$, $c$) are the crystallographic monoclinic axes, ($a$, $b$, $c^*$) are a set of useful orthogonal axes, ($a''$, $b''$, $c''$) are the antiferromagnetic axes and ($L_1$, $L_2$, $L_3$) are the paramagnetic axes. The angles between the axes are given in degrees and have been exaggerated for clarity.
1.2 Samples

when $g_1 \neq g_2$ the system is no longer a simple antiferromagnet. This mechanism was used to analyze proton NMR rotation patterns [22] [26] and low temperature magnetization curves for different directions [21], as well as to explain qualitatively the susceptibility and heat capacity measurements [27]. Each mechanism was moderately successful in explaining CFTH's magnetic behavior, but in fact it is impossible to get the whole picture without including both terms in the Hamiltonian. This full Hamiltonian was used to fit magnetization data in the Néel state [14] [28] and some reasonable estimates were made for the magnetic parameters. However, because of the complexity of the problem, only certain field directions were considered. Furthermore, the Dzyaloshinskii-Moriya exchange term used in these analyses turned out to be incorrect (see Sec. 4.2).

Despite these complications, CFTH has become a good candidate for studies on ideal 2D $S = 1/2$ square quantum antiferromagnets and the measurements have been compared to recent theoretical work. For example, at temperatures just above $T_N$ it was predicted that quantum fluctuations would simply renormalize the coupling constants [29] [30]. The correlation length in this renormalized classical regime should decay exponentially as the temperature increases. A crossover from this regime to a quantum critical regime was predicted to occur near $T = 0.36J$. Much of the experimental work was originally performed on undoped La$_2$CuO$_4$ and Sr$_2$CuCl$_2$O$_2$. However, these materials have a large coupling constant $J \sim 1500$ K and experiments at such high energy scales and temperatures are difficult. CFTH has the advantage of having a much lower $J$. Neutron scattering [31] [32], ESR [33] and NMR [34] all gave the same result: CFTH's behavior agreed well with the predictions for the renormalized classical regime. No crossover to a quantum critical regime was ever seen. CFTH has also been doped with Mg$^{2+}$ and Zn$^{2+}$ and studied with ESR [35] and susceptibility [36] to investigate the dilution properties of quantum antiferromagnets.
1.2 Samples

In our first experiments, we used fully deuterated crystals given to us by T. E. Mason and S. J. Clarke [36]. Deuterating CFTH is necessary for neutron scattering experiments and does not change the properties significantly. The magnetic properties remain the same [18] [19] and the lattice parameters will not change appreciably since increasing the mass of the nucleus does not affect the electrostatic bonding in a significant way. There will be a slight decrease in the bond lengths due to the change in the zero point energy, but it is negligible [37]. We quickly realized that we could not do Cu NMR because the relaxation rate was too fast and we decided to do D NMR instead. We would still be sensitive to the correlations between the Cu electrons by probing the D sites on the formate groups. Unfortunately, because there are also many D sites in the interplanar waters the number of NMR lines was overwhelming and we could not pick out the formate sites. We decided to make our own samples and selectively deuterate the formate groups. This was chemically easier than deuter-
I prepared the crystals by first mixing Cu$_2$(OH)$_2$CO$_3$ powder into a solution of 10% $d_1$-formic acid and 90% H$_2$O. The reaction produced Cu(DCOO)$_2$ in water:

\[
\text{Cu}_2(\text{OH})_2\text{CO}_3 + 4\text{DCOOH} \rightarrow 2\text{Cu(DCOO)}_2 + 2\text{H}_2\text{O} + \text{H}_2\text{CO}_3 \\
\text{and} \quad \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2.
\]

I then grew the Cu(DCOO)$_2$ · 4H$_2$O crystals by filtering and slowly evaporating the solution at room temperature. The first batch was often slushy but after recrystallizing and refiltering a few times [37] I managed to produce some good single crystals.
One of my samples is shown in Fig. 1.4. The crystal I used in the NMR experiments was approximately 3 mm $\times$ 3 mm $\times$ 3 mm and weighed 0.027 g. It did not appear to be twinned, based on a comparison with the known crystal habit (see Fig. 1.5). Because the crystals dehydrate very easily, I coated them with vacuum grease and stored them in the freezer when I was not using them.

1.3 Susceptibility Measurements

After producing several good CFTH single crystals, I wanted to characterize my samples before starting the NMR experiments. Initially, I modified an existing AC susceptibility probe but it turned out to be too insensitive to measure the antiferromagnetic transition. After trying and failing to resurrect the homemade SQUID system here, I went to McMaster University to use their Quantum Design SQUID. I transported the crystals in dry ice to keep them from dehydrating. With the CFTH crystal aligned roughly along the $c^*$ direction, I measured $\chi(T)$ in fields of 0.1 T and 5.0 T (see Fig. 1.6). In the low field susceptibility there is a sharp peak at $T_N \approx 17$ K as expected [9]. It is due to the 3D antiferromagnetic transition which is enhanced by the parasitic ferromagnetism. Above the Neél transition there is a much smaller broad maximum near 60 K which was also seen in earlier experiments. This bump is attributed to 2D short range correlations in the planes and is predicted by many analytical and numerical calculations [38] [39] and is also seen in the cuprates [40]. The high field susceptibility is quite different and will be compared to the NMR frequency shifts in Chapter 5.
1.3 Susceptibility Measurements

Figure 1.6: Susceptibility v/s temperature in the $c^*$ direction in a field of (a) 0.1 T and (b) 5.0 T. Inset: enlargement of the broad maximum near 60 K.
Chapter 2

Experiment and Data

In this chapter, I will first summarize the fundamentals of a nuclear magnetic resonance measurement. I will then describe the experimental techniques I used as well as the modifications I made for the set of experiments in this thesis. I will also discuss how I collected and recorded the data. Finally, I will show all the data and explain how I decomposed it into two main contributions which I will analyze in subsequent chapters.

2.1 NMR Basics

Nuclear magnetic resonance (NMR) is a technique in which a material’s nuclear spins can be used to investigate the behavior of the electrons [41] [42]. A large magnetic field lifts the degeneracy of the nuclear magnetic states and by probing the transitions between these states, both the static and the dynamic properties of the local electronic environment can be studied.

A nuclear moment \( \mu = \gamma_n \hbar \mathbf{I} \) couples to an applied magnetic field \( \mathbf{H}_0 \) through the Zeeman Hamiltonian:

\[
\mathcal{H}_Z = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{H}_0
\]  

(2.1)

where \( \mathbf{I} \) is the angular momentum operator and \( \gamma_n \) is the nuclear gyromagnetic ratio of the nucleus. With the magnetic field along the \( z \) direction, the eigenstates of this
Hamiltonian are those of the $I_\text{z}$ operator and the eigenvalues are

$$E = -\gamma_n \hbar H_0 m \quad \text{where} \quad m = I, I - 1, \ldots, -I$$

(2.2)

and $H_0$ is the magnitude of the field. The energy levels for $I = 1$ are shown in Fig. 2.1. For a macroscopic sample with many nuclei, the energy levels are populated with a Boltzmann distribution.

In standard NMR, the transitions between adjacent $\Delta m = \pm 1$ energy levels are probed. Each such transition has a resonance frequency. For a free nucleus, this is the Larmor frequency $\nu_L = \frac{1}{2\pi} \gamma_n H_0$ and it is the same for all of the transitions. But in real systems the energy levels are usually changed by the local environment. The resonance frequency $\nu$ for a given transition of a nucleus at a particular crystallographic site will no longer be equal to $\nu_L$. Some of these frequency shifts are magnetic in nature. For example, the Knight shift is due to the paramagnetic behavior of the conduction electrons in a metal and the chemical shift depends on the orbital angular momentum of nearby electrons. In a ferromagnet or an antiferromagnet, there are large fields due to the neighboring local electrons which will also shift the levels and change the resonance frequencies. In CFTH, there is no Knight shift since it is an insulator and the chemical shift is quite small compared to the large shift due to the
local antiferromagnetically ordered Cu spins. Measuring the magnetic shifts is therefore a good way to obtain information on CFTH’s static magnetic structure. The energy levels may also be changed by the coupling between the nuclear quadrupole moment and the local electric field gradient. The resulting shifts are often used for site assignment and in this experiment they were helpful when determining the alignment of the crystal.

A suitable perturbation is needed to probe the nuclear transitions. The most convenient perturbation contains operators of the type $I^+$ and $I^-$ whose matrix elements are non-zero for $\Delta m = \pm 1$ transitions. The interaction must also have energy $\Delta E = h\nu$ and it turns out that a transverse magnetic field $H_1$ alternating with frequency $\nu$ can be used. In standard pulsed NMR, $H_1$ is applied for a very short time to change the energy level populations. The transverse field is then switched off and the precessing nuclei are observed as they return to thermal equilibrium.

It is handy to consider the classical picture and treat the nuclear spins as vectors. In an external field, a spin acts like a gyroscope and its precessional frequency is equal to the transition frequency $\nu$. The macroscopic magnetization due to the collection of spins lies along the $z$ axis at equilibrium. By controlling the $H_1$ pulse, this magnetization can be tipped into the $xy$-plane. The precessing spins then return to equilibrium via two processes. The first is spin-lattice relaxation which occurs when the spins give up energy to the lattice of electrons and other excitations as they return to their equilibrium state with the magnetization along $z$. This process is exponential and characterized by a time $T_1$. The second is spin-spin relaxation which is the dephasing of the spins within the $xy$-plane and the decay of the signal might be exponential or gaussian but generally it can have any form. There are two types of spin-spin relaxation. The first is through static mechanisms such as the inhomogeneities in the external magnetic field. Since the spins all sit in slightly different fields, they will precess at different frequencies and get out of phase with one another in a time $T_2^*$. This inhomogeneous relaxation is often the fastest, but its effects can be reversed (see Sec. 2.2). The second is irreversible and is due to the dynamic coupling between
the spins. This is where the interesting physics is and it what is usually called $T_2$ or homogeneous $T_2$. Finally, the full spin-spin relaxation is a combination of both and it is inversely proportional to the NMR linewidth. Both $T_1$ and $T_2$ processes occur simultaneously but the $T_2$ processes are typically faster in solids. Both relaxations depend on local electron dynamics and are related to the frequency and wave-vector dependent magnetic susceptibility of the material.

2.2 Experiment

I used a standard pulse NMR spectrometer [43] for my experiments. Our magnet is a niobium titanium superconducting solenoid which sits in a liquid helium bath inside a cryostat. Most of my measurements were done in a field $H_0 = 7.5$ T. The sample and the NMR coil are inside a variable temperature insert which is isolated from the helium bath. Copper wire is wound about the sample can to heat it and a carbon glass resistor is attached to measure the temperature. Both the heater and the thermometer are connected to a temperature controller. The NMR resonant radiofrequency circuit is made up of the coil around the sample, a tuning capacitor to select the frequency and a coupling capacitor. The coil is used both to deliver the large pulses and to pick up the tiny NMR signal. The coil I made could be tuned to frequencies near 50 MHz which is appropriate for D nuclei in a 7.5 T field as D has a gyromagnetic ratio $\gamma_n = 0.65359 \times 2\pi$ kHz/G. The spectrometer was built by B. W. Statt. A pulse program generates pulses of different durations with four possible phases. The magnetization can therefore be tipped onto the $x$, $y$, $-x$ or $-y$ axes of a reference frame rotating at the resonance frequency. The signal is processed with a quadrature detection system which means orthogonal phases can be measured simultaneously and both real and imaginary parts of the FFT can be obtained.

To measure the NMR signal I used standard spin echo techniques. After a pulse, the signal decays away quickly mainly because of the inhomogeneity of the external field $H_0$. This is the free induction decay (FID) and it is reversible since it is due
mostly to inhomogeneous $T_2^*$ processes. If a second pulse is applied, the signal can be refocussed some time later [41]. Fig. 2.2 shows a typical $\pi/2$-$\pi$ sequence used to generate an echo. In my experiment I used times between 6-10 $\mu$sec and 12-20 $\mu$sec for the $\pi/2$ and $\pi$ pulses, respectively. After a pulse, it takes some time for the coil to recover and this will interfere with the signal. I used an add-subtract pulse sequence to get rid of this ringdown. When the phases are chosen correctly, the NMR signals will add but the ringdown signals of the coil will cancel:

\[
\begin{align*}
(p/2)_x - \tau - (p)_x - \tau - echo & \quad \text{ADD} \\
(p/2)_{-x} - \tau - (p)_x - \tau - echo & \quad \text{SUBTRACT}
\end{align*}
\]

where the subscripts are the axes in the rotating reference frame. Now the spins are also relaxing during the time $2\tau$ because of the irreversible homogeneous $T_2$ effects. This means that the echo height will decrease as $\tau$ increases until the signal is eventually wiped out. Therefore, the spin-spin relaxation can be obtained by measuring the echo height as a function of $\tau$. The spin-lattice relaxation can be measured using a technique called saturation recovery in which another $\pi/2$ pulse precedes the spin echo sequence. After this first pulse, the magnetization grows along $z$ due to the $T_1$ processes. The $\pi/2$-$\pi$ sequence is then applied to the $z$ component of the partially

Figure 2.2: Spin echo generation.
relaxed magnetization. For short times, there has not been much time for the $z$ component to build up so the signal after the echo sequence is small, but for long times, the magnetization is fully relaxed back to equilibrium so the signal is at its maximum. $T_1$ is determined by measuring the echo with fixed $\tau$ for different times between the first two pulses.

Although I did some $T_1$ and $T_2$ measurements, I was mostly interested in the frequency shifts. I wanted to measure the shifts in CFTH for many different orientations of the sample and so I rotated the crystal through $180^\circ$ and sometimes $360^\circ$ about an axis perpendicular to the main field. The original goniometer I used to rotate the
sample in the field was quite simple. Both the NMR coil and the sample inside it sat on the goniometer mount and since the wires to the coil could not be too long, it had a range of only 10°. Furthermore, I could only rotate about one axis because there was only one gear available and with nothing but a flat surface to sit the crystal on, I did not have much control over the alignment. Once I got interested in CFTH's frequency shifts as a function of field direction, I designed 3 new goniometer sample mounts so that I would be able to rotate the crystal about each of the antiferromagnetic axes $a''$, $b''$ and $c''$ (see Fig. 1.3). The goniometer mounts each have a spot for the crystal to sit in and when it is wedged in properly, I could collect rotation patterns for a given antiferromagnetic plane. In order to have the full 360° range, I made the coil big enough to fit around both the sample and the goniometer. The resulting filling factor reduction was not a problem for CFTH which has a large D NMR signal. The sample space, the NMR circuit components and the goniometer are shown in Figs. 2.3 and 2.4. I rotated the crystal in situ with the goniometer rod by hand and collected data every 10° for most of the experiments.
Figure 2.5: The 4 NMR-inequivalent D atoms in the CFTH unit cell. The pairs (D₁, D₂) and (D₃, D₄) are crystallographically inequivalent.

