To my parents and sister
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A quantum critical point (QCP), a zero-temperature singularity at which a line of continuous phase transition ends, gives rise to novel phenomena, some of which can be observed at nonzero temperatures. In this dissertation, we focus on the QCP’s of two dissimilar quantum antiferromagnets, Cr(diethylenetriamine)(O$_2$)$_2$·H$_2$O in which a transition between an antiferromagnetically ordered phase and the fully polarized state occurs at the QCP, and (CH$_3$)$_2$CHNH$_3$CuCl$_3$ whose QCP is between a quantum-mechanically disordered phase and an antiferromagnetically ordered phase. Using these two compounds, Cr(dien) and IPA-CuCl$_3$ for short, we show that nuclear spins frozen in a high-energy nonequilibrium state by temperature quenching are annealed by quantum fluctuations near a QCP. This new phenomenon, observed in a spin-1 square-lattice antiferromagnet and a spin-1/2 ladder antiferromagnet having dissimilar QCP’s, provides a powerful general tool with which to map a quantum critical region near a QCP and to investigate the dynamics of the quantum fluctuations that underlie quantum criticality.
The experiment relies extensively on a novel application of calorimetry. In Cr(dien), we have also used proton NMR to probe the quantum fluctuations of Cr$^{4+}$ spins at magnetic fields very near the QCP, a special part of a quantum critical region that is inaccessible to our calorimetric method.

As a pre-requisite for this research, we have also mapped the magnetic phase diagrams of Cr(dien) and IPA-CuCl$_3$ with a particular emphasis on finding the exact locations of the QCPs. For this purpose, we have employed specific-heat, magnetocaloric-effect, and — in the case of IPA-CuCl$_3$ — magnetic-torque measurements. We find power-law dependences of the critical field of the long-range antiferromagnetic order on temperature in both compounds. In Cr(dien), the power-law exponent is that of the three-dimensional Ising universality, for the magnetic-field direction we have investigated. In IPA-CuCl$_3$, the power-law exponents for the two magnetic-field directions we have studied indicate a Bose-Einstein condensation of magnons at the closing of the Haldane gap of the magnons by the magnetic field.
Quantum criticality is the behavior of a macroscopic system at a continuous phase transition in the limit of zero temperature \[1\]. Such a transition is produced by controlling a tunable parameter such as the magnetic field, pressure, and chemical composition. Quantum criticality is believed to underlie non-Fermi liquid behavior in some conductors and non-conventional superconductivity in cuprates, pnictides, and some heavy-fermion metals \[2, 3\]. Dynamics in the vicinity of a quantum critical point (QCP) is particularly interesting. On the one hand, critical slowing down occurs at a QCP, with a diverging equilibration time. On the other, quantum fluctuations near the QCP should enhance the energy transfer rate between different degrees of freedom.

This dissertation examines the properties of two quantum magnets, Cr(dien\(\text{O}_2\)\(_2\)\(\cdot\)\(\text{H}_2\)\(\text{O}\) and \((\text{CH}_3\)\(_2\)\(\text{CHNH}_3\)\(\text{CuCl}_3\), near their QCPs. The first compound, Cr(dien) for short, is a novel Cr\(^{4+}\) compound synthesized by Naresh Dalal’s group in the Chemistry Department of Florida State University \[4, 5\]. It is a quasi-two-dimensional antiferromagnet, in which square-lattice layers of the \(S = 1\) Cr\(^{4+}\) spins are weakly coupled. The saturation field, \(12.392 \pm 0.003\) T, in which the line of continuous phase transition between the paramagnetic phase and the antiferromagnetic phase terminates, is the QCP of this material. The second material, also known as IPA-CuCl\(_3\), is a quasi-one-dimensional antiferromagnet comprising the \(S = 1/2\) spins of Cu\(^{2+}\). These spins form two-leg ladders with antiferromagnetic leg interactions and as a result, possess a Haldane gap. The QCP of this material is at \(9.995 \pm 0.002\) T for one field direction and \(9.399 \pm 0.004\) T for another, perpendicular direction. At these critical
fields, the Haldane gap is completely suppressed by magnetic field, and interladder interactions lead to antiferromagnetic ordering.

For both compounds, we first characterized the temperature dependence of the critical field near the QCP. We have found that Cr(dien) exhibits an Ising criticality, whereas IPA-CuCl$_3$ shows a Heisenberg criticality described as a Bose-Einstein condensation of magnons.

We also discovered a new quantum critical phenomenon, quantum-fluctuation-driven release of heat from hydrogen nuclear spins, in both compounds. To observe this phenomenon, the sample is temperature quenched in a magnetic field, an operation which leaves the hydrogen nuclear spins frozen in a high-energy nonequilibrium state. Subsequently, as the magnetic field is swept towards the QCP, the divergent quantum fluctuations of the Cr$^{4+}$ or Cu$^{2+}$ spins quickly anneal the nuclear spins. We employ a calorimetric technique to examine the dynamics of the annealing and concomitant heat release from the nuclear spins. Our discovery of this phenomenon in two dissimilar antiferromagnets, differing in dimensionality and spin quantum number, suggests that it is a generic property of a variety of QCP. The results for Cr(dien) have been published in Physical Review Letters [6].

In addition, we used proton NMR to investigate the dynamics of the Cr$^{4+}$ spins in Cr(dien) near the QCP. We have found that the proton spin-lattice relaxation time $T_1$ becomes drastically short near the QCP, caused by divergent quantum fluctuations of the Cr$^{4+}$ spins. At the same time, the relaxation becomes strongly non-exponential near the QCP. We characterize the non-exponential behavior and briefly suggest a possible link between this phenomenon and the dynamic critical behavior of an Ising system.
The outline of the dissertation is as follows. Chapter 2 reviews the theoretical background of this work. Chapter 3 describes our experimental techniques: specific-heat measurements, magnetocaloric-effect measurements, magnetic-torque measurements, and NMR. Chapters 4 through 6 present the experimental results on Cr(dien) and IPA-CuCl₃. Finally, Chapter 7 summarizes the dissertation.
CHAPTER 2
THEORETICAL BACKGROUND

In this chapter, we review four theoretical concepts that form a basis of this work. They are quantum critical points, magnons, Haldane gap, and Bose-Einstein condensation.

2.1 Quantum Critical Points

Since Hertz introduced the idea of quantum criticality in 1976 [7], many people have been studying quantum critical behavior of condensed matter, theoretically and experimentally. A QCP is a point, in a phase diagram, at which a zero-temperature phase transition takes place. Such a transition is produced by tuning non-thermal parameters such as the magnetic field, pressure, and chemical composition, as illustrated in Figure 2-1. Among these, magnetic field is the most convenient parameter, which can be changed with ease without interrupting an experiment.

In general, there are two kinds of phase transitions: first-order transitions and continuous transitions, also known as higher-order transitions. A first-order transition is accompanied by an abrupt change in first derivatives of the free energy. In contrast, at a continuous phase transition, an anomaly occurs only in second or higher-order derivatives of the free energy, while the first derivatives remain continuous. For example, a transition from a paramagnet to a ferromagnet or an antiferromagnet is usually continuous, accompanied by a \( \lambda \)-peak anomaly in specific heat. Only when a continuous phase transition occurs at zero temperature is the critical point a QCP. Most often, a QCP appears in a phase diagram as the zero-temperature end point of a line of continuous transitions.
A continuous phase transition at a non-zero-temperature, classical critical point is caused by thermal fluctuations. Thermal fluctuations are absent at zero temperature, where a quantum phase transition takes place. Instead, the fluctuations at a QCP are caused purely by a quantum-mechanical effect due to the Heisenberg uncertainty. At a QCP, both spatial and temporal extents of quantum fluctuations diverge, as does the spatial extent of thermal fluctuations at a classical critical point. The divergent quantum fluctuations at a QCP are believed to be the driving mechanism behind a variety of novel phenomena, which challenge conventional theoretical approaches to collective behavior of many-body systems and may also lead to technological applications. They are responsible for the breakdown of Fermi-liquid behavior in some heavy-fermion metals [8, 9] and for the emergence of exotic states of matter such as unconventional superconductors [10, 11], nematic electron fluids in two-dimensional electron gases and in Sr$_3$Ru$_2$O$_7$ [12–14], and ‘reentrant hidden-order’ states in URu$_2$Si$_2$ [15].

Presently, many theoretical and experimental studies in condensed matter physics are devoted to the challenging task of elucidating such phenomena. Particularly important are investigations of dynamic phenomena near a QCP, such as quantum-fluctuation-driven relaxation and tunneling, because dynamic and static properties near a QCP are thought to be inseparably linked. Antiferromagnets are particularly attractive candidates for such studies, because their QCPs can be reached by applying an external magnetic field instead of varying the chemical composition of the material, a parameter difficult to control precisely as has been found in studies involving conduction electrons. However, not every antiferromagnet fills the bill. The antiferromagnet under
study must be low-dimensional and must consist of ions of a small quantum number, requirements which enhance quantum fluctuations.

2.2 Magnons

Similar to phonons, which are collective excitations of a crystal lattice, magnons are collective excitations of electron spins in a magnetic solid [16–18]. Whereas phonons are quantized sound waves, magnons are quantized spin waves. There are important differences between spin waves in a ferromagnet, illustrated in Figure 2-2, and those in an antiferromagnet. We will first describe spin waves in a ferromagnet, then those in an antiferromagnet, followed by a description of special kinds of magnons in one-dimensional quantum magnets, antiferromagnets of small spin quantum numbers.

For simplicity, we consider a one-dimensional ferromagnet described by a Heisenberg Hamiltonian:

\[ H = J \sum_i \vec{S}_i \cdot \vec{S}_{i+1}, \quad (2-1) \]

where \( J \) is the strength of the exchange interaction, and \( \vec{S}_i \) the spin operator at site \( i \).

The exchange interaction \( J \) is negative; later, for an antiferromagnet, it will be positive. It is easy to derive a dispersion relation for spin waves in a ferromagnet [19]. The Heisenberg equation of motion for the spins is

\[
\frac{d\langle \vec{S}_j \rangle}{dt} = \frac{1}{i\hbar} \left[ \langle \vec{S}_j \rangle, H \right]
\]

\[
= \frac{J}{i\hbar} \left[ \langle \vec{S}_j \rangle, \vec{S}_{j-1} \cdot \vec{S}_j \right] + \left[ \vec{S}_j, \vec{S}_{j+1} \cdot \vec{S}_j \right] \quad (2-2A)
\]

\[
= \frac{J}{i\hbar} \left\{ \langle \vec{S}_j \rangle \cdot (\vec{S}_{j-1} \cdot \vec{S}_j) - (\vec{S}_{j-1} \cdot \vec{S}_j) \cdot \vec{S}_j + \vec{S}_j \cdot (\vec{S}_j \cdot \vec{S}_{j+1}) - (\vec{S}_j \cdot \vec{S}_{j+1}) \cdot \vec{S}_j \right\} \quad (2-2B)
\]

\[
= \frac{J}{i\hbar} \left\{ \langle \vec{S}_j \rangle \cdot (\vec{S}_{j-1} \cdot \vec{S}_j) - (\vec{S}_{j-1} \cdot \vec{S}_j) \cdot \vec{S}_j + \vec{S}_j \cdot (\vec{S}_j \cdot \vec{S}_{j+1}) - (\vec{S}_j \cdot \vec{S}_{j+1}) \cdot \vec{S}_j \right\} \quad (2-2C)
\]
The components of this equation are

\[
\frac{dS_j^x}{dt} = \frac{J\hbar}{h} \left(2S_{j-1}^y - S_j^y - S_{j+1}^y\right), \quad (2-3A)
\]

\[
\frac{dS_j^y}{dt} = -\frac{J\hbar}{h} \left(2S_j^x - S_{j-1}^x - S_{j+1}^x\right), \quad (2-3B)
\]

\[
\frac{dS_j^z}{dt} = 0. \quad (2-3C)
\]

We look for a solution of the form

\[
S_j^x = u e^{i(k_j - \omega t)}, \quad (2-4A)
\]

\[
S_j^y = v e^{i(k_j - \omega t)}, \quad (2-4B)
\]

where \(u\) and \(v\) are constants, \(k\) the wave vector, and \(a\) the lattice constant. Substituting these into Eqs. 2-3A and B results in

\[
-\hbar \omega u e^{i(k_j - \omega t)} = J\hbar[2 - e^{-ika} - e^{ika} v e^{i(k_j - \omega t)}], \quad (2-5A)
\]

\[
i\hbar \omega ve^{i(k_j - \omega t)} = J\hbar[2 - e^{-ika} - e^{ika} u e^{i(k_j - \omega t)}]. \quad (2-5B)
\]

That is,

\[
\begin{pmatrix}
\hbar \omega & J\hbar(1 - \cos ka) \\
J\hbar(1 - \cos ka) & -\hbar \omega
\end{pmatrix}
\begin{pmatrix}
u \\
v
\end{pmatrix}
= 0. \quad (2-6)
\]

We can obtain the solution by using the determinant as follows:

\[
\begin{vmatrix}
\hbar \omega & 2J\hbar(1 - \cos ka) \\
2J\hbar(1 - \cos ka) & -\hbar \omega
\end{vmatrix}
= 0. \quad (2-7)
\]

Thus,

\[
\hbar \omega = 2J\hbar(1 - \cos ka). \quad (2-8)
\]
This is the dispersion relation for spin waves, i.e. magnons, in a ferromagnet. For $ka \ll 1$, Eq. 2-8 becomes
\[ \hbar \omega = |J| S a^2 k^2. \]  

(2-9)

An antiferromagnet has two sublattices, say sites A with spins pointing to the “left” and sites B with spins pointing to the “right”. We assign even indices $j$ to sites A and odd indices $j$ to sites B [19]. For even $j$,
\[ \frac{dS_j^x}{dt} = \frac{JS}{\hbar} \left( 2S^x_j - S^{y}_{j-1} - S^{y}_{j+1} \right), \]  

(2-10A)
\[ \frac{dS_j^y}{dt} = -\frac{JS}{\hbar} \left( 2S^{x}_j - S^{x}_{j-1} - S^{x}_{j+1} \right). \]  

(2-10B)

For odd $j$,
\[ \frac{dS_j^x}{dt} = \frac{JS}{\hbar} \left( 2S^x_j + S^{y}_{j-1} + S^{y}_{j+1} \right), \]  

(2-11A)
\[ \frac{dS_j^y}{dt} = -\frac{JS}{\hbar} \left( 2S^{x}_j + S^{x}_{j-1} + S^{x}_{j+1} \right). \]  

(2-11B)

Using
\[ S^+ = S^x + iS^y, \]  

(2-12)
we rewrite Eqs. 2-10 and 2-11 as
\[ \hbar \frac{dS_j^{+}}{dt} = iJS \left[ 2S_j^{+} + S_{j-1}^{+} + S_{j+1}^{+} \right] \text{ for even } j, \]  

(2-13A)
and
\[ \hbar \frac{dS_j^{+}}{dt} = -iJS \left[ 2S_j^{+} + S_{j-1}^{+} + S_{j+1}^{+} \right] \text{ for odd } j. \]  

(2-13B)

As in the ferromagnetic case, we look for a solution of the form
\[ S_j^+ = u e^{i(k_j a - \omega t)} \text{ for even } j, \quad (2-14A) \]

\[ S_j^+ = v e^{i(k_j a - \omega t)} \text{ for odd } j. \quad (2-14B) \]

Substituting Eqs. 2-14A and B into 2-13A and B results in

\[ \hbar \omega u = JS[2u + (e^{-ika} + e^{ika})v] \text{ for even } j, \quad (2-15A) \]

\[ -\hbar \omega v = JS[2v + (e^{-ika} + e^{ika})u] \text{ for odd } j. \quad (2-15B) \]

That is,

\[ \hbar \omega \begin{pmatrix} u \\ -v \end{pmatrix} = 2JS \begin{pmatrix} 1 & \cos ka \\ \cos ka & 1 \end{pmatrix} \begin{pmatrix} u \\ v \end{pmatrix}.\quad (2-16) \]

So,

\[ \begin{vmatrix} -\hbar \omega + 2JS & 2JS \cos qka \\ 2JS \cos ka & \hbar \omega + 2JS \end{vmatrix} = 0, \quad (2-17) \]

which is

\[ - (\hbar \omega)^2 + 4J^2 S^2 (1 - \cos^2 ka) = 0. \quad (2-18) \]

Therefore,

\[ \hbar \omega = 2JS |\sin ka|. \quad (2-19) \]

This is the dispersion relation for spin waves, i.e. magnons, in an antiferromagnet.