2.3 Data

I did the bulk of the experiments at 10 K and 80 K. 10 K is below $T_N \approx 16.5$ K and so CFTH is in the Néel state and the Cu moments are antiferromagnetically aligned. This leads to large internal fields and large frequency shifts. Added to this are the temperature independent shifts due to interactions with the local electric field gradient (EFG) in the crystal. At 80K, the spins are no longer statically ordered and most of the frequency shifts are due to the EFG effects. I measured the frequency shifts as a function of crystal orientation for the three planes $a"b"$, $b"c"$ and $c"a"$ at both temperatures. These rotation patterns for the 4 inequivalent D sites in Fig. 2.5 are shown in Figs. 2.8, 2.9, 2.10 and 2.11.

Although my custom-made goniometers were a definite improvement, it was still hard to align the crystal properly. Luckily, the rotation patterns at 80 K were mostly due to known EFG effects (see Chapter 3) and so I could get a pretty good idea of the misalignment in situ. I could then warm the probe, take the sample out and try again if the crystal was badly misaligned. I tried on average three times per plane.
2.1 Data

Figure 2.6: An example absorption spectrum. This spectrum was taken at 10 K in the $b''c''$-plane. The peaks correspond to the 2 data points near 250 kHz at 60° in Fig. 2.9(a).

before I was satisfied with the alignment. Furthermore, I was later able to measure how close I was from the EFG contribution to the rotation patterns (see Sec. 3.3).

To rotate the sample, I turned the goniometer rod at the top of the cryostat. One turn of the knob was 10° with an error of roughly 0.5°. The 0° starting point was somewhat arbitrary but just like with the misalignment, I could later measure where the main axes were from the EFG contributions to the patterns. In principle, the rotation patterns should have 180° symmetry. For the $a''b''$ and $b''c''$ planes, I took 180° worth of data, but for the $c''a''$ plane, I did a full 360° rotation to check for asymmetries. In fact, there were some small differences in the curves and they can be seen by comparing Fig. 2.10 and Fig. 2.11.

At low temperatures, the D NMR signal from CFTH was fortuitously large so I did not have to do much signal averaging. However, $T_1$ was 45 seconds at 10 K which is quite long and this was the main reason for the length of the experiments. $T_2$ was roughly 1.1 ms at this temperature. At 80 K, $T_1$ was 1 second which is much shorter than at low temperatures, but the signal-to-noise decreased and I had to signal average much longer which made the measurements as lengthy as at 10 K. $T_2$
was roughly 0.6 ms at 80 K.

At each angle, I swept through a range of frequencies near the Larmor frequency of D and collected spin echo data at each peak I found. I then Fourier transformed the time domain signal and recorded the peak frequency in the absorption spectrum. An example spectrum is shown in Fig. 2.6. The linewidths were approximately 8 kHz at 10 K and 10 kHz at 80 K. I chose the center of the peak by eye and recorded this as the frequency. When the lines were far apart, the error in the peak position was estimated to be ± 1-2 kHz. But at orientations with high symmetry and at 80 K where there are no large magnetic shifts, the lines got close together and it was much harder to pick out the center. The frequency error for these badly resolved lines was approximately ± 5 kHz. I did try some peak fitting and time series fitting to improve this but the errors from the fit were equal to those obtained from my original method of doing it by hand. Another source of error was the magnet drift which was roughly 5 kHz/hour at 50 MHz with the magnet in persistent mode. I needed to correct for this since my experiments could last a day or more. Instead of constantly resetting the field, I decided to record the peak position for the first angle at the end as well as at the beginning of the run and measure the drift. There was some scatter in this since I could not reset the goniometer perfectly, but since the drift was measured to be linear with time [44] I averaged the drifts for each run and then corrected all the frequencies with this average drift.

In all the rotation patterns shown in Figs. 2.8, 2.9, 2.10 and 2.11, the low temperature data are on the left and the high temperature data are on the right. The top plots (a) and (b) show the complete data sets. It was very difficult to figure out which peak belonged to which curve and it was also hard to separate the EFG contribution from the magnetic contribution. I ended up doing these simultaneously. The magnetic shifts were not known beforehand but it helped to know what the temperature independent EFG contribution should look like from theoretical considerations and from the higher temperature data (Sec. 3.3). I did a lot of guessing, averaging, subtracting, comparing and staring at the patterns to solve the puzzle.
2.1 Data

Figure 2.7: The data near the $a''$ axis in the $c''a''$-plane. The data between 130° and 160° is not used for any of the analyses.

In particular, I had a lot of problems with the $c''a''$ plane. There was an abrupt transition near $a''$ and I could not track the curves properly or even get good data points since the NMR lines were all on top of each other. When I took the data, I moved the goniometer with the smallest increments possible but I always lost track of them at the transition. In the analysis, I did not use these unassigned data points since I could not decide how to include them in the EFG and magnetic contributions. Some of these points are shown in Fig. 2.7, but they are not shown in Figs. 2.10 and 2.11. The magnetic shifts were also not as dramatic as in the other two planes and so in general the lines were quite close together. It was therefore difficult to determine what was happening at the other curve crossings in the rotation pattern. I took data in the $c''a''$ plane for a series of increasing temperatures hoping to gain some insight. This did not help, but the data are shown in Chapter 6 in which I discuss the temperature dependence of the shifts.

Eventually I was able assign almost all of the peaks correctly and separate the EFG shifts from the magnetic shifts for all planes. The EFG contributions to the data are shown in the middle plots (c) and (d) and the magnetic contributions are shown in the bottom plots (e) and (f). A good indication of the success of my line assignment is that
the EFG contributions for both temperatures are almost identical. The maximum EFG shifts are ± 60-80 kHz about the Larmor frequency. The maximum frequency separations from magnetic effects at 10 K are roughly 400, 200, and 40 kHz for the \(a'b''\)-plane, the \(b''c''\)-plane and the \(c''a''\)-plane, respectively. Although the shifts are mostly due to the EFG splittings at 80 K, there are still some magnetic effects which produce small oscillations of order 20 kHz. The EFG contribution is analyzed in detail in Chapter 3 and the magnetic contribution in Chapters 4 and 5.
Figure 2.8: Data in the $a''b''$-plane. The top plots (a) and (b) show the complete data, the middle plots (c) and (d) show the EFG contributions and the bottom plots (e) and (f) show the magnetic contribution. Note the very different frequency scales. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5. The zero on the frequency axis is the Larmor frequency of D and the dotted lines are the magnetic axes.
2.1 Data

Figure 2.9: Data in the $b''c''$-plane. The top plots (a) and (b) show the complete data, the middle plots (c) and (d) show the EFG contributions and the bottom plots (e) and (f) show the magnetic contribution. Note the very different frequency scales. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5. The zero on the frequency axis is the Larmor frequency of D and the dotted lines are the magnetic axes.

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Figure 2.10: Data in the \(c''a''\)-plane: 0° to 180°. The top plots (a) and (b) show the complete data, the middle plots (c) and (d) show the EFG contributions and the bottom plots (e) and (f) show the magnetic contribution. Note the very different frequency scales. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5. The zero on the frequency axis is the Larmor frequency of D and the dotted lines are the magnetic axes.
Figure 2.11: Data in the $c''a''$-plane: $180^\circ$ to $360^\circ$. The top plots (a) and (b) show the complete data, the middle plots (c) and (d) show the EFG contributions and the bottom plots (e) and (f) show the magnetic contribution. Note the very different frequency scales. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5. The zero on the frequency axis is the Larmor frequency of D and the dotted lines are the magnetic axes.
Chapter 3

Quadrupolar Shifts

In this chapter, I will describe how a nuclear quadrupole moment interacts with the local electric field gradient in a crystal. I will then outline the specific calculations needed in order to determine the resulting NMR shifts for each inequivalent D in CFTH. Finally, I will compare and fit these theoretical results to the data and obtain the parameters that characterize the electric field gradient at each D site. I will also determine the angles that define the orientation of the sample in the main magnetic field.

3.1 Quadrupole Interactions

Nuclei with \( I > 1/2 \) have a nonspherical charge distribution which interacts with the local electric field gradient (EFG) in the crystal. For high fields, this coupling is treated as a perturbation and one of its effects is to shift the Zeeman energy levels. The resonance frequencies of the transitions between levels will no longer be degenerate. Furthermore, these frequencies will be different for nuclei at different crystallographic sites.

The general quadrupolar Hamiltonian [41] [42] [45] [46] is

\[
\mathcal{H}_Q = \frac{1}{6} \sum_{jk} Q_{jk} V_{jk} \quad \text{where} \quad V_{jk} = \frac{\partial^2 V}{\partial x_j x_k},
\]

(3.1)
3.1 Quadrupole Interactions

\[ \Delta E_m = \frac{eQ}{4I(2I-1)} < Im|3I_z^2 - I^2|I_m > V_{zz}. \]  

\( V_{zz} \) is the component of the EFG along the main magnetic field direction \( z \) and \( Q \) is the magnitude of the quadrupole moment. For an \( I = 1 \) nucleus the frequencies are

\[ \nu_1 = \nu_L - \nu_Q \quad \text{and} \quad \nu_2 = \nu_L + \nu_Q \quad \text{where} \quad \nu_Q = \frac{3eQ}{4\hbar} V_{zz}. \]  

\( \nu_L \) is the Larmor frequency and \( \nu_1 \) and \( \nu_2 \) are the frequencies of the \(-1 \leftrightarrow 0\) and \(0 \leftrightarrow 1\) transitions, respectively. The energy levels are shown in Fig. 3.1. Note that the shifts are symmetric about the Larmor frequency in this first order calculation.
3.2 Calculating $V_{zz}$

In order to compute $\nu_1$ and $\nu_2$, the details of the EFG tensor $V_{jk} = V$ are needed for each D site in CFTH. Each tensor must be traceless and symmetric since $\nabla \cdot \mathbf{E} = 0$ and $\nabla \times \mathbf{E} = 0$ and consequently a set of principal axes $X, Y, Z$ can be found such that $V$ is diagonal:

$$V_{XYZ} = \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix}$$

(3.4)

where $V_{XX} + V_{YY} = -V_{ZZ}$. At the D sites in CFTH, the $Z$ axis is directed roughly along the C-D bond, the $X$ axis is roughly normal to the plane of the O-C-O bonds and the $Y$ axis is perpendicular to both $Z$ and $X$ [5]. These axes are shown in Fig. 3.2 and Fig. 3.3. In my experiment, the crystal is rotated in the main magnetic field $H_0$. Equivalently, the field is rotated through the crystal and $V$ must be expressed in the $H_0$ reference frame in order to obtain $V_{zz}$. The transformation from the $(X, Y, Z)$ frame to the $(x, y, z)$ field frame can be calculated using a series of coordinate rotations and reflections.

The first transformation takes the $(X, Y, Z)$ system to the $(a, b, c^*)$ system.
3.2 Calculating $V_{zz}$

The set of cartesian axes $a$, $b$ and $c^*$ are fixed with respect to the crystal: $a$ and $b$ are the crystallographic axes and $c^* = a \times b$ (see Fig. 1.3). The transformation is given by the $3 \times 3$ direction cosine matrix of the EFG but this matrix only contains three independent parameters. It is therefore convenient to use three consecutive rotations of $\alpha$, $\beta$ and $\gamma$ about three different axes [47]. A vector $\mathbf{r}$ transforms as $r_{XYZ} = \mathbf{A} \cdot \mathbf{B} \cdot \mathbf{C} \cdot r_{abc^*}$ where

$$
\mathbf{A} = \begin{pmatrix}
\cos(\alpha) & 0 & -\sin(\alpha) \\
0 & 1 & 0 \\
\sin(\alpha) & 0 & \cos(\alpha)
\end{pmatrix}
$$

(3.5)

$$
\mathbf{B} = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos(\beta) & \sin(\beta) \\
0 & -\sin(\beta) & \cos(\beta)
\end{pmatrix}
$$

(3.6)

Figure 3.3: Some of the axes used in the quadrupolar shift calculations: $(X, Y, Z)$ are the principal axes of the EFG, $(x', y', z')$ is the coordinate system in which the main field $\mathbf{H}_0$ rotates and the $(x, y, z)$ axes are fixed with respect to the field. A rotation of the field in the $x'y'$-plane is shown.
3.2 Calculating $V_{zz}$

$$C = \begin{pmatrix}
\cos(\gamma) & \sin(\gamma) & 0 \\
-\sin(\gamma) & \cos(\gamma) & 0 \\
0 & 0 & 1
\end{pmatrix} \quad (3.7)$$

The field $H_0$ is rotated nominally about the antiferromagnetic axes $a''$, $b''$ and $c''$ shown in Fig. 1.3. Because of the goniometer construction, the field was actually rotated about the $-a''$, $-b''$ and $c''$ axes and so the coordinate change is $r_{abc} = \Delta \cdot r_{a''b''c''}$ where

$$\Delta = \begin{pmatrix}
-\cos(\delta) & 0 & -\sin(\delta) \\
0 & -1 & 0 \\
-\sin(\delta) & 0 & \cos(\delta)
\end{pmatrix} \quad (3.8)$$

and $\delta = 8.5^\circ$ is the angle between $a''$ and $a$. In reality, the crystal could not be aligned with perfect accuracy and so 3 misalignment angles and 3 new axes $x'$, $y'$ and $z'$ are defined. The field $H_0$ is actually rotated about these axes. The same convention as above is used and so $r_{a''b''c''} = \Psi \cdot \Theta \cdot \Phi \cdot r_{x'y'z'}$ where

$$\Psi = \begin{pmatrix}
\cos(\psi) & 0 & -\sin(\psi) \\
0 & 1 & 0 \\
\sin(\psi) & 0 & \cos(\psi)
\end{pmatrix} \quad (3.9)$$

$$\Theta = \begin{pmatrix}
1 & 0 & 0 \\
0 & \cos(\theta) & \sin(\theta) \\
0 & -\sin(\theta) & \cos(\theta)
\end{pmatrix} \quad (3.10)$$

$$\Phi = \begin{pmatrix}
\cos(\phi) & \sin(\phi) & 0 \\
-\sin(\phi) & \cos(\phi) & 0 \\
0 & 0 & 1
\end{pmatrix} \quad (3.11)$$

for a rotation about $z'$. The last misalignment angle $\phi$ is in fact the initial angle of the goniometer as measured from the $x'$ axis. For the rotations about $x'$ and $y'$, the matrices are permuted in the appropriate way. Note that in Sec. 2.3, Sec. 3.3 and
Chapters 4 and 5 the rotation planes $x'y', y'z'$ and $z'x'$ are labelled $a''b''$, $b''c''$ and $c''a''$ which would be the case if there were no misalignment. The last transformation is from the $(x', y', z')$ system to the magnetic field system $(x, y, z)$. For an $x'y'$-plane rotation this means $r_{x'y'z'} = T \cdot r_{xyz}$ where

$$T = \begin{pmatrix}
\cos(\eta) & \sin(\eta) & 0 \\
-\sin(\eta) & \cos(\eta) & 0 \\
0 & 0 & 1
\end{pmatrix} \tag{3.12}
$$

and $\eta$ is the rotation angle shown in Fig. 3.3. Finally, the total transformation is $r_{XYZ} = \Sigma \cdot r_{xyz}$ where

$$\Sigma = A \cdot B \cdot C \cdot \Delta \cdot \Psi \cdot \Theta \cdot \Phi \cdot T \tag{3.13}$$

and the reverse transformation is given by the transpose $\Sigma^t$. The EFG in the field system is therefore

$$V_{xyz} = \Sigma^t \cdot V_{XYZ} \cdot \Sigma \tag{3.14}$$

and the quadrupolar frequency shifts are found by substituting $V_{zz}$ from this equation into Eq. (3.3). The shifts are a function of the rotation angle $\eta$, the initial angle $\phi$, the misalignments $\psi$ and $\theta$, the magnitudes $V_{XX}$ and $V_{YY}$, and the direction cosines of the principal axes of the EFG.

### 3.3 Data Analysis

The nuclear quadrupole moment's interaction with the EFG leads to a pair of resonance lines for $I = 1$. There is one pair for each $D$ in the same local EFG and so the total number of lines is determined by the number of inequivalent sites in CFTH. The sites $(D_1, D_2)$ and $(D_3, D_4)$ are crystallographically inequivalent. Hence there are 2 $V_{XYZ}$ matrices, one for each pair. The matrices will be very similar though because the crystallographic differences are quite small. More importantly, the C-D bonds for

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3.3 Data Analysis

Figure 3.4: Orientations of the C-D bond for an arbitrary field direction. \( D_1 \) and \( D_2 \) are crystallographically equivalent (as are \( D_3 \) and \( D_4 \)) but \( D_1 \) and \( D_3 \) point in almost the same direction (as do \( D_2 \) and \( D_4 \)). Note the bonds are in 3D perspective and are projected into the plane of the paper.

Each pair of equivalent formates point in different directions depending on the actual site in the unit cell (see Fig. 2.5). Although the direction cosine matrices for each will have the same values, some of the off-diagonal elements will change sign. Fig. 3.4 shows the C-D bond directions for an arbitrary field direction. The frequency shifts depend on the relative orientation of the EFG with respect to the field and so the sites \( (D_1, D_3) \) and \( (D_2, D_4) \) will have similar frequency shifts with small differences due to the crystallographic inequivalences. The number of NMR-inequivalent sites is therefore 4 and the number of resonance lines is \( 2 \times 4 = 8 \).

Using some of the numbers from previous experiments [5], atom position information [8] and assuming perfect alignment, I was able to produce theoretical rotation patterns for the \( a''b'' \), \( b''c'' \) and \( c''a'' \) planes. Note that the quadrupolar shifts are temperature independent and they are symmetric about the Larmor frequency. Furthermore, the splittings should be due mostly to the EFG at temperatures where the system is well out of the magnetically ordered state. Armed with this information, I took averages and differences of averages in both the 10 K and 80 K data until I was able to separate the raw data into the EFG contribution and the magnetic contribution (Sec. 2.3). Using the EFG contributions at both temperatures, I then fit the theoretical rotation patterns to the data using a Levenberg-Marquardt fitting.
3.3 Data Analysis

Table 3.1: EFG magnitudes in units of $h/eQ \times $kHz.

<table>
<thead>
<tr>
<th></th>
<th>$V_{XX}$</th>
<th>$V_{YY}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{1,2}$</td>
<td>$-81.8 \pm 0.5$</td>
<td>$-81.3 \pm 0.5$</td>
</tr>
<tr>
<td>$D_{3,4}$</td>
<td>$-82.7 \pm 0.4$</td>
<td>$-77.8 \pm 0.4$</td>
</tr>
</tbody>
</table>

The 19 parameters I fit to were $V_{XX}$, $V_{YY}$, $\alpha$, $\beta$ and $\gamma$ for sites $(D_1, D_2)$ and $(D_3, D_4)$, and $\psi$, $\theta$ and $\phi$ for the three rotation planes. The final parameters are listed in Tables 3.1, 3.2 and 3.3. The fit is shown with the 10 K data in Fig. 3.5 with the 80 K data in Fig. 3.6. For the $a''b''$-plane, the $b''c''$-plane and the $c''a''$-plane, the reduced $\chi^2$'s for these fits were 0.4, 0.8 and 2.0, respectively. The magnitudes and the direction cosine matrices of the EFG's agree very well with previous experiments done at higher temperatures [5]. To relate the EFG's to the actual formate groups is more difficult. It is not clear how to assign them as there are two pairs of EFG tensors and two pairs of C-D bonds pointing in roughly the same direction. A comparison between the directions of the EFG principal axes and the formate bonds for the two possible assignments is shown in Table 3.4. This means that based on the EFG analysis, I cannot distinguish between the 2 inequivalent planes in the unit cell. This conclusion is also seen in the values of the EFG direction cosines since within error $D_1$ and $D_3$ are identical, as are $D_2$ and $D_4$. The fact that the 2 planes are almost identical will be discussed further in Chapter 4. Finally, the misalignment angles $\psi$ and $\theta$ for all planes are small, indicating that the alignment of the crystal is good.

In conclusion, I was able to produce theoretical NMR rotation patterns based on the interaction between the nuclear quadrupole moment and the local electric field gradient. Once I knew roughly what the patterns should look like, I could separate the raw data into the EFG contribution and the magnetic contribution.
Table 3.2: EFG direction cosines in the \((a, b, c^*)\) coordinate system obtained from \(\alpha, \beta, \gamma\) and Eqs. (3.5), (3.6) and (3.7).

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(D_{1,2})</td>
<td>(X): 0.269 ± 0.131 (\mp 0.545 \pm 0.114)</td>
<td>(0.794 \pm 0.039)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Y) ±0.757 ± 0.052</td>
<td>(0.629 \pm 0.099)</td>
<td>(\pm 0.176 \pm 0.138)</td>
</tr>
<tr>
<td></td>
<td>(Z) −0.596 ± 0.012</td>
<td>(\pm 0.554 \pm 0.001)</td>
<td>(0.582 \pm 0.013)</td>
</tr>
<tr>
<td>(D_{3,4})</td>
<td>(X) 0.375 ± 0.054</td>
<td>(\mp 0.486 \pm 0.047)</td>
<td>(0.789 \pm 0.010)</td>
</tr>
<tr>
<td></td>
<td>(Y) ±0.725 ± 0.026</td>
<td>(0.685 \pm 0.036)</td>
<td>(\pm 0.078 \pm 0.057)</td>
</tr>
<tr>
<td></td>
<td>(Z) −0.578 ± 0.013</td>
<td>(\pm 0.543 \pm 0.001)</td>
<td>(0.609 \pm 0.012)</td>
</tr>
</tbody>
</table>

Table 3.3: Misalignment angles \(\psi, \theta\) and initial angle \(\phi\) for all rotations.

<table>
<thead>
<tr>
<th></th>
<th>(\psi)</th>
<th>(\theta)</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a''b'')</td>
<td>−0.4 ± 1.2 °</td>
<td>−0.7 ± 0.1 °</td>
<td>−59.9 ± 0.1 °</td>
</tr>
<tr>
<td>(b''c'')</td>
<td>0.4 ± 0.1 °</td>
<td>−3.5 ± 1.2 °</td>
<td>−121.9 ± 0.1 °</td>
</tr>
<tr>
<td>(c''a'')</td>
<td>1.1 ± 0.1 °</td>
<td>1.1 ± 0.1 °</td>
<td>73.4 ± 1.2 °</td>
</tr>
</tbody>
</table>

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Table 3.4: Angles between the EFG principal axes and bond directions in the formate group. The values for two possible assignments of the EFG's to the formate groups are given in (a) and (b). See text for details.

I then fit the theoretical curves to the EFG contribution and determined the EFG parameters. These compared very well to previously measured values. I also obtained the misalignment and initial angles for the sample orientation for each plane which will prove useful in the magnetic contribution analysis in Chapter 5.
Figure 3.5: Fits to the EFG contribution at 10 K for (a) the $a''b''$-plane, (b) the $b''c''$-plane and (c) (d) the $c''a''$-plane. The points are the data and the lines are the fits. The vertical axis is frequency (kHz) with zero being the Larmor frequency of D. The dotted lines are the magnetic axes.
Figure 3.6: Fits to the EFG contribution at 80 K for (a) the $a''b''$-plane, (b) the $b''c''$-plane and (c) (d) the $c''a''$-plane. The points are the data and the lines are the fits. The vertical axis is frequency (kHz) with zero being the Larmor frequency of D. The dotted lines are the magnetic axes.
Chapter 4

CFTH's Free Energy

The magnetic contribution to the low temperature NMR rotation patterns is due to the local electron spins at the Cu sites. In this chapter, I describe a $T = 0$ classical model in which the electron spins are replaced by sublattice magnetizations. The free energy of the electron system includes the anisotropic Heisenberg exchange, the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling to the external field. In the first 4 sections, I will describe the different interactions separately and discuss how they affect the local moments. In the last section, I will combine them and discuss the numerical model I used to minimize the total free energy. I will mostly use a single-plane or 2-sublattice model to calculate the NMR shifts in Chapter 5. This is appropriate since our experiments were done at 5.0 T and 7.5 T and the transition from a 4-sublattice structure to a 2-sublattice structure occurs at 0.5 T [14] [22]. However, I will also discuss a two-plane or 4-sublattice model. Not only will I use it in some of the calculations, but analyzing this more complicated system yielded many useful results.
4.1 A Simple Antiferromagnet

The isotropic antiferromagnetic Heisenberg exchange for two spins $S_1$ and $S_2$ is

$$\mathcal{H}_J = J S_1 \cdot S_2$$

(4.1)

where the coupling constant $J$ is positive. Using a zero temperature mean field theory, this exchange can be generalized to an $(i,j)$ lattice of $N$ spins where $i$ and $j$ are the indices for the perpendicular directions along 2 sides of the square plaquettes containing 4 Cu atoms (see Fig. 4.1). The quantum operators $S_{ij}$ are replaced by their expectation values $\langle S_{ij} \rangle$ and only the nearest neighbor interactions are included. Summing over the $2N$ bonds of the lattice gives

$$F_j = J M_1 \cdot M_2$$

(4.2)

where $F_j$ is free energy per bond and $M_1$ and $M_2$ are the sublattice magnetization vectors given by

$$M_1 = \frac{1}{N/2} \sum_{i+j \ even}^N \langle S_{ij} \rangle$$

and

$$M_2 = \frac{1}{N/2} \sum_{i+j \ odd}^N \langle S_{ij} \rangle.$$  

(4.3)

Since $J$ is positive, an antiparallel alignment of $M_1$ and $M_2$ is favored and the spin system is antiferromagnetic. Although this is not the only contribution to the free energy in CFTH, it is the dominant one. In the next 3 sections, I will describe the Dzyaloshinskii-Moriya interaction, the anisotropic Zeeman coupling and the anisotropic Heisenberg exchange, all of which need to be included in order to correctly model the CFTH spin system.
4.2 The Dzyaloshinskii-Moriya Interaction

The Dzyaloshinskii-Moriya interaction dates back to the 1950's. At that time, parasitic ferromagnetism was known to exist in several antiferromagnets such as $\alpha$-Fe$_2$O$_3$. A phenomenological model to explain these canted antiferromagnetic systems was first proposed by Dzyaloshinskii [23]. He showed that spin canting can exist for crystals with sufficiently low symmetry. The largest term in the free energy that leads to ferromagnetism is $D \cdot (M_1 \times M_2)$ where $D$ is called the Dzyaloshinskii vector. In contrast to the isotropic Heisenberg interaction, the cross product in this term favors a perpendicular orientation of the two sublattice magnetizations and therefore a ferromagnetic moment.

A few years later, Moriya [24] related this phenomenological model to a microscopic picture: the interaction is due to a combination of the antiferromagnetic exchange and spin-orbit coupling. He extended Anderson's superexchange theory [49] to include spin-orbit coupling and then generalized the coupling between two spins. The single-bond Hamiltonian then becomes

$$H_M = S_1 \cdot J \cdot S_2$$

Figure 4.1: A square plaquette. The black circles are the Cu atoms and $(a, b)$ are the crystallographic axes.
where $J$ is now a $3 \times 3$ tensor. The coupling can be separated into a symmetric $J^s$ exchange and an antisymmetric $J^a$ exchange such that

$$\mathcal{H}_M = S_1 \cdot J^s \cdot S_2 + S_1 \cdot J^a \cdot S_2.$$  \hfill (4.5)

The symmetric term $J^s_{ij} = J^s_{ji}$ remains the same when the spins are interchanged and it includes the isotropic exchange $J$ as well as any other symmetric anisotropies. With no other interactions around, this pseudodipolar term will set the easy, intermediate and hard axes of the spin system. The antisymmetric term $J^a_{ij} = -J^a_{ji}$ changes sign when the spins are switched and it can be written as the cross product $D \cdot (S_1 \times S_2)$. It is this term that gives rise to ferromagnetism.

As a function of the small spin-orbit coupling, the antisymmetric exchange is linear whereas the symmetric exchange is of second order. Moriya therefore argued that the antisymmetric term should dominate over the symmetric one and generalized the free energy to

$$F_M = JM_1 \cdot M_2 + D \cdot (M_1 \times M_2) + \text{other symmetric anisotropies.}$$  \hfill (4.6)

for the whole lattice. The strongest term is still the isotropic $J$ coupling which favors an antiparallel alignment of the sublattice magnetization vectors. But the antisymmetric part competes with this and prefers that $M_1$ and $M_2$ lie at right angles to each other in a plane perpendicular to $D$. Finally, the smaller symmetric part then selects particular directions in that plane for $M_1$ and $M_2$. But it turns out (see below) that this assumption of the relative strengths of the exchanges was incorrect and that there is hidden symmetry in the single-bond Moriya Hamiltonian.