For small \( k \), the dispersion has a linear dependence on \( k \) (\( \omega \approx k \)) in contrast to the \( k^2 \) dependence (\( \omega \approx k^2 \)) for a ferromagnet, as shown in Figure 2-3. In either case, magnons have no energy gap at \( k = \pi \). The quantum numbers of a magnon in a ferromagnet are known to be \( S = 1 \) and \( m_s = 1 \), whereas for a magnon in an antiferromagnet they are known to be \( S = 1 \) and \( m_s = \pm 1 \).
To derive the magnon dispersion for an antiferromagnet, we have assumed that the spins are ordered in a state comprising two sublattices. Magnetic order is often absent, however, in quantum magnets. As a result, the magnon dispersion in such a quantum magnet can greatly differ from Eq. 2-19. In the next section, we describe the case of one-dimensional antiferromagnets, a quantum magnet consisting of so-called spin dimers.

### 2.3 Haldane Gap

In the previous section, we have considered a one-dimensional (1D) Heisenberg antiferromagnet (HAF) given by Eq. 2-1 only as a model for an antiferromagnet that is spontaneously ordered with two sublattices. True 1D HAFs do not order, however, even at zero temperature, because a spin in 1D does not have enough neighbor spins and thus quantum fluctuations become overwhelming. As a result, the magnon dispersion is not given by Eq. 2-19 and depends on whether the quantum number $S$ of spins is a full integer or a half of an odd integer.

For the Hamiltonian given by Eq. 2-1 in the $S = 1/2$ case, Bethe [20] has given the exact wave functions, which lead to the following dispersion for low-lying excitations:

$$\varepsilon(k) = \frac{\pi}{2} J |\sin ka|.$$  \hspace{1cm} (2-20)

This dispersion may not appear dramatically different from Eq. 2-19. However, the spin quantum number $S$ of the excitations is $1/2$ instead of $1$. For this and other reasons, they are called spinons instead of magnons. Moreover, immediately above the dispersion given by Eq. 2-20 lies a continuum of two-spinon excitations, as shown in Figure 2-4 [21].
When the spin quantum number $S$ is an integer, the Schrödinger equation for the Hamiltonian given by Eq. 2-1 cannot be exactly solved. As was predicted by Haldane [22], however, there exists in this case an energy gap, $\Delta$, called the Haldane gap, between the quantum-mechanically disordered ground state and low-lying excitations, as shown in Figure 2-4. In particular, if $S = 1$, the Haldane gap is [23]

$$\Delta = 0.4 J.$$

Unlike in the $S = 1/2$ case, the spin quantum number $S$ of the excitations is 1, but $m_s$ can be $\pm 1$ or 0 instead of only $\pm 1$. For this reason, these excitations are sometimes called triplons rather than magnons.

Haldane’s prediction has been confirmed by a number of experiments on 1D $S = 1$ HAFs. One of the best examples is Ni(C$_2$H$_8$N$_2$)$_2$NO$_2$(ClO$_4$), also known as NENP [24]. It has been shown [25] that two-leg $S = 1/2$ Heisenberg spin ladders with an antiferromagnetic leg exchange also has a Haldane gap. One such antiferromagnet is (CH$_3$)$_2$CHNH$_3$CuCl$_3$, the subject of Chapter 6.

The presence of the Haldane gap leads to physical properties of integer-spin 1D HAFs, and two-leg $S = 1/2$ Heisenberg spin ladders such as (CH$_3$)$_2$CHNH$_3$CuCl$_3$, fundamentally different from those of half-odd-integer-spin 1D HAFs. For instance, the spatial correlation function of the integer case has an exponential decay, as opposed to a power-law decay in the half-odd-integer case [26]. Moreover, as the Haldane gap closes at a sufficiently high magnetic field, a QCP appears in the magnetic phase diagram, as explained in the next section.

### 2.4 Bose-Einstein Condensation

Bose-Einstein condensation (BEC) was initially found in liquid $^4$He [27, 28] as had been proposed as the explanation of its superfluidity [29, 30], and more recently in
ultracold atomic gases [31]. It can also occur in a system of other bosons such as gapped magnons. To explain this, we first consider the simplest quantum magnet with gapped excitations, a collection of antiferromagnetically coupled pairs of $S = 1/2$ spins with weak antiferromagnetic interpair exchanges. Such a pair is called a spin dimer.

Of this system consisting of spin dimers, the ground state is a collection of singlet dimers

$$|S = 0, m_s = 0\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle \right), \quad (2-22)$$

and low-lying excitations are mixtures of singlet dimers and triplet dimers

$$|S = 1, m_s = 1\rangle = |\uparrow\uparrow\rangle, \quad (2-23)$$

$$|S = 1, m_s = 0\rangle = \frac{1}{\sqrt{2}} \left( |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle \right), \quad (2-24)$$

$$|S = 1, m_s = -1\rangle = |\downarrow\downarrow\rangle. \quad (2-25)$$

In a magnetic field $H$, the Zeeman effect splits the triplet states, causing the energy of the $m_s = -1$ triplet to decrease linearly with $H$, with a slope $g\mu_B$, as illustrated in Figure 2-5. Here $g$ is the $g$ factor and $\mu_B$ the Bohr magneton. At a critical field

$$H_c = \frac{\Delta}{g\mu_B}, \quad (2-26)$$

the triplet reaches the ground state. Here $\Delta$ is the energy-level separation between the singlet and triplets of a dimer at zero field, analogous to the Haldane gap between the quantum-mechanically disordered ground state of an integer-spin 1D HAF and magnons. Because of the antiferromagnetic interdimer interactions, however, the ground state does not immediately become a collection of $m_s = -1$ triplets, a state in which all the spins are aligned with the magnetic field. Instead, the triplets are
delocalized — they are magnons in a general sense — and only an infinitesimal number of them will condense into the ground state at $H_c$. As the field is increased further, an increasing number of triplets will condense into the ground state, resulting in increasing magnetization. The ground state is now antiferromagnetically ordered owing to the interdimer interactions. Therefore, $H_c$ is a QCP that separates a macroscopic singlet state from an antiferromagnetically ordered state. Because delocalized triplets are bosons, the magnetic ordering can be described as a BEC of magnons [25, 32]. As this hand-waving argument for a BEC suggests, the magnetic field corresponds to the chemical potential of an ideal Bose gas or an atomic gas.

For magnons in integer-spin 1D HAFs or two-leg $S = 1/2$ Heisenberg spin ladders, the wave functions are far more complicated than Eqs. 2-22 through 2-25 and are in fact unknown. However, the effect of a magnetic field on them will be exactly the same. The only key difference is that the interactions responsible for antiferromagnetic ordering are between spin chains or spin ladders and that $\Delta$ in Eq. 2-26 is the Haldane gap.

One of the most important consequences of an antiferromagnetic ordering as a BEC of magnons is the universal power law [1–3]

$$H - H_c \propto T^\alpha,$$  \hfill (2-27)

where $H$ is the transition field at non-zero temperature $T$, and $H_c$ the critical field at zero temperature. The exponent, $\alpha$, depends on spatial dimension $d$:

$$\alpha = d/2.$$  \hfill (2-28)

For three-dimensional ordering, $\alpha = 3/2$.

The first evidence for a BEC of magnons was found in TlCuCl$_3$ [32, 33], an antiferromagnet consisting of dimers of $S = 1/2$ Cu$^{2+}$ spins. In this material, the ordering
temperature $T$ was determined at each $H$ from specific heat, and agreement with Eq. 2-27 was found with $\alpha = 1.67 \pm 0.07$, close to the theoretical value $3/2$. More recently, additional evidence for BEC has been found in a few other spin-dimer compounds, including BaCuSi$_2$O$_6$ [34], in which evidence for crossover has been observed between a three-dimensional BEC and a two-dimensional BEC due to geometric frustration. In principle, a BEC of magnons can occur also near the saturation field of a Heisenberg antiferromagnet, since an antiferromagnetically ordered state at a field just below the saturation field can be viewed as a dilute system of $m_s = 1$ magnons condensed in the background of a fully polarized “vacuum” [35].
Figure 2-1. Typical quantum critical phase diagram. $g$ is a tuning parameter such as the magnetic field, pressure, and chemical composition. At a critical value, $g_c$, a quantum phase transition occurs at $T = 0$. The solid line is a phase boundary between two phases, A and B, and the dash lines mark a crossover to the quantum critical region.

Figure 2-2. Spin wave. Top: spin wave state of a ferromagnet. $a$ is the lattice constant. Bottom: top view of the spin wave, showing a wave-like behavior.
Figure 2-3. Dispersion relations of ferromagnetic (left) and antiferromagnetic (right) magnons. For small $k$, the ferromagnetic case is $\varepsilon \approx k^2$, whereas the antiferromagnetic case is $\varepsilon \approx k$.

Figure 2-4. Dispersion relations of low-lying excitations in 1D HAF for $S = 1/2$ (left) and $S = 1$ (right). In the left panel, the shaded region is the two-spinon continuum. In the right panel, $\Delta$ is the Haldane gap. The lattice constant $a$ has been taken to be 1.
Figure 2-5. Zeeman splitting of the triplet state of a spin dimer. The critical field \( H_c \) at which the \( m_s = -1 \) triplet state reaches the ground state is \( \Delta / g \mu_B \).
CHAPTER 3
EXPERIMENTAL TECHNIQUES

Specific heat, the magnetocaloric effect, magnetic torque, and nuclear magnetic resonance (NMR) are valuable tools for the study of quantum critical behavior of magnetic materials, and often superconductors, near a QCP. These tools provide useful information on the static and dynamic properties of materials under study. In this chapter, I will describe their principles and how they were used in this work.

Most of the results presented in this dissertation were obtained in an Oxford Instruments $^3$He/$^4$He dilution refrigerator with a 20-T superconducting magnet at the Millikelvin Laboratory of the NHMFL in Tallahassee. Figure 3-1 shows another, similar refrigerator at the NHMFL. The operating temperature of the refrigerator used for this work is typically between 20 mK and 900 mK. It takes about 6 hours for the refrigerator to reach the base temperature after a top-loading probe, on which an experiment is attached, is inserted in the mixing chamber.

3.1 Specific Heat Measurements

3.1.1 Calorimeter Design

Specific heat provides an unambiguous signature at a phase transitions driven by temperature or magnetic field. As illustrated in Figure 3-2, the calorimeter used for specific-heat measurements for this dissertation consists of a sample platform, a silver block, a silver ring, and a vacuum can. This calorimeter was designed and built by Hiroyuki Tsujii, a former postdoc of our group, with components produced by our machine shop [36]. The calorimeter attaches to the bottom of the top-loading probe for the dilution refrigerator. The 6.3 mm-thick silver block and the 1.9 cm-diameter silver ring serve as a thermal reservoir. Silver is used here because, in magnetic fields, its
nuclear specific heat is one of the smallest of all metals, ensuring a short equilibration time. The sample platform is a 6.4 mm-diameter and 0.13 mm-thick sapphire disk, on which a thin film of a Ti-Cr alloy has been evaporated as a heater and a small slice of a 220 Ω Speer resistor has been attached with EPO-TEK 417® silver epoxy as a thermometer. The electrical leads for the heater and thermometer serve as a weak thermal link between the platform and the reservoir, as well as a mechanical support of the platform. The 24.6 mm-diameter vacuum can isolates the reservoir and platform thermally from the liquid helium in the mixing chamber, allowing the temperature of the experiment to be easily set anywhere between 20 mK and 7 K with a heater on the silver block. The can is made of brass in order to reduce eddy-current heating when the magnetic field is swept for a magnetocaloric-effect measurement. A grease joint with a taper of 7° provides a superfluid-tight vacuum seal [37]. The vacuum feedthroughs for the electrical leads consist of two rows of six gold-plated pins taken from a single-in-line-pin (SIP) socket and glued with Stycast 2850FT® epoxy into individual holes drilled on the lid of the vacuum can. The original spacing of the pins of the SIP socket is maintained in the feedthroughs, so that a pair of SIP sockets for the external leads and another pair for the internal leads directly plug into them from above and below, respectively. The calorimeter is evacuated at room temperature through a 1.3 mm-diameter CuNi tube and a 1/16 inch diameter stainless-steel tube, which run in series along the length of the top-loading probe.

The silver block is suspended by a rod of Vespel SP-22®, a thermal insulator, attached to the lid of the vacuum can. A weak thermal contact for the block is provided by twelve 79 µm-diameter silver leads that run to the block from the feedthroughs. The
block has sixteen silver pins for providing heat sinks to the leads; the twelve leads are attached to twelve of the pins with EPO-TEK 417® silver epoxy. The thermometer for the block is a 220 Ω Speer carbon resistors. As the block heater, a 35 cm long piece of 79 µm diameter Karma-alloy wire is wound around a silver post on the block; Karma alloy comprises Ni 74%, Cr 20%, Al 3%, and Fe 3%.

The leads for the platform thermometer and platform heater are 76 µm-diameter wires of 90%Pt-10% Rh. Each lead is soft soldered to a heat sink made of a small piece of 0.1 mm-thick silver foil that has been glued with Stycast 2850FT® to the silver ring.

3.1.2 Calorimeter Electronics and Thermometer Calibration

The electronics for the calorimeter consists of a PAR 124A lock-in amplifier, a decade resistor, three dc current sources, and a multimeter, as shown in Figure 3-3. To measure a specific heat with the relaxation method, which will be described in section 3.1.3, first the temperature of the reservoir is set at a desired value by applying a dc current to the block heater. The resistance of the block thermometer is read with the four-wire method employing one of the current sources and the multimeter used as a voltmeter. The Wheatstone bridge for the sample-platform thermometer is balanced by manually matching the decade resistor with the resistance of the thermometer, while using the lock-in amplifier as a null detector. Subsequently, the current to the platform heater is turned on to produce a temperature difference between the platform and the reservoir, resulting in an off-balance voltage across the Wheatstone bridge. The bridge is rebalanced by adjusting the decade resistor. Finally, the platform-heater current is turned off, and the ensuing relaxation of the off-balance voltage is measured by the lock-in amplifier, with the dc analog output of the lock-in amplifier recorded by a data-
acquisition board installed on a computer. The bridge is driven by the internal oscillator of the lock-in amplifier, set at 441 Hz. The excitation level is frequently checked to ensure that the platform thermometer is not overheated, while the off-balance bridge is maximized.