The Dzyaloshinskii-Moriya interaction turned up again recently in the well-studied material La$_2$CuO$_4$. Because the CuO$_6$ octahedra are tilted, the symmetry is low enough to allow an antisymmetric superexchange term. Just as in CFTH, the parasitic ferromagnetism was first seen in the susceptibility peak at $T_N$ which was much sharper than expected [50]. Neutron scattering [51] also revealed an in-plane gap in the
spin wave excitation spectrum as well as a magnetic transition from a 4-sublattice structure to a 2-sublattice structure at a critical field [52]. These results were modelled successfully by including an antisymmetric exchange term, although there was some confusion about the symmetric anisotropies which also showed up in the neutron scattering [51] and magnetoresistance [53] experiments. However, there was still an outstanding problem: the weak ferromagnetism appeared in the low temperature orthorhombic phase of La$_2$CuO$_4$ but not in the low temperature tetragonal phase. Since the CuO$_6$ octahedra are tilted in both phases, the Dzyaloshinskii-Moriya theory predicted a ferromagnetic moment in both and could therefore not account for the differences in the two phases.

Following these results, Coffey et al. [54][55] argued that the microscopic model that was used cannot possibly lead to ferromagnetism. Previous authors started with a $\mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2)$ term in the spin Hamiltonian. They then assumed two magnetic sublattices and used the phenomenological term $\mathbf{D} \cdot (\mathbf{M}_1 \times \mathbf{M}_2)$. However, when Coffey et al. carefully generalized the single-bond Hamiltonian to the whole lattice, they found that a constant $\mathbf{D}$ vector for all bonds made the canted antiferromagnetic spins spiral rather than flip back and forth from one site to the next. This means that generally there will be an infinite number of sublattices rather than two and that there can never be a net ferromagnetic moment in such a system. The correct approach is to assign a $\mathbf{D}_{ij}$ for each bond based on the symmetry of the material. A ferromagnetic moment is generated only when the $\mathbf{D}_{ij}$'s alternate in sign from bond to bond in a specific way.

Then in 1992, Shektman, Entin-Wohlman and Aharony [56] made an important correction to the old Dzyaloshinskii-Moriya theory. They did this without knowing that Kaplan [57] had in fact already worked on the problem for 1D systems in 1983. In Moriya's Hamiltonian, the antisymmetric term which has an easy-plane effect is always accompanied by a symmetric easy-axis anisotropy. For 30 years, the symmetric part was neglected or at least not treated on equal footing with the antisymmetric part. But in fact when both terms are included in the single-bond Hamiltonian,
there is a hidden symmetry and Eq. (4.5) can be mapped back onto the isotropic Hamiltonian! Shektman, Entin-Wohlman and Aharony rewrote the superexchange as

\[
H_{SEA} = J S_1 \cdot S_2 - \frac{|D|^2}{4J} S_1 \cdot S_2 \\
+ D \cdot (S_1 \times S_2) + \frac{1}{2J} S_1 \cdot D \otimes D \cdot S_2
\]

(4.7)

where \( D \otimes D \) is a diadic. The transformation that takes this into a simple scalar product is a rotation of the spins by \( \pm \theta \) about the \( D \) axis where \( \theta = \tan(|D|/2J) \) and this does not change the energy of the system. For one bond, the effects of the symmetric and antisymmetric terms must therefore cancel each other out. On the one hand, the \( D \cdot (S_1 \times S_2) \) term prefers that the antiferromagnetically ordered spins lie in the plane perpendicular to \( D \) with some canting which leads to a small ferromagnetic moment. On the other hand, the symmetric part prefers that the spins lie along \( D \) and in this case there is no canting and no ferromagnetic moment. The hidden symmetry makes the energy associated with these two terms exactly the same. There is of course an anisotropy in the interaction since \( D \) selects a special direction. But there is no energy of anisotropy as all states between the one with the canted spins lying in the plane perpendicular to \( D \) and the one with the purely antiferromagnetic spins lying along \( D \) have the same energy. This means there is no preferred orientation of the spins and there is no selected ferromagnetic moment.

It is only when more than one bond is considered that frustration can lead to symmetry breaking. Whether or not the system is frustrated depends on the individual \( D_{ij} \)'s for each bond. The question is: can all the spins on the lattice be freely rotated by \( \pm \theta \) about \( D_{ij} \) where \( \theta = \tan(|D_{ij}|/2J) \)? If so then the system is unfrustrated and its Hamiltonian can be mapped onto the isotropic Hamiltonian. For a square lattice, this is true if the 4 spins around a plaquette can be transformed in such a way that the product of the rotations is equal to 1. Then there is no frustration and the spin orientations and the ferromagnetic moment will be determined by other anisotropies in the system. This is the case when all the bonds have \( D_{ij} = D \) for example.
4.2 The Dzyaloshinskii-Moriya Interaction

If the total rotation around a plaquette is not equal to 1 then the system is frustrated. This lifts the degeneracy and breaks the symmetry of the ground state. It is the manner in which the $D_{ij}$'s vary from bond to bond that will determine the specific direction of the spins and the resulting ferromagnetic moment. However in many cases, the symmetry will be broken by other stronger sources of anisotropy and not by the frustration of the Dzyaloshinskii-Moriya interaction.

In order to obtain the corrected version of the Hamiltonian for $La_2CuO_4$ or CFTH, the $D_{ij}$'s need to be examined more closely. Although the former is orthorhombic and the latter is monoclinic, the symmetry of the individual planes is the same. Fig. 4.2 shows how the $D$ vectors are related to each other for either material. Since the Cu atoms are centers of inversion, the $D$'s will have opposite sign on either side of them. Furthermore, the $x$ and $y$ directions are different and so the $D$'s along these directions will be different too. Shektman, Entin-Wohlman and Aharony [58] used these symmetries and the updated Dzyaloshinskii-Moriya theory to obtain the new free energy in terms of the sublattice magnetizations:

$$F_{DM} = JM_1 \cdot M_2 - \frac{|D^+|^2}{4J}M_1 \cdot M_2 - \frac{|D^-|^2}{4J}M_1 \cdot M_2$$
$$+ D^+ \cdot (M_1 \times M_2)$$
$$+ \frac{1}{2J}M_1 \cdot D^+ \otimes D^+ \cdot M_2 + \frac{1}{2J}M_1 \cdot D^- \otimes D^- \cdot M_2$$

Figure 4.2: The $D$ vectors in $La_2CuO_4$ or CFTH. The open circles are Cu atoms.

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where $\mathbf{D}^\pm = \frac{1}{2}(\mathbf{D}_1 \pm \mathbf{D}_2)$. Alternatively, the free energy can be written in tensor notation as

$$F_{DM} = \mathbf{M}_1 \cdot \mathbf{J}_{DM} \cdot \mathbf{M}_2$$  \hspace{1cm} (4.9)$$

where

$$\mathbf{J}_{DM} = \left( J - \frac{|D^+|^2}{4J} - \frac{|D^-|^2}{4J} \right) \left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right) + \left( \begin{array}{ccc} D_x^+ & -D_y^+ \\ -D_x^+ & D_y^+ \\ D_y^+ & -D_x^+ \end{array} \right) + \left( \begin{array}{ccc} D_x^+D_x^- + D_y^+D_y^- & D_x^+D_y^+ + D_y^+D_y^- \\ D_y^+D_y^- + D_x^+D_x^- & D_y^+D_y^+ + D_y^+D_y^- \\ D_y^+D_x^- + D_x^+D_y^- & D_y^+D_y^+ + D_y^+D_y^- \end{array} \right) + \left( \begin{array}{ccc} D_x^+D_x^- & D_x^+D_y^- & D_y^+D_x^- \\ D_y^+D_x^- & D_y^+D_y^- & D_x^+D_y^- \\ D_x^+D_y^- & D_y^+D_x^- & D_y^+D_y^- \end{array} \right).$$ \hspace{1cm} (4.10)$$

Now if $\mathbf{D}^-$ is zero then the free energy has the same form as Eq. (4.7) and can therefore be transformed into the isotropic free energy by unfrustrated rotations of $\mathbf{M}_1$ and $\mathbf{M}_2$. When $\mathbf{D}^- \neq 0$, the symmetry is broken by frustration and the spins lie preferentially parallel and antiparallel to $\mathbf{D}^-$. The net ferromagnetic moment will then be proportional to $\mathbf{D}^- \times \mathbf{D}^+$.

For a particular material, the general form of the $\mathbf{D}^+$ and $\mathbf{D}^-$ vectors can be found through a symmetry analysis. In the low temperature orthorhombic phase of $\text{La}_2\text{CuO}_4$ for example, the CuO octahedra are tilted in bands along the $a$ direction and Coffey et al. [55] showed the result is that $\mathbf{D}_1$ and $\mathbf{D}_2$ have the same magnitude and are perpendicular to each other. This means that $\mathbf{D}^+$ and $\mathbf{D}^-$ are perpendicular to each other and since $\mathbf{D}^- \times \mathbf{D}^+$ is nonzero, there will be a ferromagnetic moment. However, in the low temperature tetragonal phase of $\text{La}_2\text{CuO}_4$ the octahedra around one plaquette are tilted toward the center of that plaquette but at the next nearest plaquette they are all tilted away. In this case, $\mathbf{D}_1$ and $\mathbf{D}_2$ point in the same direction.
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Since $\mathbf{D}^-$ is parallel to $\mathbf{D}^+$ there will be no ferromagnetic moment [55]. The weak ferromagnetism therefore depends on the orthorhombic distortion and this explains why it is present in orthorhombic $\text{La}_2\text{Cu}_0\text{O}_4$ but not in tetragonal $\text{La}_2\text{Cu}_0\text{O}_4$.

Although the ordering of the bonds in CFTH is not quite as simple as in $\text{La}_2\text{Cu}_0\text{O}_4$, I was still able to determine a general form for the $\mathbf{D}^+$ and $\mathbf{D}^-$ vectors. CFTH's space group below 236 K is $P2_1/n$ and $b$ is the unique axis. Although $P2_1/n$ is not one of the standard ones [59], its symmetry transformations can be found by rotating those of the space group $P2_1/c$ since $n$ is the bisector of $a$ and $c$. There are 2 inequivalent planes in each unit cell but in fact they are very close to being identical. Fig. 4.3 shows the $\mathbf{D}_{ij}$ vectors for each plane. $\mathbf{D}_1$ and $\mathbf{D}_2$ are associated with the bonds on the bottom plane and $\mathbf{D}'_1$ and $\mathbf{D}'_2$ are associated with those on the top one. The planes are related through the symmetry transformation that takes the monoclinic coordinates $(x, y, z)$ to $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. In other words, any object is first moved up to the next plane and shifted over in that plane. It is then inverted through the mirror plane which is the $ac$-plane and this changes the sign of the $y$-component. I transformed the vectors on the bottom plane to the top one and found that $\mathbf{D}_1$ becomes $\mathbf{D}'_2$ and $\mathbf{D}_2$ becomes $\mathbf{D}'_1$. If the components of the $\mathbf{D}$ vectors on the bottom

![Figure 4.3: The $\mathbf{D}$ vectors in CFTH on the two inequivalent planes.](image)
plane are

\[ \mathbf{D}_1 = (D_{1x}, D_{1y}, D_{1z}) \quad \text{and} \quad \mathbf{D}_2 = (D_{2x}, D_{2y}, D_{2z}), \tag{4.11} \]

then the transformed \( \mathbf{D} \) vectors on the top plane are

\[ \mathbf{D}'_1 = (D_{2x}, -D_{2y}, D_{2z}) \quad \text{and} \quad \mathbf{D}'_2 = (D_{1x}, -D_{1y}, D_{1z}). \tag{4.12} \]

This means that \( \mathbf{D}^+ \) and \( \mathbf{D}^- \) for the bottom \((b)\) and top \((t)\) planes are given by

\[
\begin{align*}
\mathbf{D}^+_b &= \frac{1}{2}((D_{1x} + D_{2x}), (D_{1y} + D_{2y}), (D_{1z} + D_{2z})), \\
\mathbf{D}^+_t &= \frac{1}{2}((D_{1x} + D_{2x}), -(D_{1y} + D_{2y}), (D_{1z} + D_{2z})), \\
\mathbf{D}^-_b &= \frac{1}{2}((D_{1x} - D_{2x}), (D_{1y} - D_{2y}), (D_{1z} - D_{2z})) \quad \text{and} \\
\mathbf{D}^-_t &= \frac{1}{2}(-(D_{1x} - D_{2x}), (D_{1y} - D_{2y}), -(D_{1z} - D_{2z}))). \tag{4.13}
\end{align*}
\]

The \( \mathbf{D} \) vectors will therefore always have the form

\[
\mathbf{D}^+_{b,t} = (D^+_{x}, \pm D^+_{y}, D^+_{z}) \quad \text{and} \quad \mathbf{D}^-_{b,t} = (\pm D^-_{x}, D^-_{y}, \pm D^-_{z}). \tag{4.14}
\]

Now since the inequivalence of the planes is small, I started by assuming that they are identical. Then \( \mathbf{D}_1 = \mathbf{D}'_1 \) and \( \mathbf{D}_2 = \mathbf{D}'_2 \) and so \( D_{1x} = D_{2x}, D_{1y} = -D_{2y} \) and \( D_{1z} = D_{2z} \). With this assumption, Eq. \( (4.13) \) for the case of a single average plane becomes

\[ \mathbf{D}^+ = (D^+_x, 0, D^+_z) \quad \text{and} \quad \mathbf{D}^- = (0, D^-_y, 0). \tag{4.15} \]

This is the form in the monoclinic coordinate system \((a, b, c)\) but it has the same form in the antiferromagnetic system \((a'', b'', c'')\) because the unique axis \(b\) is equal to \(b''\) and so \(a, a'', c\) and \(c''\) are all in the same plane (see Fig. 1.3). Although the form of the \( \mathbf{D}^+ \) and \( \mathbf{D}^- \) vectors is unchanged, the values of the components will be different.

In the calculations discussed herein, I started with the single plane assumption and then included the differences between planes by making \( D^+_y, D^-_x \) and \( D^-_z \) nonzero.
But in fact $D^-$ only appears in Eq. (4.8) as $|D^-|$ and $D^- \otimes D^-$ and so including nonzero $D_x^-$ and $D_z^-$ does not make the planes distinguishable. The same is not true for $D^+$, however.

For the case of a single average plane with only Dzyaloshinskii-Moriya interactions present, a prediction can now be made for the $H_0 = 0$ magnetic structure. First of all, the spins will lie preferentially parallel and antiparallel to $D^-$ which lies along the $b''$ axis. Secondly, the small cant generated is proportional to $D^- \times D^+$ and here that means somewhere in the $a''c''$-plane with the exact direction depending on the values of the vector components. However, it is well known experimentally that the easy axis is the $a''$ axis and that the spins cant towards the $\pm b''$ axis [16] [15]. Therefore although the Dzyaloshinskii-Moriya interaction must be present, and including it is necessary to explain many of the phenomena in CFTH, it is insufficient to predict all of the observations.

There were similar problems in the analysis of La$_2$CuO$_4$. The new corrected Hamiltonian was very successful in describing the differences in the magnetic structure of the orthorhombic and tetragonal phases of La$_2$CuO$_4$, but the symmetric anisotropies were still not well understood. For example, the magnitude of the the out-of-plane anisotropy was found to be twice as large as the in-plane anisotropy [51], whereas Shektman, Entin-Wohlman and Aharony predicted that they should be equal [58]. Furthermore, this out-of-plane anisotropy is the same in both the orthorhombic and tetragonal La$_2$CuO$_4$ [60]. In order to account for this, there must be another interaction that does not rely on the orthorhombic distortion. It turned out that the extra symmetric anisotropy can be explained by including direct Coulomb exchange in higher order calculations of the spin-orbit coupling [61] [62]. I will also include some extra symmetric exchange phenomenologically in CFTH's free energy (see Sec. 4.4).

As the investigations of magnetic materials continue, the Dzyaloshinskii-Moriya interaction is being studied more frequently in many different materials. It has been used to model 1D materials such as BaCu$_2$Si$_2$O$_7$ [63], Yb$_4$As$_3$ [64] and NaV$_2$O$_5$ [65], and is being included in theoretical work on 1D systems [66] [67]. It is also used...
in modelling 2D systems such as LaTiO₃ [68], K₂V₃O₈ [69] and Gd₂Cu₄ [70] as well as La₂CuO₄ [71]. Other interesting compounds with Dzyaloshinskii-Moriya exchange are helical structures CsCuCl₃ [72] and Ba₂CuGe₂O₇ [73], the folded chain compound Ba₃Cu₂O₄Cl₂ [74], semiconductors [75] and even the nuclear magnet PrCu₆ [76].

4.3 The Zeeman Interaction

Another mechanism for parasitic ferromagnetism in antiferromagnets was proposed in the 1950's [77] [78]. A spin S is coupled to an external magnetic field H₀ through the interaction \(-\mu_B S \cdot g \cdot H_0\). In many systems, g is assumed to be a scalar roughly equal to 2 but in complex systems, it must be treated as a tensor. Since this anisotropic Zeeman interaction depends on a combination of the spin-orbit coupling and the orbital Zeeman interactions [41], the details of the g tensor will depend on the local symmetry of the spin's crystallographic site. A system of two spins with different g tensors in a uniform field is equivalent to a system of two spins with the same g tensor in an effective staggered magnetic field [67] [79]. Inequivalent g tensors therefore lead to noncollinear antiferromagnetism or weak ferromagnetism. This mechanism is different from the Dzyaloshinskii-Moriya interaction since it is present only in an external field.

The free energy of two antiferromagnetically coupled spins in a field is

\[
F_Z = J S_1 \cdot S_2 - \mu_B S_1 \cdot g_1 \cdot H_0 - \mu_B S_2 \cdot g_2 \cdot H_0
\]

(4.16)

where the J term is usually much larger than the Zeeman terms. If \(g_1 = g_2 = g\mathbf{1}\), the energy is minimized when the spins lie mostly antiparallel to one another in a plane perpendicular to H₀. There a small cant of the spins toward the field characterized by an angle \(\theta\) given by

\[
\theta = \cos^{-1} \left( \frac{\mu_B g H_0}{2JS} \right)
\]

(4.17)

where \(S = |S_1| = |S_2|\). The set of degenerate solutions therefore lies on a cone about
4.3 The Zeeman Interaction

Figure 4.4: The inequivalent octahedra for the $g$ tensors. The thick lines are drawn to illustrate the local orientation of each octahedron. The larger oxygen atoms belong to the formate groups and the smaller ones are in the interplanar water.

If $g_1$ and $g_2$ are equal but anisotropic then $\theta$ will depend on the field direction but the solution will still be basically the same. But when $g_1 \neq g_2$, the degeneracy of the ground state will be broken. Consider for example

$$g_{1,2} = \begin{pmatrix} g_{xx} & 0 & \pm g_{xz} \\ 0 & g_{yy} & 0 \\ \pm g_{xz} & 0 & g_{zz} \end{pmatrix}$$

where the $\pm$ are for $g_1$ and $g_2$, respectively. If $H_0$ points along $z$ there will be an extra term in the free energy of $-\mu_B g_{zz}(S_{1z} - S_{2z})H_0$. This term prefers to have $S_1$ lying along $x$ and $S_2$ lying along $-x$ and so it selects a specific orientation for the spins. If all the off-diagonal elements of $g_1$ and $g_2$ are nonzero and different for each spin then the solution becomes more complicated, but the spins still point in preferred directions.
In CFTH, there are 4 sites with different \( g \) tensors (see Fig. 4.4). Since the \( g \) tensors are determined by the local bonds, they will depend roughly on the shape and orientation of the oxygen octahedron surrounding each Cu atom. There are two crystallographically inequivalent Cu atoms and octahedra but just as in the case of the electric field gradients (see Sec. 3.3), what's important is the orientation with respect to the external field \( H_0 \). This means that there are actually 4 inequivalent octahedra for a given field direction. The Cu atoms on the bottom plane have tensors \( g_1 \) and \( g_2 \) and those on the top plane have tensors \( g'_1 \) and \( g'_2 \). In terms of the resulting 4 sublattice magnetizations \( M_1, M_2, M'_1 \) and \( M'_2 \), the free energy can be written as

\[
F_Z = J M_1 \cdot M_2 + J M'_1 \cdot M'_2 - \frac{1}{4} \mu_B M_1 \cdot g_1 \cdot H_0 - \frac{1}{4} \mu_B M_2 \cdot g_2 \cdot H_0 \\
- \frac{1}{4} \mu_B M'_1 \cdot g'_1 \cdot H_0 - \frac{1}{4} \mu_B M'_2 \cdot g'_2 \cdot H_0.
\]  

To determine the form of the \( g \) tensors, I used the symmetry transformations described in Sec. 4.2 to relate the tensors on the top plane to those on the bottom plane. I found that \( g_1 \) transforms into \( g'_2 \) and \( g_2 \) transforms into \( g'_1 \). Therefore if \( g_1 \) and \( g_2 \) are given by

\[
g_1 = \begin{pmatrix} g_{xx}^1 & g_{xy}^1 & g_{xz}^1 \\ g_{xy}^1 & g_{yy}^1 & g_{yz}^1 \\ g_{xz}^1 & g_{yz}^1 & g_{zz}^1 \end{pmatrix} \quad \text{and} \quad g_2 = \begin{pmatrix} g_{xx}^2 & g_{xy}^2 & g_{xz}^2 \\ g_{xy}^2 & g_{yy}^2 & g_{yz}^2 \\ g_{xz}^2 & g_{yz}^2 & g_{zz}^2 \end{pmatrix}
\]

then by symmetry \( g'_1 \) and \( g'_2 \) are

\[
g'_1 = \begin{pmatrix} g_{xx}^2 & -g_{xy}^2 & g_{xz}^2 \\ -g_{xy}^2 & g_{yy}^2 & -g_{yz}^2 \\ g_{xz}^2 & -g_{yz}^2 & g_{zz}^2 \end{pmatrix} \quad \text{and} \quad g'_2 = \begin{pmatrix} g_{xx}^1 & -g_{xy}^1 & g_{xz}^1 \\ -g_{xy}^1 & g_{yy}^1 & -g_{yz}^1 \\ g_{xz}^1 & -g_{yz}^1 & g_{zz}^1 \end{pmatrix}. 
\]

Once again, I started by assuming that the planes are identical and that \( g_1 = g'_1 \) and \( g_2 = g'_2 \). This means that \( g_{xy}^1 = -g_{xy}^2 \) and \( g_{yz}^1 = -g_{yz}^2 \). The free energy of a single
average plane can then be written as

\[ F_Z = J M_1 \cdot M_2 - \frac{1}{4} \mu_B M_1 \cdot g_1 \cdot H_0 - \frac{1}{4} \mu_B M_2 \cdot g_2 \cdot H_0 \]  

(4.22)

with the \( g \) tensors given by

\[
\mathbf{g}_{1,2} = \begin{pmatrix}
g_{xx} & \pm g_{xy} & g_{xz} \\
\pm g_{xy} & g_{yy} & \pm g_{yz} \\
g_{xz} & \pm g_{yz} & g_{zz}
\end{pmatrix}
\]  

(4.23)

and \( M_1 \) is now the average of \( M_1 \) and \( M'_1 \), and \( M_2 \) is the average of \( M_2 \) and \( M'_2 \).

The \( g \) tensors can be measured in the paramagnetic state with electron spin resonance. The \( g \) values, which are the average diagonal elements of the tensor for the whole crystal, are determined along the paramagnetic axes \( L_1 \), \( L_2 \) and \( L_3 \) (see Fig. 1.3). These are the natural axes of the Zeeman interaction and they are found from the positions of the minima and maxima in the resonance rotation patterns. Physically, \( L_1 \) and \( L_2 \) are the bisectors of the acute and obtuse angles between the long axes of the octahedra and \( L_3 \) is normal to both \( L_1 \) and \( L_2 \) [3]. The \( g \) values were found to be \( g_{L_1} = 2.36 \), \( g_{L_2} = 2.11 \) and \( g_{L_3} = 2.07 \) [11]. More detailed experiments [80] determined the off-diagonal elements of both \( g_1 \) and \( g_2 \) and found that

\[
\mathbf{g}_{1,2} = \begin{pmatrix}
2.11 & \pm 0.002 & 0.1 \\
\pm 0.002 & 2.11 & \pm 0.1 \\
0.1 & \pm 0.1 & 2.32
\end{pmatrix}
\]  

(4.24)

in the antiferromagnetic coordinate system \((a'', b'', c'')\) which is the system I used throughout my calculations.

The free energy of Eq. (4.22) with the \( g \) tensors of Eq. (4.24) can be minimized to obtain the orientations of the sublattice magnetizations \( M_1 \) and \( M_2 \). For example

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if \( H_0 \) is along \( a'' \) then the free energy is

\[
F_{Za''} = J M_1 \cdot M_2 - \frac{2.11}{4} \mu_B H_0 (M_{1a''} + M_{2a''}) \\
- \frac{0.002}{4} \mu_B H_0 (M_{1b''} - M_{2b''}) - \frac{0.1}{4} \mu_B H_0 (M_{1c''} + M_{2c''}).
\]

(4.25)

The antiparallel magnetizations will lie preferentially in the \( b''c'' \)-plane which is perpendicular to the field direction, with most of the cant pointing in the \( a'' \) direction. This is determined by the first and second terms which are the largest. However, a small component of the cant will point in the \( c'' \) direction due to the fourth term. Within the \( b''c'' \)-plane, the magnetizations will prefer to lie such that \( M_1 \) is along \( b'' \) and \( M_2 \) is along \( -b'' \) because of the third term. Note that these orientations will be reversed for \( H_0 \) along \( -a'' \). Similar arguments can be made for the other two directions. With the field along \( b'' \), \( M_1 \) and \( M_2 \) lie mostly along \( \pm c'' \) and with the field along \( c'' \), \( M_1 \) and \( M_2 \) lie mostly along \( \pm b'' \). For intermediate directions it is more complicated, but the orientations of the magnetizations can still easily be found by minimizing the free energy in the same way.

As mentioned above, for the case of two inequivalent planes there will be 4 \( g \) tensors and 4 sublattices. Although the small differences between \( g_1 \) and \( g_1' \) (and \( g_2 \) and \( g_2' \)) have not been measured, the forms of all 4 tensors are known from the symmetry requirements. To include this in the model, I rotated \( g_1 \) away from \( g_1' \) and then used the transformations shown in Eqs. (4.20) and (4.21) to get \( g_2 \) and \( g_2' \). According to neutron scattering measurements, the orientation of the local bonds varies by only a few degrees and so \( g_1 \) and \( g_1' \) for the inequivalent planes are not expected to be very different from the single plane \( g_1 \).

In recent years, the inequivalent \( g \) tensors as a source of parasitic ferromagnetism have been investigated but have not had as much popularity as the Dzyaloshinskii-Moriya interaction. It has been studied mostly in the 1D compound Cu benzoate \( \text{Cu(C}_6\text{D}_5\text{COO})_2 \cdot 3\text{D}_2\text{O} \). Based on some old antiferromagnetic resonance and ESR experiments [81], it was suggested that two different \( g \) tensors could be used to explain
the field-induced gap in the neutron scattering excitation spectrum [82]. Following this, a theory was developed that included both the Dzyaloshinskii-Moriya exchange and inequivalent \( g \) tensors. This resulted in a staggered effective field orthogonal to the main field which produced the neutron scattering gap [79] [67]. Another 1D material that has been studied is the chain compound \([PM\cdot Cu(NO_3)_2\cdot(H_2O)_2]_n\) where PM=pyrimidine. Different \( g \) tensors were included in the Hamiltonian to explain ESR, magnetic susceptibility and specific heat measurements [83]. Although there was a suggestion that some of the phenomena in \( La_2CuO_4 \) could also be explained by including inequivalent \( g \) tensors [54], it has not been investigated very much in 2D systems. In fact, the behavior of magnetic systems in an external field has not been studied theoretically very much at all.

### 4.4 The Anisotropic Heisenberg Exchange

In a low-symmetry system like CFTH, the Heisenberg exchange is anisotropic and is described by a tensor \( J \) rather than a scalar \( J \). Some of the components of \( J \) are due to the Dzyaloshinskii-Moriya interaction and they are shown in Eq. 4.10. There are both symmetric and antisymmetric terms and they are parameterized by \( D^+ \) and \( D^- \). But even in higher symmetry materials like the 2D antiferromagnet \( Sr_2CuO_2Cl_2 \) [84] and tetragonal \( La_2CuO_4 \) [62] where there is no Dzyaloshinskii-Moriya mechanism, there is anisotropy of the easy-plane and easy-axis type. It is therefore natural to include some extra anisotropy in the exchange in CFTH. To keep things as simple as possible, I made the approximation that the principal axes of this extra anisotropic interaction are the antiferromagnetic axes \( (a'', b'', c'') \) and I wrote \( J \) as a diagonal tensor. The free energy associated with the anisotropic \( J \) term is then

\[
F_{an} = M_1 \cdot J_{an} \cdot M_2
\]

(4.26)
where

\[ \mathbf{J}_{an} = \begin{pmatrix} J_{a''a''} & 0 & 0 \\ 0 & J_{b''b''} & 0 \\ 0 & 0 & J_{c''c''} \end{pmatrix} \]  

(4.27)

I was also able to make some predictions about how the elements are related to each other based on earlier measurements. As mentioned in Sec. 4.2, if only the Dzyaloshinskii-Moriya interaction is present then \( b'' \) is the easy axis in zero field. But several experiments have shown that the easy axis is \( a'' \). Therefore I expect that \( J_{a''a''} > J_{b''b''} \) and furthermore that this anisotropy must dominate over the \( D^- \) term in zero field. Since experimentally the intermediate axis is \( b'' \) and the hard axis is \( c'' \), I also expected that \( J_{b''b''} > J_{c''c''} \) although this will depend on the other terms as well.