During an experiment, the decade-resistor values that balance the Wheatstone bridge with the platform heater off and on are converted to temperatures by using a calibration function embedded in a LabView program on the computer. Since the resistance of the platform thermometer varies slightly from run to run, however, more accurate conversions are carried out after the experiment by comparing the platform-thermometer resistance with the block-thermometer resistance, which is stable.

The resistance of the block thermometer depends not only on temperature but also on the magnetic field. Therefore, the thermometer has been calibrated at several fields in situ by measuring the relaxation times of the calorimeter with high-purity standard samples of silver, platinum, and indium. In the field range of the present experiment, calibration uncertainties are about 1.0% at 0.8 K and about 1.8% at 0.1 K. The principle of the calibration method is as follows. We choose two materials whose specific heats have quite different temperature dependences at a given magnetic field. We then measure the relaxation times of the samples of those two materials of known masses in our calorimeter, at a given temperature. The ratio of the two relaxation times will yield the temperature uniquely, provided that the phonon and electron specific heats of the samples are accurately known and their nuclear-spin specific heat and quadrupolar specific heat, if any, can be calculated. The three high-purity metals satisfy these requirements. Three instead of two are needed to cover different field and
temperature regions. The method in effect measures the heat capacities of the standard samples in magnetic field but eliminates a propagated uncertainty due to the uncertainty of the thermal conductance of the weak link by taking the ratio of relaxation times.

### 3.1.3 Relaxation Calorimetry

The calorimeter described in Sec. 3.1.1 is used to measure the specific heat of a sample with the relaxation method [38–40]. In this method, the temperature of the sample platform is raised by about 1% to 5% above the reservoir temperature by applying a dc current to the platform heater. After the platform thermometer has reached a constant temperature, the heater is turned off and the ensuing relaxation of the platform temperature is recorded. In reality, we record the off-balance signal of the Wheatstone bridge for the thermometer. The time constant $\tau$ of the relaxation yields the specific heat of the sample as follows.

The heat flow $\dot{Q}$ from the sample platform to the reservoir is given by

$$\dot{Q} = \kappa \Delta T,$$  \hspace{1cm} (3-1)

where $\kappa$ is the thermal conductance of the weak link between the sample platform and the reservoir, and $\Delta T$ the temperature difference between them (Figure 3–4(a)).

According to the definition of heat capacity,

$$dQ = -CdT,$$  \hspace{1cm} (3-2)

where $C$ is the total heat capacity of the sample and the sample platform, and $T$ the sample platform temperature. Thus,

$$\dot{Q} = -C \frac{d(\Delta T)}{dt},$$  \hspace{1cm} (3-3)

since the reservoir temperature is held constant. From Eqs. 3-1 and 3-3, we obtain
\[ \kappa \Delta T = -C \frac{d(\Delta T)}{dt}, \]  

which yields

\[ C = \kappa \tau, \]  

where \( \tau \) is the time constant of the exponential relaxation of \( \Delta T \). Here, the temperature dependences of \( C \) and \( \kappa \) have been ignored. This approximation is valid, since \( \Delta T \) with the heater on is kept small, between 1% and 5% of \( T \). Equation 3-5 is the basis of the relaxation calorimetry. Using this equation, the total heat capacity \( C \) is obtained from \( \kappa \), whose temperature dependence has been determined, and the measured \( \tau \). For \( \kappa \), we take its value at the average between the initial and final temperatures. As a result, \( C \) is the value at that average temperature. From \( C \), the known heat capacity of the sample platform, \( C_{\text{add}} \), is subtracted to obtain the heat capacity \( C_{\text{sample}} \), and thus the specific heat, of the sample.

At low temperatures, simple exponential relaxation of the sample-platform temperature is not always observed. Often, the temperature instead drops rapidly first, then decays more slowly. This rapid initial drop, the so-called \( \tau_2 \) effect, arises from either a poor thermal contact between the sample and the sample platform, as schematically shown in Figure 3-4(b), or a poor thermal conductance of the sample, as shown in Figure 3-4(c).

In the situation modeled by Figure 3-4(b), the temperature of the sample is uniform, but the thermal contact between the platform and the sample is poor so that a temperature gradient develops across the interface between the two. This causes the temperature of the platform to drop rapidly, the so-called lumped \( \tau_2 \) effect, until the temperature gradient at the interface leads to a heat flow from the sample to the
platform and thus a relaxation of the sample temperature. As a result, \( \Delta T \) follows the equation [39]

\[
\frac{\Delta T}{\Delta T_0} = a_1 e^{-t / \tau_1} + (1 - a_1) e^{-t / \tau_2},
\]

(3-6)

where \( \Delta T_0 \) is \( \Delta T \) at \( t = 0 \) — the time at which the sample-platform heater is turned off — and the parameters \( a_1, \tau_1, \) and \( \tau_2 \) depend on the individual heat capacities and conductances shown in Figure 3-4(b). The specific heat of the sample is given by

\[
C_{\text{sample}} = \kappa \frac{a_1 \tau_1 \left(1 - \frac{C_{\text{add}}}{\kappa \tau_1}\right)^2}{1 - \frac{a_1 C_{\text{add}}}{\kappa \tau_1}},
\]

(3-7)

where \( \tau_1 \) is the time constant of the slow relaxation and \( a_1 \) its weight. \( C_{\text{add}} \) is the heat capacity of the sample platform.

In the case modeled by Figure 3-4(c), the thermal conductance of the sample is poor, leading to a temperature gradient across the sample, the so-called distributed \( \tau_2 \) effect. When the heater is turned off at \( t = 0 \) a temperature gradient develops within the sample as well as between the sample and the sample platform, where \( \kappa_{\text{sample}} \) is the thermal conductance of the sample. In this case, the temperature in the sample is taken to be constant in planes parallel to the sample-to-platform boundary and to vary only with the distance from the boundary. Though the heat-flow equation may be solved analytically in terms of \( C, \kappa_s, \) and \( \kappa' \), extraction of these parameters from the relaxation data is difficult [38, 41]. However, application of conservation of energy to the problem gives the heat capacity directly, since the total energy removed from the sample and
platform must equal the total amount of heat that flows through the thermal link. This simple reasoning leads to

\[
C \Delta T_0 = \kappa \int_0^\infty \Delta T(t) dt.
\]  
(3-8)

Since the equation is based on a fundamental principle, it can be applied to all cases regardless of the source of the poor conductance [41]. In practice, however, it should be used only when the bundled-\(r_2\)-effect model is inadequate, since the numerical integration of \(\Delta T\) is susceptible to errors due to a noise.

### 3.2 Magnetocaloric-Effect Measurements

A peak in specific heat is an unambiguous indicator of a phase transition. However, mapping out a phase diagram with specific-heat measurements requires a great amount of time. Also, the specific-heat anomaly usually becomes weak, as a phase boundary becomes flat, meaning that the temperature dependence of the transition field becomes weak as the temperature approaches zero. To supplement specific-heat measurements which suffer from these limitations, the magnetocaloric effect provides a very convenient, fast probe that works over a wide range of temperatures. Often, magnetocaloric-effect measurements are made before specific-heat measurements to make a quick survey of the phase diagram of a new magnetic material, followed by specific-heat measurements for close inspection of temperature and field regions of particular interest with a higher accuracy. Magnetocaloric-effect measurements employ the same relaxation calorimeter and ancillary electronics used in specific-heat measurements. However, the principle of magnetocaloric-effect measurements is different from specific-heat measurements, as explained below.
The magnetocaloric effect is the response of the temperature or entropy of a magnetic material to a change in the applied magnetic field. This effect finds applications in the technique of adiabatic nuclear demagnetization that provides ultralow temperatures below 10 mK, as well as in the conventional magnetic-refrigeration technology [42, 43].

When a magnetic field applied to a magnetic material placed on a thermally isolated sample platform is changed by $dH$, the platform temperature will change by

$$dT = \left( \frac{\partial T}{\partial H} \right)_S \, dH = -\left( \frac{\partial S}{\partial T} \right)_H \, dH = - \frac{T}{C_H} \left( \frac{\partial M}{\partial T} \right)_H \, dH . \quad (3-9)$$

Here, $S$ is the entropy, $M$ the magnetization, i.e., the total magnetic dipole moment of the sample. In deriving Eq. 3-9, Maxwell’s relation

$$\left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H \quad (3-10)$$

and the expression for the constant-field heat capacity

$$C_H = T \left( \frac{\partial S}{\partial T} \right)_H \quad (3-11)$$

have been used.

For the relaxation calorimeter described in Sec. 3.1.1, Eq. 3-9 does not strictly hold, since the sample platform of the calorimeter is weakly coupled to the thermal reservoir rather than thermally isolated, as depicted in Figure 3-5. Equation 3-1 again governs the heat flow through the weak link from the platform to the reservoir. On the other hand,
\[ dQ = -TdS = -T \left( \frac{\partial S}{\partial T} \right)_H dT + \left( \frac{\partial S}{\partial H} \right)_T dH \]  
(3-12)

From Eqs. 3-1 and 3-12, we obtain

\[ \kappa \Delta T = -C_H \frac{d(\Delta T)}{dt} - T \left( \frac{\partial M}{\partial T} \right)_H \frac{dH}{dt} \]  
(3-13)

for \( \Delta T \) due to the magnetocaloric effect during a field sweep at the rate \( dH/dt \). Here, Eqs. 3-10 and 3-11 have been used along with the fact that the reservoir temperature is held constant. By rearranging the terms in the above equation, the evolution of the temperature deviation is given by

\[ \Delta T + \tau \frac{d(\Delta T)}{dt} = -T \left( \frac{\partial M}{\partial T} \right)_H \frac{dH}{dt}, \]  
(3-14)

where \( \tau = C_H / \kappa \) is the thermal relaxation time of the platform.

As this equation shows, the magnetocaloric effect during a field sweep results in a temperature difference between the sample platform and the reservoir, a temperature difference whose field dependence reflects the dependence of the entropy on the magnetic field or, equivalently, the temperature dependence of the magnetization. Thus, the magnetocaloric effect is a sensitive probe of a magnetic phase transition, at which the entropy and magnetization exhibit anomalies. Furthermore, this effect can distinguish a first-order transition from a continuous transition. In practice, it is found that the sweep rate of the applied field affects the reservoir temperature, which in turn affects the sample-platform temperature. Since the reservoir is made of silver, eddy current generated by a field sweep causes heating, proportional to the square of the sweep rate. To account for the heating effects, the field must be swept both upward and
downward, and the resulting temperature variations referenced to the average background temperature.

3.3 Magnetic-Torque Measurements

Magnetic torque is another tool that allows quick detection of a magnetic phase transition, although it is often a blunt probe that does not give the precise location of the transition. To measure this quantity, we have used a capacitive cantilever magnetometer built by Timothy Murphy at the NHMFL. The measurements were made in collaboration with him. Figure 3-6 illustrates his magnetometer, comprising a 12.7 µm-thick CuBe beam (the cantilever), a fixed electrode, and a header. A thermometer and heater that read and regulate the temperature of the sample are located on the mounting stage (not shown) of the magnetometer.

The sample is attached to the cantilever with GE varnish to prevent it from falling off in response to an applied field and the gravity. The position of the sample should be close to the tip of the cantilever, as far from the fulcrum as possible, to maximize the magnetometer sensitivity, and on the symmetry line of the cantilever to minimize the effect of an unwanted torque that twists instead of bends the cantilever.

The cantilever technique was developed by Brooks et al. [44], among others. When a uniform magnetic field is applied to a magnetic sample, the direction of the sample magnetization usually differs slightly from that of the magnetic field. This will result in a torque

\[ \tau = \vec{M} \times \vec{H}, \]

where \( \vec{M} \) is the magnetization, and \( \vec{H} \) the applied field. This torque on the sample bends the cantilever, whose deflection changes the capacitance between the cantilever
and the fixed electrode [45]. For a small deflection, the capacitance change is proportional to the torque.

The misalignment of the magnetization with respect to the magnetic field, a necessary condition for torque magnetometry, can arise from a number of sources. The magnetic ions in the sample may have an anisotropic $g$ tensor or the so-called single-ion anisotropy due to spin-orbit interaction. The exchange interaction between the magnetic ions may contain a Dzyaloshinskii-Moriya term [46, 47], which is anisotropic. Even in a sample that lacks such sources of anisotropy, a non-uniform demagnetization field will cause a misalignment of the magnetization, unless the sample is an ellipsoid.

The capacitance of the cantilever magnetometer is measured with an Andeen-Hagerling 2700A automatic capacitance bridge, operated at 1 kHz with a 1 V$_{\text{rms}}$ excitation. Typical measured capacitances of the magnetometer at the NHMFL are 0.9 to 1.1 pF. Typical sensitivities range from $10^{-7}$ emu to $10^{-9}$ emu for measurements at 20 T.

### 3.4 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is used in the work reported in Chapter 5, in order to measure the spin-lattice relaxation time $T_1$ of hydrogen nuclear spins in a magnetic sample placed in a magnetic field. In this section, I will describe the principle of the spin-echo method, and its use in $T_1$ measurements and NMR spectra measurements.

Figure 3-7 is a schematic representation of the experimental geometry, in which a sample is placed inside an rf coil inserted in the bore of a superconducting magnet. The magnet produces a static magnetic field along the $z$ axis. The $z$ component of the angular momentum — loosely called the spin — of an atomic nucleus in the sample is
then quantized, with allowed values of the quantum number, $m$, ranging from $-I$ to $I$, where $I$ is the spin quantum number of the nucleus. For example, $^1$H has $I = 1/2$ so that $m$ can be either $+1/2$ or $-1/2$. When there is no applied field, the spin states of different $m$ are degenerate. In applied magnetic field $\vec{H}$, however, the Zeeman effect will split the energy of these states as shown in Figure 3-8 for $I = 1/2$, with the energy of each state given by

$$E = -\bar{\mu} \cdot \vec{H},$$

(3-16)

where $\bar{\mu}$ is the nuclear magnetic moment. This quantity is written as

$$\mu = \frac{geI}{2m_p},$$

(3-17)

where $g$ is the nuclear $g$ factor, $e$ the fundamental charge, $\hbar$ the Planck constant, and $m_p$ the proton mass. The energy is quantized according to

$$E = -m \gamma H,$$

(3-18)

where $\gamma$ is the gyromagnetic ratio $ge/2m_p$. Consequently,

$$\omega = \gamma H$$

(3-19)

is the frequency of a photon that is absorbed or emitted during a transition between the two states. This frequency is typically 1 MHz to 1 GHz, in the range of radio frequency [48]. The photons that are absorbed or stimulate an emission are produced by an rf coil shown in Figure 3-7. This coil also detects the photons emitted by the nuclear spins. Macroscopically, the detection occurs as an induced emf across the coil due to precession of nuclear magnetization around the $z$ axis, the direction of the applied magnetic field $H$. 