### 4.5 The Numerical Model

I will now combine all the magnetic interactions described in the previous sections to obtain the total free energy for CFTH and describe the numerical model I used to minimize this free energy. For a single plane and 2 magnetic sublattices, the total free energy due to all the interactions is

\[
F = M_1 \cdot \mathbf{J}_{an} \cdot M_2 - \frac{|D^+|^2}{4J} M_1 \cdot M_2 - \frac{|D^-|^2}{4J} M_1 \cdot M_2 \\
+ D^+ \cdot (M_1 \times M_2) \\
+ \frac{1}{2J} M_1 \cdot D^+ \otimes D^+ \cdot M_2 + \frac{1}{2J} M_1 \cdot D^- \otimes D^- \cdot M_2 \\
- \frac{1}{4} \mu_B M_1 \cdot g_1 \cdot H_0 - \frac{1}{4} \mu_B M_2 \cdot g_2 \cdot H_0
\]  

(4.28)

where \( J = \sqrt{J_{a''a''}^2 + J_{b''b''}^2 + J_{c''c''}^2} \). I wanted to minimize this with respect to \( M_1 \) and \( M_2 \) for many values of the coupling parameters. I chose to decompose the magnetizations into components in the polar coordinate system shown in Fig. 4.5.
M_1 and M_2 can then be written as

\[ M_1 = |M| (\sin \theta_1 \cos \varphi_1, \sin \theta_1 \sin \varphi_1, \cos \theta_1) \] and
\[ M_2 = |M| (\sin \theta_2 \cos \varphi_2, \sin \theta_2 \sin \varphi_2, \cos \theta_2) \] (4.29)

with the assumption that |M_1| = |M_2| = M. I therefore minimized the free energy with respect to \( \theta_1, \theta_2, \varphi_1 \) and \( \varphi_2 \).

I initially tried techniques such as using Lagrange multipliers and coordinate transformations on a simpler model in an attempt to find an analytic solution. Unfortunately, it was not possible except in the very simplest of cases. I therefore decided to work on finding solutions numerically [48]. For the 2-sublattice model in Eq. (4.28), the parameters needed are the exchange parameters J_{an}, D^+ and D^-, the Zeeman tensors g_1 and g_2, the magnitude M of the magnetizations and the external magnetic field H_0. I used the experimentally determined values of g_1 and g_2 from Eq. (4.24) and I did not allow these to vary. The field used in the model depended on the plane. In the a''b''-plane, the data was taken in a field of \( H_0 = 5.0 \) T whereas both the b''c''-plane and the c''a''-plane experiments were done at \( H_0 = 7.5 \) T. I normally varied J_{an}, D^+, D^- and M and I started with values that I obtained or estimated from previous work on CFTH. Finally, I included the misalignment of the crystal.
4.5 The Numerical Model

and the initial orientation by using the angles I obtained from the EFG analysis (see Sec. 3.3). With all of these terms in the numerical model, I let the magnetic field rotate about all three axes $a''$, $b''$ and $c''$. For every $10^\circ$, I minimized the free energy and determined the 4 angles $\theta_1, \theta_2, \varphi_1$ and $\varphi_2$ that define the orientation of the sublattice magnetizations. Once I had found the solution, I could plot the components of $M_1$ and $M_2$ along several directions in order to study them.

Before calculating the NMR shifts, I analyzed how each term in the Hamiltonian affected the orientations of $M_1$ and $M_2$. At the same time, I checked all the predictions made in the previous sections. For the case of a simple antiferromagnet with an isotropic $J$ and an isotropic Zeeman coupling such that $g = g\mathbf{1}$, the spins lie perpendicular to the field with some canting leading to a ferromagnetic moment in the field direction. Keeping $J$ isotropic but including the anisotropy in the Zeeman terms, I confirmed that the magnetizations prefer to lie along $\pm b''$, $\pm c''$ and $\pm b''$ for $H_0$ along $a''$, $b''$ and $c''$, respectively. I could also extend this and calculate the orientations of $M_1, M_2$ and the ferromagnetic moment due to the canting of the spins for general directions. The size and orientation of the ferromagnetic moment depends on the field direction, but on average the maximum value of the ferromagnetic moment along the field direction is roughly $0.03M$ for $J \approx 7$ meV. There is also a smaller component of the ferromagnetic moment which lies perpendicular to the field direction.

I also investigated the effects of the Dzyaloshinskii-Moriya terms. At zero field, the solutions with only the Dzyaloshinskii-Moriya terms included were as predicted with the $b''$ axis being the easy axis. I could then add in the $J_{an}$ term and for some estimates of $D^+$ and $D^-$, I could determine how much extra anisotropy I needed to force the solution to have its easy axis along $a''$. For example, with $J_{a''a''} \approx 7$ meV, $D^+ \approx (-0.1, 0.0, -0.25)$ meV and $D^- \approx (0.0, 0.1, 0.0)$ meV, the easy axis switched from $b''$ to $a''$ when $J_{b''a''} \leq 0.996J_{a''a''}$. I then let $D^+ \neq 0$ but kept the Zeeman interaction isotropic. When the field is parallel to $D^+$, the solution is the same as that for a simple antiferromagnet. But if $D^+$ is not in the field direction, the spins lie parallel and anti-parallel to $D^+ \times H_0$ and the cant along $H_0$ is increased. Adding in...
4.5 The Numerical Model

$D^-$ and making the Zeeman terms anisotropic, the solution becomes too complicated to describe here and depends very much on the details of each exchange interaction. I will discuss this further in the next chapter. In conclusion, the numerical model I created generated all the expected results and extended our understanding of the behavior of $M_1$ and $M_2$ in CFTH.

Although I mostly used the single-plane model, I also created and used a model which included the 2 inequivalent planes and 4 sublattices. The free energy for this system is

$$F = F_b + F_t + F_{int} \tag{4.30}$$

where the free energy $F_b$ for the bottom plane is

$$F_b = M_1 \cdot J_{an} \cdot M_2 - \frac{|D_b^+|^2}{4J} M_1 \cdot M_2 - \frac{|D_b^-|^2}{4J} M_1 \cdot M_2$$

$$+ D_b^+ \cdot (M_1 \times M_2)$$

$$+ \frac{1}{2J} M_1 \cdot D_b^+ \otimes D_b^- \cdot M_2 + \frac{1}{2J} M_1 \cdot D_b^- \otimes D_b^+ \cdot M_2$$

$$- \frac{1}{4} \mu_B M_1 \cdot g_1 \cdot H_0 - \frac{1}{4} \mu_B M_2 \cdot g_2 \cdot H_0, \tag{4.31}$$

the free energy $F_t$ for the top plane is

$$F_t = M'_1 \cdot J_{an} \cdot M'_2 - \frac{|D_t^+|^2}{4J} M'_1 \cdot M'_2 - \frac{|D_t^-|^2}{4J} M'_1 \cdot M'_2$$

$$+ D_t^+ \cdot (M'_1 \times M'_2)$$

$$+ \frac{1}{2J} M'_1 \cdot D_t^+ \otimes D_t^- \cdot M'_2 + \frac{1}{2J} M'_1 \cdot D_t^- \otimes D_t^+ \cdot M'_2$$

$$- \frac{1}{4} \mu_B M'_1 \cdot g' \cdot H_0 - \frac{1}{4} \mu_B M'_2 \cdot g' \cdot H_0 \tag{4.32}$$

and the free energy $F_{int}$ due to the coupling between the planes is

$$F_{int} = J_p(M_1 \cdot M'_1 + M_2 \cdot M'_2) + J_d(M_1 \cdot M'_2 + M_2 \cdot M'_1) \tag{4.33}$$

where $J_p$ is the perpendicular interplanar coupling constant and $J_d$ is the constant.

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associated with the diagonal next nearest neighbor coupling between $M_1$ and $M'_2$ and $M'_1$ and $M_2$. The parameters that now need to go into the model in order to determine the orientations of $M_1$ and $M_2$ are $J_{an}$, $D_t^+$, $D_t^-$, $D_6^+$, $D_6^-$, $J_p$, $J_d$, $M$, $H_0$ and the 4 $g$ tensors.

I also attempted to include the dipole-dipole interactions between the sublattice magnetizations in the model for completeness. I added the terms

$$
M_1 \cdot g_1 \cdot A \cdot g_1 \cdot M_1 + M_2 \cdot g_2 \cdot A \cdot g_2 \cdot M_2 + \\
M'_1 \cdot g'_1 \cdot A \cdot g'_1 \cdot M'_1 + M'_2 \cdot g'_2 \cdot A \cdot g'_2 \cdot M'_2 + \\
M_1 \cdot g_2 \cdot B \cdot g_2 \cdot M_2 + M'_1 \cdot g'_2 \cdot B \cdot g'_2 \cdot M'_2 + \\
M_1 \cdot g_1 \cdot C \cdot g'_1 \cdot M'_1 + M_2 \cdot g_2 \cdot C \cdot g'_2 \cdot M'_2 + \\
M_1 \cdot g_1 \cdot D \cdot g_2 \cdot M'_2 + M_2 \cdot g_2 \cdot E \cdot g'_1 \cdot M'_1
$$

(4.34)

where the Cu-Cu dipole tensors $A$, $B$, $C$, $D$ and $E$ were calculated in the same way as the Cu-D ones for the NMR shifts (see Sec. 5.1). Unfortunately, the model never ran properly when it got this complicated and so in the end I had to remove these terms.

Finally, there are some other sources of anisotropy that I did not include. A common one is single-ion anisotropy which is due to the ion’s interaction with the crystalline electric field [24]. The single-ion anisotropy energy sets the local easy axis for a spin at a given site. If the spins have different easy axes then they will cant with respect to one another and this will lead to weak ferromagnetism. However, this type of mechanism only exists in $S > 1/2$ systems and so it is not included in CFTH [16]. Another anisotropy not included in this work is a cyclic or ring exchange around the plaquettes which was recently suggested to explain neutron scattering results in La$_2$CuO$_4$ [85]. This may also be present in CFTH but was omitted in this work.

In the next chapter, I will describe how I used both the 2-sublattice and the 4-sublattice numerical models to calculate the NMR shifts due to the resulting magnetizations and then fit these shifts to the data to obtain values for the different
parameters in CFTH's free energy.
Chapter 5

Magnetic Shifts

In this chapter, I will calculate the NMR rotation patterns due to the local magnetic moments using the results of the free energy minimization described in the previous chapter. I will first summarize the two ways in which the D nuclei couple to the Cu electrons. The first and largest coupling is through the direct dipole-dipole interaction and the second is through the hyperfine exchange. For generality, I will describe these interactions for the 4-sublattice case but the results are easily reduced to the 2-sublattice case. I will then explain how I compared and fit the resulting NMR shifts to the 10 K data and determined the different parameters in CFTH's free energy. In the last two sections, I will briefly discuss the 80 K magnetic data and the shifts as a function of temperature.

5.1 Direct Dipolar Coupling

In CFTH, the dominant coupling mechanism between the D nuclei and the Cu electrons is through the direct dipole-dipole exchange. The dipolar Hamiltonian can be written as

\[ \mathcal{H}_d = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{H}_d \]  

(5.1)

and since this is a small perturbation to the much larger nuclear Zeeman Hamiltonian of Eq. 2.2, only the secular part is considered. The shift from the Larmor frequency
5.1 Direct Dipolar Coupling

due to dipole-dipole interaction is then

$$\Delta \nu_{\text{dip}} = -\frac{\gamma_n \mathbf{H}_d \cdot \mathbf{H}_0}{2\pi |\mathbf{H}_0|}.$$  \hfill (5.2)

In order to calculate $\Delta \nu_{\text{dip}}$, the local field $\mathbf{H}_d$ at each site needs to be known. The magnetic field $\mathbf{H}_d$ due to a magnetic dipole $\mathbf{m}$ is

$$\mathbf{H}_d(r) = \frac{3\mathbf{r}(\mathbf{r} \cdot \mathbf{m}) - \mathbf{m}|\mathbf{r}|^2}{|\mathbf{r}|^5}$$  \hfill (5.3)

where $\mathbf{r}$ is the position vector measured from the dipole [86]. I found it convenient to rewrite this so that all the spatial information is contained in a tensor and I therefore express the dipole field as

$$\mathbf{H}_d(r) = \mathbf{R} \cdot \mathbf{m}$$  \hfill (5.4)

where $\mathbf{R}$ in Cartesian coordinates is given by

$$\mathbf{R} = \frac{1}{|\mathbf{r}|^5} \begin{pmatrix}
3r^2_x - |\mathbf{r}|^2 & 3r_xr_y & 3r_xr_z \\
3r_yr_x & 3r^2_y - |\mathbf{r}|^2 & 3r_yr_z \\
3r_zr_x & 3r_zr_y & 3r^2_z - |\mathbf{r}|^2
\end{pmatrix}.$$  \hfill (5.5)

To calculate the details of the spatial tensor $\mathbf{R}$, I generated atomic positions from the coordinates obtained by neutron scattering measurements [8]. Since the monoclinic axes are not orthogonal, I transformed the positions into a Cartesian coordinate system with

$$\mathbf{r}_{abc'} = \begin{pmatrix} 1 & 0 & -\sin(\sigma) \\ 0 & 1 & 0 \\ 0 & 0 & \cos(\sigma) \end{pmatrix} \cdot \mathbf{r}_{abc}$$  \hfill (5.6)

where the angle between $c$ and $c'$ is $\sigma = \beta - 90^\circ = 11.28^\circ$. I then transformed these positions into the antiferromagnetic coordinate system $(a'', b'', c'')$ that I work in. The
5.1 Direct Dipolar Coupling

Figure 5.1: The 4-sublattice magnetizations $M_1$, $M_2$, $M'_1$ and $M'_2$. The 2-sublattice structure is obtained when $M_1 = M'_1$ and $M_2 = M'_2$.

transformation is

$$r_{a''b''c''} = \begin{pmatrix} -\cos(\delta) & 0 & -\sin(\delta) \\ 0 & -1 & 0 \\ -\sin(\delta) & 0 & \cos(\delta) \end{pmatrix} \cdot r_{abc^*}. \quad (5.7)$$

where $\delta = 8.5^\circ$. With these atomic positions, I calculated all the elements of $R$ for each inequivalent D atom due to all dipoles $m = g \cdot M$ of one sublattice (see Fig. 5.1). I summed the contributions to $R$ out to $16 \times 16 \times 16$ unit cells at which point the values of the tensor elements had clearly levelled off. All the $R$ tensors are given in Table 5.1. Once I had determined $M_1$, $M_2$, $M'_1$ and $M'_2$ from the free energy minimization, I calculated the dipole fields at the D nuclei. For example, the field at site D$_1$ is given by

$$H_d = R_{D_1,M_1} \cdot g_1 \cdot M_1 + R_{D_1,M_2} \cdot g_2 \cdot M_2 +$$

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### Table 5.1: The spatial tensors in Å⁻³ for the direct dipolar coupling due to each sublattice $M$ for each inequivalent $D$.