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The dynamics of nuclear spins in a sample are characterized by two relaxation times, the spin-lattice relaxation time $T_1$ and the spin-spin relaxation time $T_2$. The spin-lattice relaxation is a longitudinal magnetic relaxation, the recovery of the longitudinal component of the nuclear magnetization, $M_z$, to equilibrium after tipping of the nuclear spins by an rf pulse. $T_1$ characterizes this relaxation as

$$M_z(t) = M_z(0)(1 - e^{-t/T_1}).$$

(3-22)

The spin-spin relaxation, on the other hand, is a transverse magnetic relaxation of the $xy$ component of the nuclear magnetization, $M_{xy}$. $T_2$ characterizes this process as

$$M_{xy}(t) = M_{xy}(0)(1 - e^{-t/T_2}).$$

(3-23)

in a frame rotating around the $z$ axis at frequency $\omega$ given by Eq. 3-21.

The transverse relaxation is caused by interactions between nuclear spins as well as by an inhomogeneity of the static field $H$ providing slightly different precession frequencies to local nuclear magnetizations in different parts of the sample. To remove this second, uninteresting effect, the spin-echo method is used. Figure 3-9 explains this method [49]. First, a $90^\circ$ pulse tips the nuclear spins in the sample by $90^\circ$ into the $xy$ plane, in the rotating frame. Immediately after this pulse, all spins point in the same direction in the $xy$ plane, but after a while their directions in the rotating frame will spread out because a slight inhomogeneity in $H$ causes the spins in different parts of the sample to precess at different rates. The $180^\circ$ pulse, applied at time $\tau$ after the $90^\circ$ pulse, flips all the spins by $180^\circ$ in the rotating frame. This flipping places slower spins ahead of faster spins, causing all the spins to line up once again in the $xy$ plane at time $2\tau$. At this point, all the spins precess in phase in the laboratory frame, inducing an rf
emf across the coil that has generated the tipping pulses. This signal is the spin echo.

The intensity of the spin-echo signal plotted against $2\tau$ decays only with intrinsic $T_2$ due to time-dependent fluctuating random fields arising from interactions between nuclear spins, not with a shortened time constant that includes the uninteresting effect of the inhomogeneous magnetic field.

Spin echoes are not only used for $T_2$ measurements. Since an echo signal appears with a delay after the last rf pulse, it does not suffer from a slow recovery of the amplifier after a pulse, unlike a free-induction signal which immediately follows an rf pulse. For this reason, spin echoes are widely used for NMR spectra measurements as well as $T_1$ measurements.

Figure 3-10 shows the basic pulse sequence for $T_1$ measurements with the spin-echo technique [48]. First, several 90° pulses are applied in order to saturate $M_z(0)$ of all spins to zero. After a delay, $t_R$, the recovery of $M_z$ is monitored by a 90°-180° pulse pair that produce a spin echo, whose intensity is proportional to the recovering $M_z$. The sequence is repeated many times, by varying $t_R$ while holding $\tau$ constant, and $T_1$ is determined from the recovering intensity of the spin echo as a function of $t_R$. In our experiment, to be described in Chapter 5, $t_R$ ranged from 10 µs to 10 s, and $\tau$ was 45 µs.
Figure 3-1. $^3$He/$^4$He dilution refrigerator at the NHMFL Millikelvin Laboratory.
Figure 3-2. Calorimeter for specific-heat and magnetocaloric-effect measurements. The bottom view shows the sample platform made of a thin sapphire disk at center, attached to the silver ring via the leads for the heater and thermometer on it. The photograph to the right shows the actual calorimeter, with the vacuum can removed. Adapted from Ref. [36].
Figure 3-3. Schematic of the calorimeter electronics setup for the specific-heat and magnetocaloric-effect measurements. A Wheatstone bridge is used to measure the resistance of the sample-platform thermometer. Data is obtained by a data acquisition board (DAQ) on a computer. Via a GP-IB bus, the computer also controls the current sources for the block and platform heaters and for the block thermometer, and reads the voltage across the block thermometer.
Figure 3-4. Models for the analysis of a relaxation of the platform temperature in a specific-heat measurement [50]. (a) Simple one-dimensional heat-flow model with only one relaxation time. (b) Model for the lumped $\tau_2$ effects, with two relaxation times, $\tau_1$ and $\tau_2$, arising from a poor thermal contact between the sample and the platform, represented by the limited thermal conductance $\kappa'$ in series with the thermal conductance $\kappa$ of the weak link between the platform and the reservoir. (c) Model for the distributed $\tau_2$ effects. The two time constants in this case arise from the limited thermal conductance of the sample. [Adapted from Sherline, T.E. 2006. Antiferromagnetism in cesium Tetrabromocuprate(II) and Body-Centered-Cubic Solid Helium Three. Ph.D. dissertation (Page 23, Figure 2.4). University of Florida, Gainesville, Florida.]

Figure 3-5. Illustration of the principle of the magnetocaloric effect due to a field sweep [50]. When the magnetic field on a sample is changed by $dH$ over an infinitesimal time $dt$, the temperature of the sample changes by $d(\Delta T)$. [Adapted from Sherline, T.E. 2006. Antiferromagnetism in cesium Tetrabromocuprate(II) and Body-Centered-Cubic Solid Helium Three. Ph.D. dissertation (Page 30, Figure 2.6). University of Florida, Gainesville, Florida.]
Figure 3-6. Schematic view of the cantilever magnetometer. A sample (a) is glued with GE varnish on the flexible CuBe beam (b). The beam is separated from the fixed electrode (c), which is embedded in the base plate (d), by the spacer (e). As explained in the text, when the magnetization ($M$) of the sample is misaligned with respect to the external magnetic field ($H$), a magnetic torque ($\tau$) is exerted on the sample, bending the cantilever beam and thus leading to a change in the capacitance between b and c.
Figure 3-7. Schematic arrangement for NMR.

Figure 3-8. Energy diagram of a nuclear spin \((I = 1/2)\) in an applied field \(H\). The energy difference \(\Delta E\) between the two spin states is proportional to \(H\) and the gyromagnetic ratio \(\gamma\) of the spin.
Figure 3-9. Principle of the spin-echo technique. The precession of magnetization, shown with arrows, is depicted in the rotating frame. (a) At $t = 0$, the equilibrium magnetization points in the $z$ direction parallel to the applied field $H$. (b) A 90° pulse brings the magnetization to the $xy$ plane. (c) Magnetizations at different parts of the sample rotate at slightly different rates due to an inhomogeneity of the applied field, causing the magnetizations to spread out in the rotating frame. (d) This spreading becomes more extensive with passing time. (e) A 180° pulse along the $x$ axis flips the magnetizations by 180°, reversing their order. (f) Finally, a faster magnetization catches up with a slower magnetization, so that all magnetizations become once again in phase and produce an induced emf (the spin echo) across the rf coil.
Figure 3-10. NMR pulse sequence for $T_1$ measurements. Five 90° pulses (only two are shown for clarity) saturate the magnetization, followed by a 90°-180° pulse pair that monitors magnetization recovery by spin echo. $t_R$, known as a recovery time, is varied whereas $\tau$ — the time between the 90° and 180° pulses for the spin echo — is fixed. Free-induction-decay signals immediately after the 90° pulses have been omitted for clarity.
4.1 Basic Properties of Cr(diethylenetriamine)(O$_2$)$_2$·H$_2$O

At a classical critical point, of a continuous phase transition occurring at a non-zero temperature, only the spatial extent of order-parameter fluctuations diverges [51]. In contrast, the divergence occurs both spatially and temporally at a QCP, inextricably linking dynamic and static properties [52, 53]. A spectacular demonstration of this linkage is the quantum annealing — the quantum-fluctuation-driven relaxation of quenched disorder — of an Ising spin glass near its QCP, a phenomenon with broad implications in efficient algorithms for solving optimization problems in circuit designs and logistics [54, 55]. Despite the importance of the dynamics of quantum fluctuations near QCPs, experimental studies of such dynamics have been scarce, largely limited to inelastic neutron scattering to which not all materials that possess QCPs are amenable.

In our work, we have observed heat release from hydrogen nuclear spins caused by the quantum fluctuations of Cr$^{4+}$ ionic spins near the magnetic-field-driven QCP. This phenomenon opens up a unique avenue to investigate the dynamics of quantum fluctuations that underlie quantum criticality.

For this study, we have chosen the inorganic coordination compound Cr(diethylenetriamine)(O$_2$)$_2$·H$_2$O, hereafter referred to as Cr(dien), because it contains a large number of hydrogen nuclear spins [4, 56]. Cr(diethylenetriamine)(O$_2$)$_2$, the key building block of this compound, is an oblate, elongated disk-shaped molecule, in which Cr$^{4+}$ is located on the mirror-symmetry plane, as shown in Figure 4-1. In the monoclinic crystal structure of Cr(dien), also shown in Figure 4-1, the $S = 1$ spins of Cr$^{4+}$ form a square lattice parallel to the crystallographic $ac$ plane, with an exchange energy $J$ of
2.71–2.88 K according to magnetic susceptibility at temperatures between 1.8 K and 300 K \cite{4}. The spins order antiferromagnetically at $T_N = 2.55$ K in zero magnetic field \cite{4}. Application of a high magnetic field depresses the ordering temperature, driving it to zero at a critical field, which we have found to be $12.392 \pm 0.003$ T. Heat release from hydrogen nuclear spins occurs near this QCP.

4.2 Experimental

The single-crystal sample of Cr(dien), shown in Figure 4-2, was grown by Narpinder Kaur at the Chemistry Department of Florida State University, by chemical synthesis in an ice bath, followed by slow evaporation of water, as described in Ref. \cite{4}. The crystal weighed 1.02 mg.

The experiment, done primarily at the NHMFL in Tallahassee, used the relaxation calorimeter described in section 3.1.1. In this calorimeter, the sample temperature can be raised with the heater with ease and allowed to drop rapidly to the reservoir temperature by turning off the heater. Heat released in the sample, if any, can be readily detected as a spontaneous temperature difference between the sample and the reservoir. The calorimeter was inserted in the mixing chamber of a top-loading dilution refrigerator equipped with a 20-tesla superconducting magnet.

4.2.1 Specific Heat and Magnetocaloric Effect

Prior to heat-release measurements, we first determined the magnetic phase diagram of Cr(dien) by means of specific-heat and magnetocaloric-effect measurements

\footnote{The values of $J$ differ from those given in Ref. \cite{4} by a factor of 2, because we write — unlike the authors of that reference — the spin hamiltonian as

$$H = J \sum_{<i,j>} \vec{S}_i \cdot \vec{S}_j$$

where each nearest-neighbor spin pair $\langle i,j \rangle$ appears only once in the sum.}
at temperatures ranging from 0.2 K to 3 K in magnetic fields up to 12.5 T. To minimize the addenda heat capacity, the sample was directly glued on the calorimeter platform with Wakefield compound. The field was applied parallel to the crystallographic $b$ axis, perpendicular to the $ac$ plane of the monoclinic crystal. For the magnetocaloric-effect measurements, the magnetic field was swept at the rate of 0.2 T/min.

### 4.2.2 Heat Release from Proton Spins near the QCP

Figure 4-3 describes the procedure of the experiment. First, the sample is heated from the thermal-reservoir temperature, $T_0$, to temperature $T_q$ ranging from 266 mK to 1.52 K, in magnetic field $H_q$ parallel to the $b$ axis, the same direction as in the specific-heat and magnetocaloric-effect measurements. After 1.4 min at $T_q$, the sample is rapidly cooled back to $T_0$ in 1.8 s by turning off the heater. This temperature quenching leaves the hydrogen nuclear spins, the proton spins, frozen in a high-energy nonequilibrium state corresponding to $T_q$. Subsequently, the magnetic field is swept at 0.2 T/min or 0.1 T/min through the critical field, while the temperature difference $\Delta T$ between the sample and the thermal reservoir is continuously measured to detect heat release from the proton spins. The field sweeps were made at four different $T_0$ ranging from 96 mK to 261 mK. Each sweep was immediately repeated, and $\Delta T$ of the second sweep — in which heat release from the proton spins no more occurs — was subtracted from $\Delta T$ of the first sweep in order to remove uninteresting contributions of the magnetocaloric effect (at most 1.1 mK) and eddy-current heating (3 mK at $T_0 = 96$ mK and 8 mK at $T_0 = 181$ mK).

We have also measured the relaxation time $\tau$ of the proton spins during the heat release. This was done by stopping the field sweep in the middle, at field $H$, and recording the subsequent relaxation of the sample temperature toward $T_0$. Again, the
sweep was immediately repeated to the same field, and the ensuing relaxation of $\Delta T$
from the magnetocaloric effect and eddy-current heating alone was recorded and
subtracted from the data. The measurements were carried out only at $T_0 = 181$ mK, after
the sample had been quenched from $T_q = 796$ mK at $H_q = 13.5$ T or from $T_q = 761$ mK at
$H_q = 10$ T. $\tau$ measured in this manner is approximately $T_1 + C_n/\kappa$ [57], where $T_1$ is the
nuclear spin-lattice relaxation time and $C_n$ the nuclear heat capacity. At 181 mK, where
the measurements were made, $C_n/\kappa = 11.1$ s at 12.1 T.

4.3 Analysis of the Results

4.3.1 Specific Heat and Magnetocaloric Effect

Figure 4-4 shows the result of specific-heat measurements. Peaks indicate an
antiferromagnetic transition. As the magnetic field is raised, both the transition
temperature and peak height decreases. Above 12 T, the peak becomes too small to
detect. To overcome this limitation, we made magnetocaloric-effect measurements from
10.5 T to 12.5 T.

As described in section 3.2, the magnetocaloric effect is a sensitive, convenient
tool for detecting a magnetic phase transition. However, it is usually unclear which
feature of a $\Delta T$ curve during a field sweep stands for a transition, if the transition is
continuous as opposed to first-order. This ambiguity in the exact location of a
continuous magnetic transition is a problem common to all techniques that measure,
directly or indirectly, a magnetization. As in those cases, one needs to rely on specific-
heat results as a guide in choosing the correct feature. In the $\Delta T$ curves for Cr(dien), a
peak or a dip appears depending on whether the field is swept upward or downward, as
shown in Figure 4-5. It turns out that the average temperature and field of these two
features in a pair of curves for upward and downward field sweeps for a fixed reservoir temperature give the correct transition point.

From the specific-heat and magnetocaloric-effect data, we have determined the magnetic phase diagram of Cr(dien) in terms of magnetic field and temperature, as shown in Figure 4-6. If Cr(dien) is a Heisenberg antiferromagnet, then the boundary of the ordered phase should obey a power law, Eq. 2-27, with the critical exponent \( \alpha = 3/2 \). Fitting the data up to 0.838 K, we obtain \( H_c = 12.392 \pm 0.003 \) T with \( \alpha = 2.01 \pm 0.02 \). This exponent is in close agreement with \( \alpha = 2 \) predicted for the 3D Ising universality class [2], ruling out a BEC of magnons in Cr(dien). To identify the origin of the Ising anisotropy in this compound, further studies are required.