<table>
<thead>
<tr>
<th></th>
<th>$M_1$</th>
<th>$M_2$</th>
<th>$M_3$</th>
<th>$M_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>-0.005042  -0.000443  -0.004415</td>
<td>-0.006302  -0.000184  -0.002203</td>
<td>-0.008131  0.043298  0.022259</td>
<td>0.014686  0.022259  -0.038044</td>
</tr>
<tr>
<td></td>
<td>-0.000443  -0.005302  0.000417</td>
<td>-0.000184  -0.007118  -0.001645</td>
<td>0.043298  0.046175  0.022259</td>
<td>-0.0001645  0.013420</td>
</tr>
<tr>
<td></td>
<td>-0.004415  0.000417  0.010344</td>
<td>0.002203  -0.001645  0.013420</td>
<td>-0.000413  0.005276  0.0001652</td>
<td>0.013423  0.010332</td>
</tr>
<tr>
<td>$D_2$</td>
<td>0.047794  0.045971  -0.002604</td>
<td>-0.008131  0.043298  0.022259</td>
<td>0.014686  0.022259  -0.038044</td>
<td>-0.002203  0.013420</td>
</tr>
<tr>
<td></td>
<td>0.045971  -0.004112  -0.003422</td>
<td>0.043298  0.046175  0.022259</td>
<td>0.014686  0.022259  -0.038044</td>
<td>0.000417  0.012259</td>
</tr>
<tr>
<td></td>
<td>-0.002604  -0.003422  -0.043682</td>
<td>0.000417  0.012259  0.000447</td>
<td>-0.000413  0.005276  0.0001652</td>
<td>0.013423  0.010332</td>
</tr>
<tr>
<td>$D_3$</td>
<td>-0.009711  -0.043101  0.014632</td>
<td>0.047702  -0.044005  -0.002515</td>
<td>0.005055  0.000457  -0.004483</td>
<td>-0.002515  0.003383  -0.042657</td>
</tr>
<tr>
<td></td>
<td>-0.043101  0.047912  -0.022912</td>
<td>-0.044005  -0.005046  0.0003383</td>
<td>0.000457  -0.005276  -0.000444</td>
<td>0.010331  0.001652  -0.038044</td>
</tr>
<tr>
<td></td>
<td>0.014632  -0.022912  -0.038201</td>
<td>-0.002515  0.003383  -0.042657</td>
<td>0.000457  -0.005276  -0.000444</td>
<td>0.010332  0.001652  -0.038044</td>
</tr>
<tr>
<td>$D_4$</td>
<td>-0.006284  0.000193  -0.002112</td>
<td>0.005055  0.000457  -0.004483</td>
<td>-0.043105  -0.005276  -0.000444</td>
<td>0.010332  0.001652  -0.038044</td>
</tr>
<tr>
<td></td>
<td>0.000193  -0.007142  0.001656</td>
<td>0.000457  -0.005276  -0.000444</td>
<td>-0.043105  -0.005276  -0.000444</td>
<td>0.010332  0.001652  -0.038044</td>
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<td>-0.002112  0.001656  0.013426</td>
<td>0.004483  -0.000444  0.010332</td>
<td>-0.043105  -0.005276  -0.000444</td>
<td>0.010332  0.001652  -0.038044</td>
</tr>
</tbody>
</table>

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Finally, I calculated the resulting NMR shifts using Eq. (5.2) for each inequivalent D nucleus.

5.2 Hyperfine Coupling

Not only are the D sites coupled to the Cu sites through direct dipolar interactions, but they are also coupled indirectly through the overlapping orbitals of the Cu atoms and the formate groups. This is the hyperfine exchange and the general hyperfine Hamiltonian for a nuclear spin I interacting with an electron spin S is

$$\mathcal{H}_h = -\mathbf{I} \cdot \mathbf{A}' \cdot \mathbf{S}$$

(5.9)

where $\mathbf{A}'$ is the hyperfine tensor. In CFTH, the unpaired electron in the Cu $3d^9$ orbital is coupled to the D nuclear spin through the O-C-D bonds (see Fig. 1.2). Since the exchange is through the D's $1s$ orbital, it is isotropic and can be parameterized by a constant $A'$ rather than a tensor. I assumed that the coupling involves only the nearest neighbor atoms and therefore each D is coupled to two Cu electrons. Since the D's are situated at the center of the formate groups which is roughly halfway between the two nearest neighbor Cu atoms, I normally used the same constant for the bonds in both directions. However, I also allowed for small differences between the hyperfine constants for each nearest neighbor Cu atom. Furthermore, since there are two inequivalent formate groups in each unit cell there would in fact be a total of 4 different hyperfine constants. $D_1$ and $D_2$ will have the same two hyperfine constants for the two closest Cu atoms, as will $D_3$ and $D_4$. Taking the secular part of the Hamiltonian, the resulting NMR shift in the classical limit with a single hyperfine constant is

$$\Delta \nu_{hyp} = -\frac{\gamma_n}{2\pi} A \left( \frac{\mathbf{g}_a \cdot \mathbf{M}_a \cdot \mathbf{H}_0}{|\mathbf{H}_0|} + \frac{\mathbf{g}_b \cdot \mathbf{M}_b \cdot \mathbf{H}_0}{|\mathbf{H}_0|} \right)$$

(5.10)
where
\[ A = \frac{A'}{\gamma_e \gamma \hbar^2} \]  
and \( \gamma_e \) is the electron gyromagnetic ratio. For a single plane, \( M_a \) and \( M_b \) are \( M_1 \) and \( M_2 \). If there are two inequivalent planes, then \( M_a \) and \( M_b \) are \( M_1 \) and \( M_2 \) or \( M'_1 \) and \( M'_2 \), depending on the plane. The same is true for the tensors \( g_a \) and \( g_b \).

## 5.3 Data Analysis

In this section, I will explain the procedure for calculating the NMR shifts and fitting them to the experimental data using the free energy of the local electronic moments and the interactions between the Cu electrons and the D nuclei. For illustrative purposes, I will describe the method using the 2-sublattice model but the method remains the same for the 4-sublattice model.

I first minimized the magnetic free energy as described in the previous chapter and once I had determined the orientations of \( M_1 \) and \( M_2 \), I calculated the resulting NMR shifts. The parameters needed for this are the dipolar tensors \( R \) for each D site and the hyperfine coupling constant \( A \). I varied \( A \) but the dipole tensors \( R \) were fixed at the values given in Table 5.1. Furthermore, the Larmor frequencies \( \nu_{La''c'} \), \( \nu_{La''c''} \) and \( \nu_{La''c''} \) were not accurately known. This was a result of some inaccuracy in \( H_0 \) caused by the magnetic ramping procedure. I therefore chose to vary the Larmor frequencies in the numerical model. The NMR shifts were obtained for each plane by adding the contributions from Eqs. (5.2) and (5.10) to the Larmor frequency.

To summarize, the parameters that were always held fixed in the numerical model were the field magnitude \( H_0 \), the Zeeman tensors \( g_1 \) and \( g_2 \) and the dipole tensors \( R \). The parameters I allowed to vary and eventually fit for were the exchange parameters \( J_{an} \), \( D^+ \) and \( D^- \), the magnetization magnitude \( M \), the hyperfine coupling constant \( A \) and the Larmor frequencies \( \nu_{La''c''} \), \( \nu_{La''c''} \) and \( \nu_{La''c''} \). Note that for the 2-sublattice model, the form of the \( D \) vectors is given by Eq. 4.15. The only components needed are therefore \( D_{x}^+ \), \( D_{z}^+ \) and \( D_{y}^- \) and the others were set to zero. I also chose to
parameterize the anisotropic Heisenberg exchange with the variables $J_{a''a''}$, $\eta_{a''b''} = (J_{b''b''} - J_{a''a''})/J_{a''a''}$ and $\eta_{a''c''} = (J_{c''c''} - J_{a''a''})/J_{a''a''}$.

Once I had determined the NMR shifts numerically, I compared them to the experimental data. For simplicity, I started by averaging the data (see Fig. 5.3). I chose to do this in order to correctly model the largest frequency splittings in the rotation patterns. Some of the smaller splittings in the data are due to the crystallographic differences of the D positions and these are reproduced in the model. However, there are other splittings that are not reproduced by the 2-sublattice model (see below) and I did not want to include these in the fitting. I averaged the D₁ and D₃ shifts and the D₂ and D₄ shifts in both the $a''b''$-plane and $b''c''$-plane. In the $c''a''$-plane, I averaged the shifts from all 4 D sites. For both the numerical and experimental shifts, the 4 rotation pattern curves for each inequivalent D were then set to be equal to their averages. By trying several different sets of parameters and comparing the theoretical curves to the experimental data, I determined roughly what range of parameters were needed to approximately reproduce the data. I also found that the g tensors and the $D^+_x$ and $D^+_z$ parameters had the most significant effect on the overall shape of the curves whereas $D^-_y$, $\eta_{a''b''}$ and $\eta_{a''c''}$ modified the shape to a much lesser degree.

After comparing the numerical shifts and the data qualitatively, I designed and performed Monte Carlo numerical experiments in which I varied the parameters randomly. I could therefore quantitatively determine the sets of values that optimally reproduced the data. After minimizing the free energy for each set of parameters and calculating the NMR shifts, I compared them to the data by creating a $\chi^2$. For example, in the $a''b''$-plane I let

$$\chi^2_{a''b''} = \frac{1}{\sigma_{\exp}^2} \frac{1}{N-n} \sum_{\phi=0^\circ}^{360^\circ} \sum_{D=1}^{4} (\Delta \nu^\text{num}_{\phi,D} - \Delta \nu^\text{exp}_{\phi,D})^2$$ (5.12)

where $\Delta \nu^\text{num}_{\phi,D}$ is the numerically calculated shift, $\Delta \nu^\text{exp}_{\phi,D}$ is the experimentally measured shift, $N$ is the number of data points and $n$ is the number of fitted parameters. $\sigma_{\exp}$ is
the error on each data point which in this case was estimated to be 3 kHz. I summed over all 4 shifts from each D site and all rotation angles \( \phi \). Finally, I summed over the 3 planes such that \( \chi^2 = \chi^2_{a''b''} + \chi^2_{b''c'} + \chi^2_{c''a''} \) and repeated this from 100 to 15000 times depending on the run. I then plotted and analyzed all the successful sets of parameters for which \( \chi^2 \) was lower than a critical value as well as all the unsuccessful sets for which \( \chi^2 \) was higher than this value. This enabled me to determine the range of good parameters and helped me decide where to look next in phase space. An example of a Monte Carlo run is shown in Fig. 5.2. I could also determine whether any parameters were correlated which helped refine the search. For example, both \( D_x^+ \) and \( D_z^+ \) are correlated with \( J_{a''a''} \) as seen in the top two plots in Fig. 5.2. I modified the phase space I searched and reduced the critical value of \( \chi^2 \) until I found satisfactory fits. However, I kept the phase space large compared to the expected values of the various parameters. The global minimum was then much more accurately found with the Powell minimization routine [48]. This particular method was used since it did not require analytic derivatives. \( \chi^2 \) was minimized starting from many different sets of parameters obtained from the Monte Carlo results. Although several local minima were found, there was a clear global minimum [87]. Therefore, with this combined technique of Monte Carlo sampling and Powell minimization, I obtained final values for the various parameters and they are given in Table 5.2. A comparison between the experimental data and model results is shown in Fig. 5.3. The model reproduces the data very well in the \( a''b'' \)-plane and the \( b''c' \)-plane. In the \( c''a'' \)-plane, the fit is not quite as good but is still successful. Note that the dip in the numerical curve near \( a'' \) in the \( c''a'' \)-plane is due to a rapid transition where the spins go from lying antiparallel along \( b'' \) to lying antiparallel along the axis perpendicular to both \( b'' \) and the field direction. I did not fit to any data here because of the line tracking problem mentioned in Sec. 2.3 which in fact had suggested an abrupt transition of the kind shown by the numerical model.

Since the model does not reproduce the data perfectly, there are systematic errors which are larger than those due to the statistical errors in the data. However, the
reduced $\chi^2$ can give some estimate of the success of the fit. For the $a''b''$-plane, the $b''c''$-plane and the $c''a''$-plane the $\chi^2$'s were found to be 2.0, 7.8 and 13.4, respectively. The statistical uncertainties on the parameters listed in Table 5.2 were found by calculating the values for an increase $\Delta\chi^2 = 1$.