4.3.2 Heat Release from Proton Spins near the QCP

Figures 4-7 shows the temperature difference \( \Delta T \) between the sample and the thermal reservoir during field sweeps through the critical field \( H_c \), when the thermal reservoir was held at \( T_0 = 181 \) or 96 mK. Curves obtained at \( T_0 = 261 \) and 219 mK are shown in Figure 4-8. As the field approaches \( H_c \), heat is released in the sample, manifesting itself as a pronounced peak in \( \Delta T \). The heat release occurred only during the first field sweep after the temperature quenching of the sample from \( T_q \), not during subsequent sweeps.

The amount of released heat \( Q \) is obtained from the data via

\[
Q = \int \kappa \Delta T dH / \dot{H},
\]  

where \( \kappa \) is the thermal conductance of the weak link between the sample and the thermal reservoir, and \( \dot{H} \) the field-sweep rate. As shown in Figure 4-9, \( Q \) depends on
both \( T_q \) and \( H_q \). These dependences indicate unambiguously that the heat is indeed released from the proton spins, as the following analysis shows.

The energy of nuclear spins per mole at temperature \( T \) in magnetic field \( H \) is

\[
U(T, H) = -Ra \frac{H^2}{T},
\]

(4-2)

where the constant \( a \) is

\[
a = \frac{(h\gamma)^2 I(I + 1)}{3k_B^2}.
\]

(4-3)

\( R \) is the gas constant, and \( k_B \) the Boltzmann constant. For the proton, \( I = 1/2 \). In the second step of the experiment, the sample is cooled rapidly in magnetic field \( H_q \) from temperature \( T_q \), at which the proton spins are thermalized with the lattice, to \( T_0 \), at which the nuclear spin-lattice relaxation time is long. This causes the proton spins to freeze in a non-equilibrium state determined by \( T_q \). At this point, the energy of the proton spins is \( U(T_q, H_q) \). In the third step, where the magnetic field is swept to \( H \), the energy changes to \( U(T_qH/H_q, H_q) \) because the entropy of the proton spins stays constant and, as a result, the temperature that characterizes the non-equilibrium state of the proton spins changes from \( T_q \) to \( T_qH/H_q \). (Note that the entropy of nuclear spins is a function of only \( H/T \).) If this field is close to the QCP, then rapidly fluctuating dipolar fields and transferred hyperfine fields due to quantum fluctuations of the \( \text{Cr}^{4+} \) spins will cause the proton spins to thermalize with the lattice. The heat released by the proton spins to the lattice will be then

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\[ Q = U(T_q H / H_q, H) - U(T_0, H) \]
\[ = RaH^2 \left( - \frac{H_q}{HT_q} + \frac{1}{T_0} \right) \]
\[ = R \left( \frac{h \gamma}{k_B} \right)^2 \frac{I(I+1)}{3} \left( \frac{H}{T_0} - \frac{H_q}{T_q} \right) H. \]

(4-4)

In \( n \) moles of sample, if the number of proton spins that participate in such heat release is \( n_H \) per formula unit, then Eq. 4-4 must be multiplied by \( n_H n \):

\[ Q = n_H n R \left( \frac{h \gamma}{k_B} \right)^2 \frac{I(I+1)}{3} \left( \frac{H}{T_0} - \frac{H_q}{T_q} \right) H. \]

(4-5)

At \( T_0 = 261 \) and 219 mK, the temperatures of the data shown in Figure 4-8, the agreement between the amount of released heat and Eq. 4-5 is poor, suggesting that the proton spins had partly equilibrated with the lattice before the field sweeps. For \( T_0 = 181 \) mK, good agreement between experiment and Eq. 4-5 is obtained with \( n_H = 10 \), as shown in Figure 4-9(a), except for a few points for which \( H_q \) is 18 T or 16 T. For those points, 1.4 min of waiting was probably insufficient to thermalize the proton spins at \( T_q \).

At \( T_0 = 96 \) mK, the peak that appears at 12.76 T in Figure 4-7(b) during the downward field sweeps from 13.5 T is very sharp while \( \Delta T > 36 \) mK, \( i.e., \) while the sample temperature \( T_0 + \Delta T \) is higher than 132 mK. This indicates that proton spins whose relaxation times \( \tau \) are too short when \( T_0 > 132 \) mK now participated in heat release.

When \( T_0 = 181 \) mK, they had evidently reached thermal equilibrium with the lattice before each field sweep started and therefore did not participate in heat release. As shown in Figure 4-9(b), good agreement between Eq. 4-5 and the \( T_0 = 96 \) mK data for \( H_q = 13.5 \) T is obtained with \( n_H = 15 \), of which five whose \( \tau \) are very short at \( T_0 > 132 \) mK are assumed to freeze at a high-energy nonequilibrium state at 132 mK instead of at \( T_q \).
Evidently, those five proton spins do not participate in heat release even at $T_0 = 96$ mK when quenched at $H_q = 10$ T, in the antiferromagnetic phase.

Cr(dien) contains fifteen hydrogen atoms per formula unit, as shown in Figure 4-1(b). Among the thirteen in the Cr(diethylenetriamine)(O$_2$)$_2$ molecule, the five bonded to nitrogens are closer to the Cr$^{4+}$ ion than eight that are bonded to carbons. The five hydrogens bonded to the nitrogens are located at 2.40 – 2.52 Å from the Cr$^{4+}$, whereas the eight that are bonded to the carbons fall into two groups of four, each at 3.08 – 3.29 Å and 3.77 – 3.79 Å from the Cr$^{4+}$. The water hydrogens are at 3.29 and 3.48 Å from the closest Cr$^{4+}$ ions. It is very likely that the five proton spins with short nuclear-spin $\tau$ are of the hydrogens bonded to the nitrogens and thus experience stronger fluctuating dipolar field and transferred hyperfine field of the Cr$^{4+}$ ion, whereas the ten proton spins with longer $\tau$ are of the eight hydrogens bonded to the carbons and the two in the water molecule.

The temperatures and fields of the peaks in Figures 4-7 and 4-8 are shown in the diagram given in Figure 4-10, along with the phase boundary between the highly polarized antiferromagnetic phase and similarly highly polarized paramagnetic phase. Since the peak position depends slightly on the quenching conditions, $T_q$ and $H_q$, the peaks chosen for the figure are for similar $T_q$ and $H_q$ as much as possible for consistency, as listed in Table 4-1. This diagram suggests that the loci of the peaks converge on the QCP in the zero-temperature limit. These loci delimit the region in which $\tau$ is shorter than the timescale of the experiment, a quantum critical region.
Figure 4-11 shows the relaxation of $\Delta T$ at $T_0 = 181$ mK at various $H$. Six of the eleven curves exhibit exponential relaxation whereas five exhibit stretched exponential relaxation:

$$\Delta T(t) = \Delta T(0)e^{-(t/\tau)^v},$$

where $t$ is time. The stretching exponent $v$ ranges from 0.61 to 0.78.

The relaxation rate $1/\tau$ diverges as the field approaches $H_c$, as shown in Figure 4-12, indicating that divergent quantum fluctuations of the Cr$^{4+}$ spins near the QCP drive the relaxation of the nuclear spins. The divergence is asymmetric around $H_c$, faster for $H > H_c$ than for $H < H_c$. This asymmetry is also seen in Figure 4-10 as a wider quantum critical region for $H > H_c$ than for $H < H_c$.

The amount of heat released during the relaxation measurements is shown as a function of $|H-H_c|$ in Figure 4-13. The result indicates that the ten proton spins that release heat at $T_0 = 181$ mK contain two groups, each comprising four to six spins per formula unit. Above $H_c$, one group relaxes at $|H-H_c|$ of about 0.8 T, whereas the other group relaxes at fields closer to $H_c$. Similarly, below $H_c$, the first group relaxes at $|H-H_c|$ of about 0.6 T, whereas the second group relaxes at fields closer to $H_c$. The result is consistent with the molecular structure of Cr(diethylenetriamine)(O$_2$)$_2$ shown in Figure 4-1(b): the eight hydrogens bonded to the four carbons — with longer proton-spin $\tau$ — fall into two groups, each consisting of four hydrogens, with distinct ranges of distances from the Cr$^{4+}$.

4.4 Discussion

Our results provide unambiguous evidence that temperature quenching of Cr(dien) leaves the proton spins frozen in a high-energy nonequilibrium state and, as the
magnetic field is then brought close to the QCP, quantum fluctuations of the $\text{Cr}^{4+}$ ionic spins quickly anneal them to reach thermal equilibrium with the lattice. These results imply that the quantum-fluctuation-driven heat release from nuclear spins is a generic phenomenon to be found near a variety of QCP.

Because of the inextricable link between dynamic and static properties in quantum criticality, quantum-critical systems are predicted to exhibit interesting, non-trivial relaxation phenomena during and after a sweep of a control parameter such as magnetic field and pressure through a QCP [58] and also after temperature quenching near the QCP [59]. Our results warn, however, that the response of nuclear spins — which are nearly ubiquitous — to those changing parameters and to quantum fluctuations must be carefully taken into account in real solids. At the same time, heat release from nuclear spins promises to be a useful probe for the dynamics of quantum fluctuations that underlie quantum criticality in a variety of systems.
Figure 4-1. Crystal structure and basic unit of Cr(diethylenetriamine)(O$_2$)$_2$ and H$_2$O molecules. (a) (top panel) Crystal structure of Cr(dien), with H$_2$O molecules and H atoms omitted for clarity [60]. The blue arrows indicate nearest-neighbor distances between Cr$^{4+}$ ions, 5.64 Å on average, within a square-lattice layer. The interlayer spacing is approximately 6.9 Å. (b) (bottom panel) Basic unit of the crystal: a pair of Cr(diethylenetriamine)(O$_2$)$_2$ and H$_2$O molecules. Yellow is Cr, red O, blue N, black C, and gray H. Drawn by Ronald Clark. [Top panel reprinted with permission from Ramsey, C.M. 2004. Thermo-magnetic and EPR Probing of Magnetism in Low-Dimensional Lattices and Single-Molecule Magnets. Ph.D. dissertation (Page 77, Figure 5.3). Florida State University, Tallahassee, Florida.]
Figure 4-2. Image of the Cr(dien) sample.

Figure 4-3. Procedure of the heat-release experiment. The sample is heated from point $P_1$ to $P_2$ in the nearly completely polarized paramagnetic phase, or from $P_1'$ to $P_2'$ in the antiferromagnetic phase, whose boundary (broken line) terminates in a QCP at $T = 0$. After rapid temperature quenching, the magnetic field is swept through the critical field, and the evolution of the sample temperature is recorded.
Figure 4-4. Specific heat as a function of temperature at different magnetic fields [5]. Peaks indicate clearly the transition at fields between 0 T and 11.5 T. At 12 T, the peak is barely visible. Magnetocaloric-effect measurements were used at high fields, where specific-heat peaks are small or barely visible. [Adapted from Kaur, N. 2010. Magnetic and Thermodynamics Studies on Spin 1 Compounds. Ph.D. dissertation (Page 89, Figure 5.11). Florida State University, Tallahassee, Florida.]
Figure 4-5. Magnetocaloric-effect curves of Cr(dien) at different reservoir temperatures [5]. Red and blue curves represent, respectively, the sample temperature during upward and downward field sweeps. Specific-heat measurements guarantee that the peaks and dips in the curves are transitions. [Adapted from Kaur, N. 2010. Magnetic and Thermodynamics Studies on Spin 1 Compounds. Ph.D. dissertation (Page 86, Figure 5.10). Florida State University, Tallahassee, Florida.]
Figure 4-6. Magnetic phase diagram of Cr(dien), determined by specific-heat and magnetocaloric-effect measurements [5]. The critical field, $H_c$, is $12.392 \pm 0.003$ T. [Adapted from Kaur, N. 2010. Magnetic and Thermodynamics Studies on Spin 1 Compounds. Ph.D. dissertation (Page 95, Figure 5.17). Florida State University, Tallahassee, Florida.]
Figure 4-7. Temperature difference $\Delta T$ between the sample and the thermal reservoir as a function of the magnetic field during field sweeps. (a) The thermal reservoir was held at 181 mK, as the field was swept at 0.2 T/min. Temperature $T_q$ from which the sample has been quenched ranges from 266 mK to 1.52 K. The quenching fields were 6 T (black), 9 T (purple), 11.5 T (green), 13.5 T (orange), 16 T (magenta), and 18 T (red). (b) The thermal reservoir was held at 96 mK, as the field was swept at 0.1 T/min. $T_q$ ranged from 300 mK to 797 mK. The quenching fields were 10 T (blue) and 13.5 T (red). In both frames, the peaks to the right were observed during downward field sweeps and those to the left during upward sweeps. The critical field, $H_c$, is $12.392 \pm 0.003$ T, as shown in Figure 4-6.
Figure 4-8. Temperature difference $\Delta T$ between the sample and the thermal reservoir during field sweeps at 0.1 T/min. For (a), the thermal reservoir was held at $T_0 = 261$ mK during the field sweeps as well as during temperature quenching of the sample. Blue and green: upward field sweeps after temperature quenching from $T_q = 764$ mK (blue) and 1.01 K (green) at $H_q = 10.5$ T; red: downward field sweep after temperature quenching from $T_q = 796$ mK at $H_q = 13.5$ T. For (b), the thermal reservoir is held at $T_0 = 219$ mK. Blue: upward field sweep after temperature quenching from $T_q = 1.00$ K at $H_q = 10$ T; red: downward field sweep after temperature quenching from $T_q = 1.04$ K at $H_q = 13.5$ T.
Figure 4-9. Amount of heat released at (a) 181 mK and (b) 96 mK as a function of $T_q$, the temperature from which the sample was rapidly quenched. In (a), the sample was quenched at 6 T (black), 9 T (purple), 11.5 T (green), 13.5 T (orange), 16 T (magenta), and 18 T (red). The lines represent Eq. 4-5 with $n_H = 10$, each corresponding to the data points of the same color. In (b), the sample was quenched at 10 T (blue) and 13.5 T (red). The lines of corresponding colors represent Eq. 4-5. $n_H = 10$ for the 10 T line; $n_H = 15$, of which five are assumed to freeze only at 132 mK, for the 13.5 T line.
Figure 4-10. Magnetic fields and temperatures of the peaks in the $\Delta T$ curves (squares), marking a quantum critical region of Cr(dien) delimited by two straight lines through the data points. Solid squares are for peaks at a sweep rate of 0.1 T/min, open squares at 0.2 T/min. Circles represent the phase boundary — detected by the magnetocaloric effect — between the antiferromagnetic (AF) and nearly completely polarized paramagnetic (P) phases, with the broken line from a power-law fit of data points up to 0.84 K.
Figure 4-11. Relaxation of $\Delta T$, the temperature difference between the sample and the thermal reservoir, after a field sweep at 0.1 T/min is stopped at $t = 0$. The reservoir is held at $T_0 = 181$ mK. The sample has been prepared by temperature quenching (a) from $T_q = 796$ mK at $H_q = 13.5$ T and (b) from $T_q = 761$ mK at $H_q = 10$ T. In (a), the curves were taken at 13.1 T, 13.0 T, 12.9 T, 12.85 T, 12.8 T, and 12.7 T (from top to bottom), after a downward field sweep from $H_q$ toward $H_c = 12.392 \pm 0.003$ T stopped. In (b), the fields at which the curves were taken are 12.1 T, 12.0 T, 11.9 T, 11.8 T, and 11.7 T (from top to bottom), after an upward field sweep from $H_q$ toward $H_c$ stopped. For clarity, successive curves have been shifted by 1 mK.
Figure 4-12. Relaxation rate $1/\tau$ vs. the field at which field sweep was stopped. Solid symbols are data from curves showing exponential relaxation, and open symbols from curves showing stretched-exponential relaxation. Lines are guides to the eye.

Figure 4-13. Amount of heat released vs. the field at which field sweep was stopped. Horizontal lines indicate the amounts of heat released during complete field sweeps through $H_c$. Blue and red squares are for $T_q = 761$ mK at $H_q = 10$ T and $T_q = 796$ mK at $H_q = 13.5$ T, respectively.
Table 4-1. $T_0$, $T_q$, and $H_q$ of the data points demarcating a quantum critical region in the $H$-$T$ diagram shown in Figure 4-10.

<table>
<thead>
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<th>$T_0$ (mK)</th>
<th>$T_q$ (K)</th>
<th>$H_q$ (T)</th>
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CHAPTER 5
PROTON NMR IN THE S=1 SQUARE-LATTICE ANTIFERROMAGNET
Cr(DIETHYLENETRIAMINE)(O2)2·H2O NEAR THE QUANTUM CRITICAL POINT

5.1 Motivation

In Chapter 4, we studied heat release from proton spins in temperature-quenched Cr(dien) near the QCP between the antiferromagnetically ordered phase and the fully polarized state. This study provided insight to quantum fluctuations of the Cr\(^{4+}\) spins, demarcating a quantum critical region near the QCP. However, our calorimetric method involving a field sweep could not measure a proton-spin relaxation time shorter than about 27 s. This limited our studies to a magnetic-field region at least 0.2 T away from the QCP. To investigate the spin dynamics of Cr\(^{4+}\) at magnetic fields closer to the QCP, a region in which the protons relax faster, we have used proton NMR, which directly probes the proton spins and is able to measure fast proton-spin relaxation.

The experiment was done at the NHMFL with Tiglet Basala, Phillip Kuhns, and Arneil Reyes, at temperatures between 1.35 K and 300 mK in a \(^3\)He cryostat with a 17 T superconducting magnet. Using a spin-echo technique at frequencies between 511.0 MHz and 540.7 MHz, we have primarily focused on measuring \(T_1\) in a very narrow field range around the QCP, 12.0 T – 12.7 T. In addition, we have taken NMR spectra in this field range, as well as at 11.0 T, partly to study the effect of magnetic ordering on NMR peak positions. In all measurements, the magnetic field was applied parallel to the crystallographic \(b\) axis, the same as in all the experiments described in Chapter 4.

5.2 Results and Discussions

5.2.1 Field Sweeps

We first took proton NMR spectra of Cr(dien) at 1.30 K, in the nearly completely polarized paramagnetic phase, by sweeping the magnetic field at several fixed
frequencies. The field was swept upward, typically over a 0.4 T wide range, at a rate of 0.25 T/min to ensure thermal equilibrium. We observed six peaks as shown in Figure 5-1, which shows the spin-echo intensity at 540.7 MHz as a function of the field.

As described in section 4.3.2, in Cr(dien) there are thirteen hydrogen sites contained in a Cr(diethylenetriamine)(O$_2$)$_2$ molecule and two sites in a water molecule. Within the Cr(diethylenetriamine)(O$_2$)$_2$ molecule, the distances to the hydrogen sites from Cr$^{4+}$ are 2.40 Å – 2.52 Å to the five hydrogen sites (H2, H1C, H1D, H3C, and H3D) attached to the three nitrogen atoms and 3.08 Å – 3.79 Å to the eight hydrogen sites attached to the four carbon atoms. (Ref. [4] for the labeling of the hydrogen sites.) The water hydrogen sites are at 3.29 Å and 3.48 Å from the closest Cr$^{4+}$. The hydrogen sites attached to the nitrogen atoms are much closer to Cr$^{4+}$ than are all the other hydrogen sites, and thus experience the strongest dipolar fields and transferred hyperfine fields. For our magnetic-field direction, $H||b$, the dipolar field of the Cr$^{4+}$ spin at H2 attached to the middle nitrogen raises the total field, whereas the dipolar fields on the four sites attached to the two corner nitrogen atoms lower the total fields. As a result, the small isolated peak in Figure 5-1, appearing at the lowest field, comes from H2, and the peak at the highest field probably comes from the four hydrogen sites attached to the corner nitrogen atoms.

To assign peaks to the water hydrogen sites and the hydrogen sites attached to carbon atoms, at larger distances from the nearest Cr$^{4+}$, we need to consider the contribution of more than one Cr$^{4+}$ spin to the dipolar fields. Our calculations of the dipolar fields due to all Cr$^{4+}$ spins that are within 12 Å of each hydrogen site suggest that the small peak at the second lowest field in Figure 5-1 comes from one of the water
hydrogen sites (H5B) and one of the two hydrogen sites (H4A) attached to one of the two corner carbon atoms, the third peak from the left comes from the remaining water hydrogen (H5A) and two of the hydrogen sites (H2A and H3B) attached to two non-corner carbon atoms, the second tallest peak comes from three hydrogen sites (H1A, H1B, and H4B) attached to the two corner carbon atoms, and the tallest peak comes from the two remaining hydrogen sites (H2B and H3A). In these peak assignments, we have ignored transferred hyperfine fields, whose computation is beyond the scope of this dissertation.

5.2.2 Frequency Sweeps

In NMR spectra taken with the field-sweep technique, different points in the spectra correspond to different points in the magnetic phase diagram. To examine the effect of magnetic ordering on the NMR spectra, a frequency-sweep technique in which the magnetic field is fixed is therefore superior, although it requires frequent tuning of the tank circuit for the rf coil and thus takes longer to perform. We have taken frequency-sweep spectra at 12.7 T and 11.0 T, as shown in Figures 5-2 and 5-3, which present integrated spin-echo signals as well as summed-up fast Fourier transforms (FFTs) of the signals. At 12.7 T, the frequency was changed in 0.1 MHz steps, which were decreased to 0.05 MHz at 11.0 T.

At 12.7 T, above $H_c$ and thus in the nearly completely polarized paramagnetic phase, the spectra were taken at 1.30 K and 0.36 K. The 1.30 K spectra agree very well with the field-sweep spectra, Figure 5-1, taken at the same temperature. Moreover, the spectral shape and widths show no change upon cooling to 0.36 K, as expected for a nearly completely polarized paramagnetic phase.
At 11.0 T, the spectra were taken at three temperatures — 2.50 K, 1.55 K, and 0.50 K — corresponding to the paramagnetic phase, near the phase boundary, and the antiferromagnetically ordered phase, respectively. To facilitate better comparison of the spectra at the three temperatures, Figure 5-4 shows each spectra scaled with the area under the curve. Comparison of the sweeps at 0.50 K and 2.50 K reveals that all the peaks in the paramagnetic phase split in two in the ordered phase, as marked in Figure 5-3, except the small isolated peak at the highest frequency. (We will call this peak, which does not split, the baby peak.) This splitting indicates that the Cr$^{4+}$ spins in the ordered phase have two orientations, as expected for a square-lattice antiferromagnet, in which spins form two magnetic sublattices, one with the spins tilted slightly to the “left” and the other with the spins tilted slightly to the “right” with respect to the magnetic field.

Why does the baby peak remain unsplit in the ordered phase? Because this peak comes from a single proton site and because that site, attached to the middle nitrogen of the Cr(diethylenetriamine)(O$_2$)$_2$ molecule and thus the closest (2.40 Å) to Cr$^{4+}$, is dominated by the dipolar field produced by just one Cr$^{4+}$ spin. Moreover, along our field direction, $H || b$, this site happens to be almost directly above or below the Cr$^{4+}$. Consequently, the dipolar field there does not depend, to the first order, on the direction to which the Cr$^{4+}$ spin tilts in the antiferromagnetically ordered phase and thus to which of the two sublattices the Cr$^{4+}$ spin belongs.

Incidentally, except for the effect of the dipolar field and transferred hyperfine field of the Cr$^{4+}$ ions, the NMR peak heights should obey Curie’s law for the proton spins and, as a result, should be inversely proportional to temperature. However, the peak
heights of the spectra at different temperatures shown in Figures 5-2 and 5-3 cannot be compared with each other, since we tuned the tank circuit at each temperature and thus the quality factor $Q$ of the rf tank circuit varied slightly from spectra to spectra.

### 5.2.3 Site Dependence of the Spin-Lattice Relaxation Time $T_1$

To further confirm the assignment of the resonance peaks to proton sites, $T_1$ is a powerful tool, since it is strongly influenced by fluctuations in the dipolar field and transferred hyperfine field, fluctuations whose strength varies from proton site to proton site. For this purpose, 12.7 T is a convenient field since the temperature dependence of $T_1$ is weak at this field, as will be discussed in the next subsection, and thus we do not need to worry about a temperature drift during measurements. The measurements were made at 1.31 K and 0.36 K, near the highest and lowest temperatures of our experiment; within the temperature range of our experiment, the relaxation is closest to being exponential in the high temperature end, becoming increasingly non-exponential as the temperature decreases — as will be discussed in the next subsection. Examples of nearly exponential and strongly non-exponential relaxations are shown in Figure 5-5.

Figure 5-6 shows $T_1$ at 12.7 T as a function of frequency. At this field, 540.7 MHz is the unshifted frequency. The figure shows that the more shifted is the resonance, the shorter is $T_1$, indicating that the peaks with the largest shifts come from proton sites closest to Cr$^{4+}$ as discussed in section 5.2.1. The baby peak and the low-frequency shoulder have the shortest $T_1$, as expected, since they come from the proton sites closest to Cr$^{4+}$, one attached to the middle nitrogen and four attached to the two corner nitrogen atoms of the Cr(diethylenetriamine)(O$_2$)$_2$ molecule.

In section 4.3.2, we argued on the basis of heat-release results that it is very likely that the five proton sites that are attached to nitrogen atoms in Cr(dien) have shortest
relaxation times. The NMR $T_1$ data verify that interpretation. Moreover, the heat-release measurements in which field sweeps were stopped before reaching $H_c$ indicated that the longer relaxation times of the eight proton sites attached to carbon atoms and the two sites within the water molecule comprise two groups, each containing four to six sites. The longer $T_1$'s in Figure 5-6(b) do divide into two such groups. $T_1$'s are shorter for two peaks, at 539.7 MHz and 543.8 MHz, which according to our dipolar-field calculation come from four proton sites, H5B, H4A, H2B, and H3A.

5.2.4 Dependence of $T_1$ on Temperature and Magnetic Field

For the $T_1$ measurements to investigate Cr$^{2+}$ spin dynamics near the QCP, we chose the second highest peak in the NMR spectra, since at 1.3 K this peak has almost no shift due to the dipolar field and transferred hyperfine field (Figure 5-1). At 540.7 MHz, the frequency-to-field ratio of the peak is $540.7 \text{ MHz} / 12.7 \text{ T} = 42.575 \text{ MHz/T}$, very close to the gyromagnetic ratio $42.577468 \text{ MHz/T}$ of the proton. We therefore expected that this peak would split by the smallest amount in the antiferromagnetically ordered phase near the QCP. More important, this peak will not shift in the ordered phase, to the lowest order. Therefore, the frequency can be held constant at a given magnetic field, as the temperature is varied.

To estimate the frequencies of this peak at eight other field values we have chosen for $T_1$ measurements, we used the frequency-to-field ratio determined at 540.7 MHz. For example, for 12.1 T, we estimated the frequency of the peak to be $12.1 \text{ T} \times 42.575 \text{ MHz/T} = 515.2 \text{ MHz}$. To confirm our estimates, we then made a field sweep at each calculated frequency at 1.27 K – 1.50 K, as shown in Figure 5-7. The field was again swept upward at a rate of 0.25 T/min to guarantee thermal equilibrium. These spectra ensured that the frequency estimate for each field is correct.
As described in section 3.4, the spin-echo technique was used to monitor the proton-magnetization recovery after saturation and thus to measure $T_1$. Two typical relaxation curves are shown in Figure 5-5, as mentioned before, one of them approximately exponential (Eq. 3-22) and the other strongly non-exponential, exhibiting a stretched-exponential behavior given by

$$M_z(t) = M_z(0) \left( 1 - e^{-(t/T_1)^{\nu}} \right).$$ (5-1)

Figures 5-8 and 5-9 show, as a function of temperature, the relaxation time $T_1$ obtained from such data by fitting them to exponential curves and stretched-exponential curves, respectively. At 12.7 T, in the nearly completely polarized paramagnetic phase above the QCP, $T_1$ increases gradually and monotonically as the temperature is lowered. In contrast, at fields smaller than 12.4 T, there is a shallow minimum near the transition temperature, $T_c$, followed by a steep increase with decreasing temperature in the antiferromagnetically ordered phase. The data points at and very near 0.3 K, the lowest temperature of the $^3$He cryostat, may suffer from temperature instability. However, this does not affect the majority of the data, which were taken at higher temperatures.

Figure 5-10 shows the stretching parameter $\nu$ of Eq. 5-1 as a function of temperature. The data points at different fields fall on a common curve labeled “empirical line”, decreasing with decreasing temperature except near $T_c$, where a downward deviation from the common curve occurs. This means that the relaxation becomes less exponential as temperature decreases and also near $T_c$. Combining these two general trends suggests that the relaxation will be most strongly non-
exponential as $T_c$ approaches zero, that is, at the QCP. At an Ising critical point, the autocorrelation function that characterizes fluctuations decays with a stretched-exponential time dependence, with the stretching exponent $(d - 1)/(d + 1)$, where $d$ is the system dimensionality \[61\]. It is very likely that our observation is related to this behavior of fluctuations, but more theoretical work is needed to connect the two dots together.

To present $T_1$ and the stretching parameter as a function of temperature and magnetic field, two-dimensional (2D) contour plots and three-dimensional (3D) graphs are useful, as shown in Figures 5-11, 5-12, and 5-13. In particular, as shown in Figure 5-12, $1/T_1T$ exhibits a sharp peak, indicating the transition from the nearly completely polarized paramagnetic phase to the antiferromagnetically ordered phase. In the 2D contour plots, the red line and the black circles, taken from Figure 4-6, mark the phase boundary determined from specific heat and the magnetocaloric effect, and shown in black is the same line shifted by 0.14 T to indicate the probable phase boundary for the NMR sample. The difference between the two curves probably comes from different remanent fields of the magnets used in the two sets of measurements and, possibly, a slight difference in the crystal orientation. In Figure 5-9(b), the stretching parameter exhibits a dip near the QCP, suggesting that there is indeed an intrinsic stretched-exponential relaxation driven by quantum fluctuations.