The average value of the Heisenberg coupling $J = \sqrt{J_{a''a''}^2 + J_{b''b''}^2 + J_{c''c''}^2}$ is $4.0 \pm 0.4$ meV or $47 \pm 4$ K. This value falls slightly below the $J$'s found by other authors which have been anywhere from 50-70 K [11] [14] in magnetization and static susceptibility measurements to as high as 110-120 K in neutron scattering and ESR experiments [33] [88]. This wide range may be due to the type of model used in the measurement to extract $J$. The coupling may also be energy dependent and would therefore be different for probes of different energies. This may explain why the neutron scattering results are consistently higher than results from other experiments. The anisotropies $\eta_{a''b''}$ and $\eta_{a''c''}$ are very small. The Monte Carlo results gave values of roughly $\pm 0.0005$ for both and were therefore set to zero in the Powell minimizations. The anisotropy $\eta_{a''b''}$ is lower by more than an order of magnitude than the value required to force the easy axis to be $a''$ when $H_0 = 0$. $D^+$ is $(-0.03 \pm 0.01, 0.0, -0.18 \pm 0.02)$ meV and hence $|D^+| \simeq J/22$ which is larger than the original estimate of $J/200$ [25] but close to the more recent estimate of $J/14$ [31]. $D^- = (0.0, 0.00 \pm 0.06, 0.0)$ meV was not well determined from this particular measurement. This is because the anisotropy from the field-dependent Zeeman terms is much stronger and dominates over the $D^-$ term. The average moment for the sublattices is found to be $0.571 \pm 0.004 \mu_B$ which is not much bigger than the previous value of $0.48 \mu_B$ [15]. The hyperfine coupling $A = 57 \pm 45$ Oe/$\mu_B$ is 3 orders of magnitude smaller than the hyperfine coupling between the O nucleus and the Cu atom in YBa$_2$Cu$_3$O$_7$ [89], but this is not surprising since the coupling is through the Cu-O-C-D bonds instead of a simple Cu-O bond. The Larmor frequencies can be compared to the experimental differences between the NMR shifts at $a''$, $b''$ and $c''$ in each plane, although this will be inaccurate because of the imperfect alignment of the crystal. Very roughly, $\nu_{Lb''c''}$ should be 35 kHz above $\nu_{Lb''c''}$ which in turn should be
5.3 Data Analysis

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<td>$M$</td>
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<td>$A$</td>
<td>$57 \pm 44$ Oe/$\mu_B$</td>
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<td>$\nu_{La''b''}$</td>
<td>$-19 \pm 7$ kHz</td>
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<td>$\nu_{Lb''c''}$</td>
<td>$10 \pm 8$ kHz</td>
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<td>$\nu_{Le''a''}$</td>
<td>$39 \pm 9$ kHz</td>
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Table 5.2: Final values for the fitted parameters for the 2-sublattice model.

35 kHz above $\nu_{La''b''}$. This agrees with the numerically determined Larmor frequencies since $\nu_{La''c''} - \nu_{Lb''c''} = 29$ kHz and $\nu_{Lb''c''} - \nu_{La''b''} = 29$ kHz. Finally, the calculated ferromagnetic moment along the field direction is shown in Fig. 5.4 and it is clearly very field dependent. The maximum value is roughly 7% of the total moment and is of order $0.04 \mu_B$ which is similar to the previously measured value of 0.05 $\mu_B$ in a 1.2 T field [15].

The contributions to the NMR rotation patterns from the dipolar coupling and the hyperfine exchange are shown in Fig. 5.5. I calculated them using the coupling parameters given in Table 5.2. I also set $\nu_{La''b''} = \nu_{Lb''c''} = \nu_{La''c''} = 0$ and did not include any misalignment. The shifts resulting from the dipolar coupling are larger than those due to the hyperfine exchange and the rotation patterns in the data most closely resemble those from the dipolar shifts with a much smaller contribution due to hyperfine shifts.
In Fig. 5.6, the separate effects of the inequivalent $g$ tensors and the Dzyaloshinskii-Moriya interaction are shown. I calculated the rotation patterns using the same parameters as above. To determine the shifts for the inequivalent $g$ tensors, $D^+$ and $D^-$ were set to zero. For the shifts due to the Dzyaloshinskii-Moriya exchange alone, I made the Zeeman coupling isotropic and set $g = g_1$ where $g = 2$ for all tensors. The anisotropic Zeeman interaction reproduces the shifts in the experimental data to a reasonable degree for the $b''c''$-plane and $c'a''$-plane, but shows discrepancies for the case of the $a''b''$-plane. In contrast, the Dzyaloshinskii-Moriya interaction reproduces the $a''b''$-plane splitting reasonably well, but fails to reproduce the $b''c''$-plane and $c'a''$-plane splittings. Therefore, I have found that contrary to the results of previous work, neither interaction is sufficient on its own and both the inequivalent $g$ tensors and the Dzyaloshinskii-Moriya exchange are needed to model the data.

Finally, I investigated the 4-sublattice model in an attempt to reproduce some of the less prominent features seen in the unaveraged data. The smallest splittings come from the crystallographic differences in the positions of the D atoms and these can easily be calculated for either model. However, there are other larger splittings that were not seen in the results of the 2-sublattice model, in particular near $c''$ in both the $c'a''$-plane and the $b''c''$-plane rotation patterns. These can be seen in Fig. 5.7 and are roughly 10% of the largest splittings. In an effort to understand these, I implemented the 4-sublattice model of Eq. 4.30 which contains two inequivalent planes. I fixed all the 2-sublattices parameters to the fitted values listed in Table 5.2 and varied only the extra 4-sublattice parameters. I first included interlayer coupling in the form of $J_p$ and $J_d$ (Eq. 4.33). If $J_p$ was negative, the interlayer coupling was ferromagnetic and the results were essentially unchanged since the solution was already ferromagnetic along the $c$-axis because of the $g$ tensors. In fact as long as $J_p < 0.01$ meV, the rotation patterns were not significantly different from those calculated in the absence of interlayer coupling. However, if $J_p$ was greater than 0.01 meV, the forced antiferromagnetism along the $c$ axis overcame the $g$ tensor-induced ferromagnetism and the NMR shifts changed drastically. Therefore, adding the interlayer coupling did not
produce any small extra splittings. A similar behavior was seen when the diagonal coupling was ferromagnetic and $J_d$ was less than $-0.004$ meV. I next studied the effects of the $D$ vectors. For the 4-sublattice model, the form of the $D$ vectors is given by Eq. 4.14. I therefore included the Dzyaloshinskii-Moriya parameters $D_+^x$, $D_-^x$ and $D_-^z$ which I had previously set to zero. Although certain combinations of these produced some extra splittings, none reproduced the features in the data nor made any significant improvement to the fit. With the parameters in Table 5.2 fixed, I found the best-fit values were $D_+^x \approx 0.0$, $D_-^x \approx 0.0$ and $D_-^z \approx 0.0$. I next included some symmetry differences in the $g$ tensors as explained in Sec. 4.3, but none produced the desired splittings. I also tried the 4 different hyperfine constants described in Sec. 5.2. Although they did produce some extra splittings, no variations of these produced features with the right symmetry. Finally, I tried including the full dipole-dipole interactions of Eq. 4.34, but no realistic solutions for the minimization of the free energy were found. In conclusion, more work will be needed to produce a 4-sublattice model that predicts all the details of the experimental NMR shifts. Due to the extremely large parameter space, the most optimal combination of parameters may have been missed. Also, the physical effects that are responsible for the small unexplained splittings may not be included in my model. Currently, these small extra splittings remain of unknown origin.

5.4 Shifts at High Temperature

The magnetic contribution to the experimentally measured frequency shifts at 80 K is shown in Fig. 5.8. The data has been averaged in the same manner as the 10 K data (see Sec. 5.3). It is clear that there is still some remanent magnetism at this temperature which results in the small frequency shifts. The maximum splitting in the rotation patterns is approximately 20 kHz and the oscillations are a result of the anisotropic dipole coupling but may also have a component due to the anisotropic behavior of the local spins. Note that at this temperature, CFTH is is not yet in
the Curie limit and the susceptibility at 80 K is still in the broad maximum (see Fig. 1.6(a)). Unfortunately, since this is in the intermediate temperature regime of CFTH, I do not have an adequate model for the magnetism which I would need in order to analyze the shifts quantitatively.

5.5 Shifts versus Temperature

The rotation patterns in the $c''a''$-plane for eight different temperatures are shown in Fig. 5.9. As temperature increases, the frequency shifts decrease. The sharp transition near $a''$ disappears between 20 K and 25 K. Below 30 K, the shifts at $c''$ are larger than those at $a''$, but between 30 K and 40 K this is reversed. The frequency splittings are due to a combination of the anisotropic magnetic behavior of the spins and anisotropic coupling between the nuclei and the electrons. Without a model for the magnetism at intermediate temperatures, I could not analyze these rotation patterns. However, it is interesting to note that static moments at the Cu sites appear to persist to temperatures well above $T_N \approx 16.5$ K.

The frequency shifts as a function of temperature are shown for 4 different rotation angles in Fig. 5.10. The $c''$ axis is at 73° degrees which is near 70°, and the $a''$ axis is at 163° degrees which is near 160°. There is a shoulder near 20 K. In some plots, it appears to be an artifact, but as the behavior at 160° is very pronounced, this is no doubt a real effect. Again, without an adequate model for the magnetism at intermediate temperatures, the behavior of these shifts remains unexplained. Along $c^*$ which is perpendicular to the planes, the shifts can be compared to the measured susceptibility. The shape is similar as shown in Fig. 5.11 in which the susceptibility has been scaled to match the NMR shifts and the baseline seen in Fig. 1.6 (b) has been subtracted. At $T = 10$ K, the numerical model predicts that the component of the magnetization along $c^*$ is 0.03 $\mu_B$, and the calculated susceptibility is therefore 0.00040 $\mu_B$/kOe. This is in good agreement with the measured susceptibility of 0.00031 $\mu_B$/kOe at 10 K. Note that the low field peak in the susceptibility has been
broadened considerably at the higher field. There is almost no evidence of a transition at $T_N \simeq 16.5$ K, but instead there seems to be evidence of static magnetism persisting up to 30 K. I was unable to find any quantitative description of this broadening in the literature and it would be worth exploring in greater detail.
Figure 5.2: Examples of Monte Carlo type searches for several parameters. The large black points are from successful sets of parameters and the smaller grey points are from unsuccessful sets of parameters.
Figure 5.3: The final fits for the 10 K magnetic data. The curves are the numerically calculated shifts and the points are the experimental data which have been averaged as described in the text.
Figure 5.4: The magnitude of the ferromagnetic moment in the field direction for (a) the $a''b'$-plane, (b) the $b''c'$-plane and (c) the $c''a''$-plane.

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Figure 5.5: A comparison between the calculated shifts due to dipolar coupling and hyperfine coupling for (a) (d) the \( a''b'' \)-plane, (b) (e) the \( b''c'' \)-plane and (c) (f) the \( c''a'' \)-plane. The left hand column is with dipolar coupling only and the right hand column is with hyperfine coupling only. Note the different frequency scales.
Figure 5.6: A comparison between the effects of the inequivalent g tensors and the Dzyaloshinskii-Moriya mechanisms on the calculated NMR shifts for (a) (b) the $a''b''$-plane, (c) (d) the $b''c''$-plane and (e) (f) the $c''a''$-plane. Also plotted is the averaged data for each plane.

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Figure 5.7: The 2-sublattice shifts for all 4 D sites. The curves are numerically calculated using the parameters in Table 5.2 and the points are the experimental data.
Figure 5.8: 80 K rotation patterns and numerical results. The solid lines are guides to the eye.
Figure 5.9: Rotation patterns versus temperature in the $c^{''}a^{'''}$-plane. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5. The vertical axis is frequency (kHz) and where zero is the Larmor frequency of D. The dotted lines are the magnetic axes.

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Figure 5.10: NMR shifts versus temperature for 4 different angles. The vertical axis is frequency (kHz) with zero being the Larmor frequency of D. The solid lines are guides to the eye and the colors match those of the D sites in Fig. 2.5.

Figure 5.11: Susceptibility and NMR shifts along the \( c^* \) axis as a function of temperature. The susceptibility has been scaled to match the NMR shifts.

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Chapter 6

Conclusions

I have determined from NMR experiments the ground state properties of the 2D $S=1/2$ square antiferromagnet CFTH. I measured the NMR frequency shifts for the deuterium nuclei in the formate groups as a function of field orientation. At low temperatures, the shifts depend on the orientation of the local moments at the Cu sites. I analyzed these shifts by creating a $T = 0$ numerical model of the free energy. This model contains the anisotropic Heisenberg exchange, the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling to the external field. The inclusion of all of these terms is of particular interest since previous authors used less complete models of the free energy to analyze their data and the few that used the full model only analyzed certain high symmetry directions. As a result, the magnetism in CFTH was poorly understood. This is the first time that the full Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling have been used in a model which allows an arbitrary direction of the magnetic field. The use of both the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling was found to be crucial in modelling the data and understanding the magnetic ground state of CFTH.

The numerical model was compared and fit to the experimental frequency shift data to obtain the various parameters in the magnetic free energy of the 2-sublattice model. The Heisenberg exchange coupling $J$ is $4.0 \pm 0.4$ meV or $47 \pm 4$ K and the extra anisotropies in this coupling were found to be very small. The two Dzyaloshinskii-
Moriya vectors are $D^+ = (-0.03 \pm 0.01, 0.0, -0.18 \pm 0.02) \text{ meV}$ and $D^- = (0.0, 0.00 \pm 0.06, 0.0) \text{ meV}$. The magnitude of $D^+$ agrees with earlier estimates and this is the first time that all components of the vectors have been measured. The average moment of the antiferromagnetically ordered spins is $0.571 \pm 0.004 \mu_B$ and the maximum ferromagnetic moment due to the small cant of the spins was found to be roughly $0.04 \mu_B$. I have shown that the low temperature magnetic ground state of CFTH is very dependent on the orientation of the external magnetic field and I believe it would be important to include the Dzyaloshinskii-Moriya interaction and the anisotropic Zeeman coupling in any future analysis of CFTH.

In this series of experiments, there remain a few outstanding problems. At 10 K, although the major frequency splittings are now understood in terms of the interactions that govern the magnetic ground state, the smaller unexplained splittings need further investigation. If the source of the splitting involves physics that is not currently incorporated in the model, it would be important to study this new effect in order to complete the picture of the magnetism of CFTH at low temperatures. It would also be beneficial to develop a model of the magnetism of CFTH for higher temperatures, since both our NMR data and the broadening of the transition in the high field susceptibility indicate that there is static magnetic behavior above the Néel temperature. Unfortunately, this type of theoretical work at intermediate temperatures is hard even for an ideal 2D $S=1/2$ square antiferromagnet and it would be very difficult if the complex magnetic interactions present in CFTH were included. There has been some work done recently on 1D systems with both the Dzyaloshinskii-Moriya interaction and the anisotropic g-tensors [67] for $T > 0$, but the 2D case remains much more difficult and uninvestigated as far as I know [90]. Additionally, the ideal 2D $S=1/2$ square antiferromagnet above $T_N$ is not predicted to have any antiferromagnetic fluctuations that are time-averaged to non-zero values. Our data suggests that it may be worth exploring whether the Dzyaloshinskii-Moriya interaction or the inequivalent g-tensors can lead to small static moments above $T_N$.

The types of magnetic anisotropies in CFTH are also seen in many other mate-
rials. In the cuprates for example, the magnetic behavior of undoped \( \text{La}_2\text{CuO}_4 \) was only understood after the Dzyaloshinskii-Moriya exchange was included correctly in the magnetic Hamiltonian. It is essential to correctly include all the relevant interactions, study the symmetries of these interactions in detail and properly quantify their relative strengths in order to fully understand these types of magnetic systems.
References


REFERENCES