5.3 Summary

We have probed the spin dynamics of Cr$^{4+}$ ions in Cr(dien) by means of proton NMR near the QCP. The results reveal increasingly stretched-exponential behavior of proton spin-lattice relaxation as the QCP is approached. How the quantum fluctuations of ionic spins near a QCP leads to such a behavior of nuclear spins is an interesting
question whose answer will require theoretical investigation. Contrary to our expectation based on the calorimetric results described in section 4.3.2, the relaxation rate, $1/T_1$, does not diverge as the QCP is approached, although $T_1$ does reach a minimum at $T_c$. 
Figure 5-1. NMR spectra at 540.7 MHz, showing the spin-echo intensity as a function of magnetic field. The arrows indicate the six peaks discussed in the text. The vertical line mark the position of the unshifted peak, at 12.7 T. The spin-lattice relaxation of this peak was studied as a function of temperature and magnetic field near the QCP.
Figure 5-2. Frequency-sweep NMR spectra at 12.7 T at 1.30 K and 0.36 K. Shown are (a) FFT sums and (b) integrated intensity, of spin-echo signals.
Figure 5-3. Frequency-sweep NMR spectra at 11.0 T at 2.50 K, 1.55 K, and 0.50 K. Shown are (a) FFT sums and (b) integrated intensity, of spin-echo signals. The arrows indicate splitting of peaks, as the sample is cooled from nearly completely polarized paramagnetic phase to the antiferromagnetically ordered phase. In (a), A represents the main group of peaks, which split in the ordered phase, and B represents the baby peak, which does not split.
Figure 5-4. Scaled plots of the data shown in Figure 5-3. The data have been scaled with the area under the curve at each temperature, for comparison.
Figure 5-5. Two examples of proton NMR relaxation curves, both taken at 12.7 T. Circles are integrated spin-echo signals in arbitrary units; the horizontal axis, which is in a logarithm scale, is time in microseconds. (a) (top panel) At 1.30 K, the deviation from an exponential fit (blue line) is small. (b) (bottom panel) At 320 mK, a stretched-exponential fit (blue line) with $\nu = 0.50$ is required to describe the relaxation.
Figure 5-6. Proton NMR $T_1$ as a function of frequency at 1.31 K and 0.36 K at 12.7 T. $T_1$ has been extracted from data by (a) an exponential fit and (b) a stretched-exponential fit.
Figure 5-7. NMR spectra obtained at 1.27 K – 1.50 K from integrated spin echoes at nine frequencies. The arrow in each frame indicates the unshifted peak chosen for $T_1$ measurements. These spectra were taken to confirm the estimated frequency at each chosen field of $T_1$ measurements. The field ranged from 12.0 T to 12.7 T, from (a) to (i) in 0.1 T increments except for (h), which is for 12.65 T.
Figure 5-8. Proton NMR $T_1$ in Cr(dien) as a function of temperature in fields ranging from 12.0 T to 12.7 T. $T_1$ has been determined from exponential fits of relaxation curves. Lines are guides to the eye.

Figure 5-9. Proton NMR $T_1$ in Cr(dien) as a function of temperature in fields ranging from 12.0 T to 12.7 T. $T_1$ has been determined from stretched-exponential fits of relaxation curves. Lines are guides to the eye.
Figure 5-10. Stretching parameter $\nu$ as a function of temperature at various magnetic fields. An empirical line (black solid line) indicates a general trend, from which the data deviate downward near the phase transition.
Figure 5-11. 2D contour plot and 3D plot of proton $T_1$, determined from stretched-exponential fits, as a function of temperature and magnetic field. In (a), red line and black circles mark the phase boundary between the antiferromagnetically ordered phase and the nearly completely polarized paramagnetic phase, determined from specific heat and the magnetocaloric effect in section 4.3.1. The black line is the same as the red line, but shifted to indicate a probable phase boundary for the NMR sample.
Figure 5-12. 2D contour plot and 3D plot of $1/T_1T$ as a function of temperature and magnetic field. As shown in (a), the maxima in $1/T_1T$ indicate the phase transition. Black circles, red line, and black line are the same as in Figure 5-11.
Figure 5-13. 2D contour plot and 3D plot of the stretching parameter as a function of temperature and magnetic field. Black circles, red line, and black line are the same as in Figure 5-11. A dark blue dip, a region of small stretching parameter, appears near the QCP.
6.1 Previous Work on (CH$_3$)$_2$CHNH$_3$CuCl$_3$

(CH$_3$)$_2$CHNH$_3$CuCl$_3$, abbreviated IPA-CuCl$_3$, forms a triclinic lattice (the $P\overline{1}$ space group) with lattice constants $a = 11.692 \pm 0.008$ Å, $b = 7.804 \pm 0.004$ Å, $c = 6.106 \pm 0.003$ Å, $\alpha = 79.00 \pm 0.04^\circ$, $\beta = 122.60 \pm 0.04^\circ$, and $\gamma = 116.47 \pm 0.04^\circ$ [62].

The convention among researchers who study the magnetism of IPA-CuCl$_3$ is to specify the direction of the applied magnetic field with respect to the so-called $A$, $B$, and $C$ planes — the three orthogonal faces of a single crystal — rather than with respect to the crystallographic axes. The $A$ plane is perpendicular to the $c$ axis, and the $C$ plane is the $bc$ plane. The $B$ plane is perpendicular to the $A$ and $C$ planes, thus perpendicular to the $bc$ plane and parallel to the $c$ axis [62–64]. Manaka and co-workers [63, 64], who have extensively studied the magnetism of this compound for more than a decade, choose the unit cell differently from Roberts et al. [62], who were the first to determine the crystal structure. In this dissertation, we instead refer to the crystallographic axes defined by the latter authors.

The magnetism of IPA-CuCl$_3$ arises from $S = 1/2$ Cu$^{2+}$ ions. In early experiments, the compound was thought, naively on a structural ground, to comprise ferromagnetic-antiferromagnetic alternating chains running along the $c$ axis [63]. Instead, it was found later by inelastic neutron scattering [65] to consist of two-leg spin ladders, which run parallel to the $b$ axis as shown in Figure 6-1(b). A simple spin ladder has only two kinds of exchange interactions: a rung exchange and leg exchange. But the ladders in IPA-CuCl$_3$ have four exchanges, including an interladder exchange, as depicted in Figure 6-1(a). The rung exchange $J_1$, responsible for the formation of $S = 1$ composite spins, is
ferromagnetic, and the leg exchange $J_2$ is antiferromagnetic. The diagonal exchange $J_3$ is also antiferromagnetic, whereas the interladder exchange $J_4$ is ferromagnetic.

According to inelastic neutron scattering and magnetic susceptibility [63, 65], $J_1 = -27 \pm 7$ K, $J_2 = 14 \pm 2$ K, $J_3 = 34 \pm 1$ K, and $J_4 = -3.39 \pm 0.01$ K [66]. The negative signs for $J_1$ and $J_4$ indicate ferromagnetic exchange.

Theoretically, $S = 1/2$ two-leg Heisenberg spin ladders with an antiferromagnetic leg exchange belong to the same universality class as $S = 1$ linear-chain Heisenberg antiferromagnets and should therefore have a Haldane gap between the quantum-mechanically disordered ground state and the triplet magnon excitations, as pointed out in section 2.3. As a result, the ground state below a critical field $H_c$ will be a spin liquid, with no long-range order. Above $H_c$, which is a QCP, the composite $S = 1$ spins will order antiferromagnetically owing to interladder interactions, and this ordering can be described as a BEC of magnons, as explained in section 2.4. These theoretical expectations have been borne out by a number of neutron experiments on IPA-CuCl$_3$ [65, 67, 68]. However, only a small number of data points were taken in these experiments to determine the critical exponent of Eq. 2-27.

To determine the magnetic phase diagram of IPA-CuCl$_3$ in detail, particularly near the QCP, we have measured the specific heat and the magnetocaloric effect — the method used for Cr(dien), as described in section 4.3.1. Preliminary results have been published as a short report [69]. In addition, we have measured the magnetic torque in an attempt to extend the phase diagram to about 24 mK, considerably lower than possible with the calorimetric method. We find a power-law dependence of the critical field on temperature, with an exponent indicative of a BEC of magnons. Near the QCP,
we also find heat release from proton spins after temperature quenching, demonstrating that the phenomenon we have first observed in Cr(dien) is probably a generic property of a variety of QCP.

### 6.2 Experimental

All measurements were performed in a dilution refrigerator with a 20-tesla superconducting magnet at the NHMFL in Tallahassee. The specific-heat and magnetocaloric-effect measurements were carried out in the relaxation calorimeter described in section 3.1, at temperatures down to 49.9 mK in magnetic fields up to 18 T. In order to minimize the addenda heat capacity, the sample was directly glued on the calorimeter platform with Wakefield compound. The applied magnetic field was perpendicular to the $B$ plane or $C$ plane of the crystal.

Magnetic torque was measured by a cantilever beam magnetometer described in section 3.3. The sample was glued on the flexible CuBe beam with GE varnish and covered with a stretched piece of Teflon® tape for protection. Using a rotating probe at the NHMFL, we oriented the sample so that the magnetic field was perpendicular to either the $B$ plane or $C$ plane, as in the specific-heat and magnetocaloric-effect measurements.

The calorimeter for the specific-heat and magnetocaloric-effects measurements was also used for the heat-release experiment. In this experiment, the magnetic field was applied only perpendicular to the $B$ plane. The procedure of the experiment was the same as in the heat-release experiment on Cr(dien), described in section 4.2.2.

The single-crystal samples of IPA-CuCl$_3$ used in these experiments were grown by Akira Oosawa’s group in Tokyo by dissolving $(\text{CH}_3)_2\text{CHNH}_2\cdot\text{HCl}$ and CuCl$_2$ in isopropanol and allowing the solvent to evaporate slowly at 30°C [63].
6.3 Results and Analysis

6.3.1 Specific Heat and Magentocaloric Effect

Figures 6-2 and 6-3 show the specific heat in the two field directions. The peak at each magnetic field indicates an antiferromagnetic transition. The peak height, as well as the transition temperature, decreases with decreasing magnetic field. The peak disappears completely at 10 T, when the applied field is perpendicular to the $B$ plane, and at 9.5 T when $H \perp C$ plane, indicating that these fields are close to the QCP at which the antiferromagnetic order disappears. The rapid upturn below about 0.4 K at these fields is due to the nuclear specific heat of copper and hydrogen, which makes it difficult to detect a transition peak at a temperature less than about 0.4 K.

To overcome this limitation of the specific-heat technique, we used the magnetocaloric effect at temperatures below 0.8 K as a complementary tool, as shown in Figure 6-4. As in Cr(dien), whose results were described in section 4.3.1, comparison of the magnetocaloric-effect data and specific-heat peak positions indicated that the correct transition point is given by the average temperature and field of the peak and dip in a pair of curves for upward and downward field sweeps at a fixed reservoir temperature.

From specific heat and the magnetocaloric effect, we have determined the phase diagram in terms of magnetic field and temperature for each applied field direction. As shown in Figure 6-5, there is no magnetic ordering below a critical field $H_c$; near zero temperature, this field region is presumably a spin-liquid phase, in which magnon excitations are gapped. Above $H_c$, 3D antiferromagnetic long-range order appears due to weak interladder exchange.
If IPA-CuCl$_3$ is an ideal Heisenberg antiferromagnet, then its antiferromagnetic ordering is expected to be a BEC of magnons, near the QCP, as described in section 2.4. The universal power law for a BEC is given by Eq. 2-27 with an exponent $\alpha$. To determine $\alpha$ for IPA-CuCl$_3$, we have fitted the data shown in Figure 6-5 to Eq. 2-27 by letting $H_c$ and $\alpha$ to be fitting parameters and by limiting the maximum temperature to which the fit is made. Figure 6-6 shows the exponent value versus the maximum temperature of the fit. From this analysis, we find $H_c = 9.995 \pm 0.002$ T and $\alpha = 1.47 \pm 0.06$ for $H \perp B$ plane and $H_c = 9.399 \pm 0.004$ T and $\alpha = 1.50 \pm 0.06$ for $H \perp C$ plane, by fitting the data up to 0.6 K and 0.8 K, respectively [69]. The critical exponents are in excellent agreement with $\alpha = 3/2$ expected for 3D BEC.

The energy gap $\Delta$ at zero field is related to the critical field $H_c$ by Eq. 2-26. The $g$ factor of IPA-CuCl$_3$ is slightly anisotropic, with $g_A = 2.11$, $2.06 < g_B < 2.11$, and $g_C = 2.26$, according to ESR [63, 64]. With these and from our $H_c$, we find $13.831 \pm 0.003$ K $< \Delta < 14.166 \pm 0.003$ K for $H \perp B$ plane and $\Delta = 14.268 \pm 0.006$ K for $H \perp C$ plane, in good agreement with the value directly obtained by zero-field inelastic neutron scattering, $\Delta = 13.589$ K [65]. Moreover, Figure 6-7, which shows the magnetic phase diagrams for the two field directions scaled with the $g$ factor, indicates that the anisotropy of the phase diagram comes from the $g$-factor anisotropy alone within our experimental uncertainties. Such a scaling was noted earlier by Manaka et al. [70], who compared the phase diagrams for $H \perp A$ plane and $H \perp C$ plane. Their phase diagrams extended, however, only down to about 0.7 K.

6.3.2 Magnetic Torque

Magnetic torque is a convenient tool to qualitatively measure magnetization as a function of magnetic field and to thereby determine a magnetic phase diagram, albeit
not a quantitatively accurate tool. Figures 6-8 and 6-9 show the magnetic torque, divided by the magnetic field, on IPA-CuCl₃ for $H \perp B$ plane and $H \perp C$ plane. This quantity, $\tau / H$, is roughly proportional to the sample magnetization, as can be understood from Eq. 3-15. For both field directions, $\tau / H$ is nearly zero in the quantum-mechanically disordered phase below $H_c$. Since magnon excitations are gapped in this phase, the magnetization is zero at low temperatures. Above $H_c$, $\tau / H$ increases rapidly, as the magnetization increases with the magnetic field.

In an attempt to precisely determine the critical field at each temperature from the torque data, we examine the derivatives $d(\tau / H) / dH$ and $d^2(\tau / H) / dH^2$, which are shown as a function of magnetic field in Figures 6-10 and 6-11 for $H \perp B$ plane, and in the inset to Figures 6-9 and in Figure 6-12 for $H \perp C$ plane. The peak in the second derivative, $d^2(\tau / H) / dH^2$, occurs systematically about 0.1 T below the transition determined from the magnetocaloric effect, whereas the shoulder in the first derivative closely follows the transition. However, we have not yet found a quantitatively unique way to define this feature in the first derivative and thus cannot use the torque to extend the phase diagram from 0.17 K to about 24 mK.

6.3.3 Heat Release from Proton Spins near the QCP

Like in Cr(dien), results for which were discussed in section 4.3.2, we have found that proton spins in temperature-quenched IPA-CuCl₃ release heat near the QCP. In this experiment, the magnetic field was applied perpendicular to the $B$ plane of the crystal. For the procedure of the experiment, which was similar to the Cr(dien) experiment, refer to section 4.2.2. The quenching temperature $T_q$ ranged from 225 mK to 1.33 K. The waiting time for thermal equilibrium at $T_q$ was typically 2 min for high $T_q$.
and 30 min for low \( T_q \), after which the sample was rapidly cooled to the reservoir temperature \( T_0 \) in less than 1 min. The field sweeps through the critical field \( H_c \) were made at seven different \( T_0 \) ranging from 56.2 mK to 271 mK, at the rate of 0.1 T/min or 0.2 T/min.

As the field is swept toward \( H_c \), a pronounced peak appears in the temperature difference \( \Delta T \) between the sample and the thermal reservoir, as shown in Figure 6-13, indicating heat being released in the sample. As was found in Cr(dien), the heat release occurs only during the first field sweep after the temperature quenching of the sample from \( T_q \).

The amount of released heat \( Q \) is obtained from the data by using Eq. 4-1. As shown in Figure 6-14, \( Q \) depends on both \( T_q \) and \( H_q \), the quenching field, in a manner very similar to the results for Cr(dien) discussed in section 4.3.2, clearly indicating that the heat is released from the proton spins. As has been derived in that section, \( Q \) is given by Eq. 4-5. For the thermal-reservoir temperature \( T_0 = 180 \text{ mK} \), good agreement between experiment and the equation is obtained with \( n_H = 7 \), as shown in Figure 6-14(a), except for a few points for which \( H_q \) is 6 T. As shown in Figure 6-14(b), good agreement between the equation and the \( T_0 = 99.7 \text{ mK} \) data for \( H_q = 9 \text{ T} \) is obtained with \( n_H = 5 \), whereas \( n_H = 4 \) gives the best fit for \( H_q = 11 \text{ T} \).

IPA-CuCl\(_3\) contains ten hydrogen atoms per formula unit, as shown in Figure 6-15. Among them, seven are significantly closer to a Cu\(^{2+}\) ion — at 3.37 Å, 3.57 Å, 3.72 Å, 3.80 Å, 3.99 Å, 4.09 Å, and 4.30 Å — than other three, which are at 4.71 Å, 4.94 Å, and 5.20 Å from the closest Cu\(^{2+}\) ion. It is very likely that these seven hydrogen atoms, which experience stronger fluctuating dipolar field and transferred hyperfine field of the
Cu$^{2+}$ spins than other three do, are those whose nuclear spins release heat at $T_0 = 180$ mK. Among them, only four or five that are closest to a Cu$^{2+}$ ion evidently release heat at $T_0 = 99.7$ mK.

The positions of the heat-release peaks are shown in Figure 6-16 along with the phase boundary between the spin-liquid phase and the antiferromagnetically ordered phase. As in the case of Cr(dien), the diagram suggests that the loci of the peaks converge on the QCP in the zero-temperature limit. These loci delimit the quantum critical region in which $\tau$ is shorter than the timescale of the experiment.

As in Cr(dien), we have also investigated the variation of $\tau$, the relaxation time of proton spins, within the quantum critical region. The measurements were carried out at $T_0 = 180$ mK after the sample had been quenched from $T_q = 779$ mK at $H_q = 9$ T or from $T_q = 826$ mK at $H_q = 12.5$ T. The relaxation rate $1/\tau$ diverges as the field approaches $H_c$, as shown in Figure 6-17, indicating that divergent quantum fluctuations of the Cu$^{2+}$ spins near the QCP drive the relaxation of the proton spins. The divergence is asymmetric around $H_c$, faster for $H > H_c$ than $H < H_c$. This asymmetry is also seen in Figure 6-16 as a wider quantum critical region for $H > H_c$ than for $H < H_c$.

The amount of heat released during the relaxation-time measurements is shown as a function of $|H-H_c|$ in Figure 6-18. The result indicates that the seven hydrogen atoms whose nuclear spins release heat at this temperature consist of two groups, each comprising three or four hydrogens within our uncertainties. Below $H_c$, one group releases heat at $|H-H_c|$ larger than about 0.45 T, whereas the other group does so at fields closer to $H_c$. This result is consistent with the distribution of hydrogen-copper distances discussed earlier to explain the $T_0$ dependence of the number of proton spins.
that participate in heat release. Above $H_c$, there is no evidence for grouping in the field region of our study.

### 6.4 Conclusions

We have determined the magnetic phase diagram of IPA-CuCl$_3$ for two magnetic-field directions, $H \perp B$ plane and $H \perp C$ plane, from specific heat and the magnetocaloric effect. The phase boundaries, $H(T)$, between the gapped, spin-liquid phase and the antiferromagnetically ordered phase scale with the anisotropic $g$ factor, indicating that IPA-CuCl$_3$ is an ideal Heisenberg antiferromagnet, with negligible single-ion anisotropy or Dzyaloshinskii-Moriya interaction. As a result, the antiferromagnetic ordering near zero temperature can be described as a 3D BEC of magnons, as testified by the critical exponents for the phase boundaries.

Like in Cr(dien), temperature quenching of IPA-CuCl$_3$ leaves the hydrogen nuclear spins frozen in a high-energy nonequilibrium state and, as the magnetic field is then brought close to the QCP, quantum fluctuations of the Cu$^{2+}$ ionic spins quickly anneal them to reach thermal equilibrium with the lattice. But unlike in Cr(dien), where the QCP is between an antiferromagnetically ordered phase and a state completely polarized by the magnetic field, the QCP in IPA-CuCl$_3$ occurs between a gapped, spin-liquid phase and a field-induced, antiferromagnetically ordered phase. Taken together with our result for Cr(dien), our result for IPA-CuCl$_3$ strongly suggests that the heat release from nuclear spins driven by quantum fluctuations is a generic phenomenon near a wide variety of QCPs.
Figure 6-1. Schematic diagram and the crystal structure of IPA-CuCl$_3$. (a) (top panel) Schematic representation of spin ladders in IPA-CuCl$_3$ with four exchanges: ferromagnetic rung exchange $J_1$ (black solid lines) responsible for the formation of composite $S = 1$ spins, antiferromagnetic leg exchange $J_2$ (blue dot lines), antiferromagnetic diagonal exchange $J_3$ (orange dot line), and ferromagnetic interladder exchange $J_4$ (long dash line). Brown circles represent the $S = 1/2$ spins of Cu$^{2+}$ ions. (b) (bottom panel) Crystal structure of IPA-CuCl$_3$, with the exchanges indicated. Brown spheres and green spheres represent Cu$^{2+}$ ions and Cl$^-$, respectively. Ladders extend along the $b$ axis. For clarity, IPA ions are not shown. The structure has been drawn with Balls & Sticks [71].
Figure 6-2. Specific heat of IPA-CuCl$_3$ in magnetic fields normal to the $B$ plane. From 10.3 T to 11.0 T, near the QCP, the data were taken in small field increments. Bottom panel shows the low temperature region below 1.5 K. Lines are guides to the eye.
Figure 6-3. Specific heat of IPA-CuCl₃ in magnetic fields normal to the C plane. Bottom panel shows the low-temperature region below 1.0 K. Lines are guides to the eye.
Figure 6-4. Magnetocaloric-effect curves at various temperatures. (a) (left panel) $H \perp B$ plane and (b) (right panel) $H \perp C$ plane. Red traces are for upward field sweeps and blue traces for downward field sweeps. In the left panel, temperature variation has been amplified by a factor of 2 for clarity.
Figure 6-5. Magnetic phase diagram of IPA-CuCl$_3$. Red squares are for $H \perp B$ plane and purple circles for $H \perp C$ plane. Above the critical field, at which the energy gap of triplet magnons becomes zero, 3D long-range order appears. Solid line for $H \perp B$ plane and dash line for $H \perp C$ plane are power-law fits for BEC.
Figure 6-6. Exponent of the power-law fit as a function of the highest transition temperature, for $H \perp B$ plane and $H \perp C$ plane.
Figure 6-7. Transition field scaled with the $g$ factor for the two applied field directions. Red squares and purple circles are for $H \perp B$ plane and $H \perp C$ plane, respectively. The scaled phase diagrams are almost the same for the two field directions.
Figure 6-8. Magnetic torque divided by magnetic field at various temperatures, for field applied perpendicular to the $B$ plane. Blue lines are data below 100 mK, red lines at and above 124 mK, and magenta for 121 mK. For clarity, curves at different temperatures have been shifted by arbitrary amounts.
Figure 6-9. Magnetic torque for $H \perp C$ plane. For comparison, all curves are forced to be zero at 8.6 T. Inset: the second derivative of torque divided by $H$, with respect to $H$. 

IPA-CuCl$_3$

H $\perp$ C plane
Figure 6-10. Derivatives of magnetic torque divided by magnetic field for $H \perp B$ plane at various temperatures. (a) the first derivative and (b) the second derivative.
Figure 6-11. Comparison of the magnetic-torque data shown in Figure 6-10 with the phase boundary determined from specific heat (solid squares) and the magnetocaloric effect (open squares), shown in Figure 6-5. Blue lines are the power-law fit. (a) The first derivative and (b) the second derivative of the torque data. Each curve has been drawn so that the value at 9.1 T indicates the temperature at which the data were taken.
Figure 6-12. Comparison of the magnetic-torque data for $H \perp C$ plane, partly shown in the inset to Figure 6-9, with the phase boundary determined from the magnetocaloric effect (open circles), shown in Figure 6-5. Dash lines are the power-law fit. (a) The first derivative and (b) the second derivative of the torque data. Each curve has been drawn so that the value at 8.6 T indicates the temperature at which the data were taken.
Figure 6-13. Temperature difference $\Delta T$ between the sample and the thermal reservoir as a function of the magnetic field during field sweeps at 0.1 T/min. The peaks to the right were observed during downward field sweeps and those to the left during upward sweeps. (a) The thermal reservoir was held at 180 mK. Temperature $T_q$ from which the sample has been quenched ranged from 253 mK to 1.42 K. The quenching fields were 6 T (green), 9 T (blue), 12.5 T (red), and 15.5 T (magenta). (b) The thermal reservoir was held at 99.7 mK. $T_q$ ranges from 222 mK to 796 mK. Quenching fields were 9 T (blue) and 11 T (red). The QCP is at $H_c = 9.995 \pm 0.002$ T.
Figure 6-14. Amount of heat released at (a) 180 mK and (b) 99.7 mK as a function of $T_q$, the temperature from which the sample was quenched. Quenching fields $H_q$ are given in the legends. The lines represent Eq. 4-5 with $n_H = 7$ for (a), and $n_H = 5$ (9 T) and $n_H = 4$ (11 T) for (b).
Figure 6-15. Crystal structure of IPA-CuCl$_3$. Brown spheres are Cu, green Cl, gray C, blue N, and white H. The triclinic unit cell, indicated by thin lines, contains two chemical-formula units. Drawn with Balls & Sticks [71].
Figure 6-16. Magnetic fields and temperatures of the peaks in the $\Delta T$ curves (triangles and circles), marking a quantum critical region of IPA-CuCl$_3$ delimited by two lines through the data points. Squares represent the phase boundary — detected by the specific heat and the magnetocaloric effect (MCE) — between the antiferromagnetic (AF) and quantum-mechanically disordered (P) phases. The line through the squares is a power-law fit of data points up to 0.6 K.
Figure 6-17. Relaxation rate $1/\tau$ vs. the field at which field sweep was stopped. Blue and red squares are for $T_q = 779$ mK at $H_q = 9$ T and $T_q = 827$ mK at $H_q = 12.5$ T, respectively.

Figure 6-18. Amount of heat released at $T_0 = 180$ mK as a function of the field at which field sweep ended. Horizontal lines indicate the amounts of heat released in complete field sweeps through $H_c$. Blue and red squares are for $T_q = 779$ mK at $H_q = 9$ T and $T_q = 827$ mK at $H_q = 12.5$ T, respectively.
We have studied phase transitions, thermodynamics, and magnetic properties of two quantum magnets, Cr(dien) and IPA-CuCl₃. These compounds are excellent laboratory models of quantum magnets to investigate quantum critical phenomena.

The first material, Cr(dien), is a quasi-two-dimensional square-lattice antiferromagnet with a saturation field of 12.392 T ± 0.003 T, at which the quantum phase transition occurs between the antiferromagnetically ordered phase and the fully polarized state. The critical exponent of the phase boundary is $\alpha = 2.01 \pm 0.02$, indicating a 3D Ising criticality instead of a BEC of magnons.

Our most significant finding in this material is heat release from proton spins caused by divergent quantum fluctuations of Cr⁴⁺ near the QCP. The results present clear evidence that temperature quenching of Cr(dien) leaves the proton spins frozen in a high-energy non-equilibrium state and, as the magnetic field is then brought near the QCP, quantum fluctuations of Cr⁴⁺ spins quickly anneal them.

We have also used NMR to probe the dynamics of Cr⁴⁺ spins very near the QCP. The results show that the spin-lattice relaxation time, $T₁$, of the proton spins becomes significantly shorter near the QCP with increasingly stretch-exponential behavior. These are caused by the divergent quantum fluctuations of the Cr⁴⁺ spins. How the quantum fluctuations of ionic spins near a QCP lead to stretched-exponential relaxation of nuclear spins is a question whose answer will require theoretical investigation.

The second compound, IPA-CuCl₃, is a quasi-one-dimensional antiferromagnet. Although the spin quantum number of Cu²⁺ is 1/2, low-lying excitations in this material have a Haldane gap, usually associated with integer-spin quasi-one-dimensional
antiferromagnets, because the spins form two-leg ladders with antiferromagnetic leg interactions. The QCP of IPA-CuCl$_3$ is at $9.995 \pm 0.002$ T for $H \perp B$ plane and $9.399 \pm 0.004$ T for $H \perp C$ plane [69]. These critical fields translate to a Haldane gap of $13.831 \pm 0.003$ K $< \Delta < 14.166 \pm 0.003$ K for $H \perp B$ plane and $\Delta = 14.268 \pm 0.006$ K for $H \perp C$ plane, in good agreement with the value directly obtained by zero-field inelastic neutron scattering, $\Delta = 13.589$ K [65]. Above the critical fields, the spins order antiferromagnetically. The critical exponent of the boundary between the ordered phase above and the quantum-mechanically disordered spin-liquid phase below is $\alpha = 1.47 \pm 0.06$ for $H \perp B$ plane and $\alpha = 1.50 \pm 0.06$ for $H \perp C$ plane, in excellent agreement with $\alpha = 3/2$ expected for 3D BEC of magnons.

As in Cr(dien), temperature quenching of IPA-CuCl$_3$ leaves the proton spins frozen in a high-energy non-equilibrium state and, as the magnetic field is then brought close to the QCP, quantum fluctuations of the Cu$^{2+}$ spins quickly anneal them to reach thermal equilibrium with the lattice. Our discovery of heat release from proton spins in Cr(dien) and IPA-CuCl$_3$, involving two different kinds of QCPs with different dimensionality and spin quantum numbers, strongly suggests that it is a generic phenomenon near a QCP. This phenomenon promises to be a useful probe for the dynamics of quantum fluctuations that underlie quantum criticality in a variety of systems.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Younghak Kim was born in Daegu, Korea. He graduated from Kyungpook National University. While an undergraduate student at the university, majoring in physics, he decided to continue his study of the subject abroad as a graduate student. He came to the University of Florida in the fall of 2005 to pursue Ph. D. in physics with interest in experimental condensed-matter research. He joined Prof. Yasumasa Takano’s group in 2006 and graduated in the spring of 2011 with Ph. D. in physics.