High Field NMR Investigation of Kitaev Spin Liquid Candidate  $\rm Cu_2 IrO_3$ 

# High Field NMR Investigation of Kitaev Spin Liquid Candidate ${\rm Cu_2 IrO_3}$

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# Abstract

The search for quantum spin liquids (QSLs) introduces some of the most challenging and interesting problems in contemporary physics. The recently discovered iridate  $Cu_2IrO_3$ , which contains a honeycomb lattice of  $Ir^{4+}$  ions with effective spin 1/2 coupled by frustrated Ising interactions, presents itself as a promising candidate for a Kitaev QSL.

In this study, we use nuclear magnetic resonance (NMR), a spectroscopic technique based on the energy levels of nuclear spin states, to probe the intrinsic spin excitations of Cu<sub>2</sub>IrO<sub>3</sub>. By measuring the NMR frequency shift of <sup>63</sup>Cu from 4.2 K to 298 K, we demonstrate that its spin susceptibility  $\chi_{spin}$  behaves nearly identically to its parent compound Na<sub>2</sub>IrO<sub>3</sub>, without showing evidence of magnetic ordering at low temperatures. We showed that the upturn of bulk susceptibility  $\chi$  below T = 50 K is due to the contribution of defect spins. The hyperfine coupling constant  $A_{hf}$  between Cu and Ir<sup>4+</sup> was also estimated by comparing the Knight shift <sup>63</sup>K to  $\chi$ .

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### Chapter 1

## Introduction

#### 1.1 Background and Motivation

One of the most exotic phases of matter is known as a quantum spin liquid (QSL). While magnetic moments in conventional materials are usually either dominated by thermal fluctuations (paramagnets), or exhibit long range ordering (ferromagnets and antiferromagnets). QSLs in contrast, remain paramagnetic and behave like a highly entangled and fluctuating "liquid" in the absence of thermal energy as its spins do not order to a static ground state [1].



FIGURE 1.1: Three neighboring spins in a triangular lattice interacting antiferromagnetically. Since all three spins cannot be simultaneously antiparallel to each other, there is no single energetically favoured configuration for the three spins to align. This principle applies to every set of 3 neighboring spins in the entire lattice.

A typical example of a QSL involves a material with layers of 2-dimensional triangular lattices of Ising spins interacting antiferromagnetically, resulting in what is known as geometric frustration. As demonstrated in figure (1.1), there is no way to satisfy every pair of nearest neighbor Ising interactions, thus leading to a near-infinite number of possible ways to orient the spins in the ground state of the system.

Quantum mechanically, the ground state of a QSL is a superposition of these orientations in which the spins are highly correlated [1].

Though we have yet to confirm its existence, identifying a QSL may prove to be greatly beneficial to the field of condensed matter, as studying its unconventional properties will further our understanding of the quantum nature of materials and present new possibilities for technological innovation.

#### 1.2 Kitaev Quantum Spin Liquids

There exists many potential QSL candidate materials such as those possessing Kagomé [2] or Pyrochlore [3] lattices. Recently in 2006, theoretical calculations by Alexei Kitaev demonstrated that a honeycomb lattice of spin 1/2 fermions dominated by bonddependent ferromagnetic interactions with their nearest neighbors can lead to a quantum spin liquid ground state [4].

The Kitaev Hamiltonian is defined as

$$\hat{\mathcal{H}}_K = \sum_{\langle i,j \rangle} J_K^{\gamma} S_i^{\gamma} S_j^{\gamma}, \qquad (1.1)$$

where  $J_K^{\gamma}$  is the energy of the anisotropic, bond-dependent Ising interactions. The indices i and j represent nearest neighbors in the honeycomb lattice.  $\gamma$  is defined for each pair of nearest neighbors to be the x-, y-, or z- axis oriented in the direction of their bond, as illustrated by Takagi *et al.* in figure (1.2).



FIGURE 1.2: Diagram of bonds on a Kitaev honeycomb lattice. The 3 bonds adjacent to each lattice point has their easy axes parallel to the x-, y-, or z- axes. Figure from [5]

Since each spin in the Kitaev lattice is only able to energetically satisfy one of its 3 neighboring spins by aligning with it according to the direction of their bond. The countless ways to pair up these spins leads to geometric frustration and a highly degenerate ground state, as illustrated in figure (1.3).



FIGURE 1.3: The Kitaev spin-liquid state as a superposition of the many possible arrangements of spin pairs. Figure from [5]

However, realistic materials exhibit additional interactions between their neighboring spins and may be described by the Kitaev-Heisenberg model. Their spin Hamiltonians contain the isotropic Heisenberg exchange term

$$\hat{\mathcal{H}}_H = \sum_{\langle i,j \rangle} J_H \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \qquad (1.2)$$

and the symmetric off-diagonal exchange term

$$\hat{\mathcal{H}}_{\Gamma} = \sum_{\langle i,j \rangle} \Gamma(S_i^{\alpha} S_j^{\beta} + S_i^{\beta} S_j^{\alpha}), \qquad (1.3)$$

where  $\alpha$  and  $\beta$  are defined as Cartesian directions not equal to the direction of the bond  $\gamma$ .

The Kitaev-Heisenberg Hamiltonian is written as the sum of the Kitaev, Heisenberg, and symmetric off-diagonal exchange Hamiltonians [6]

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$$\hat{\mathcal{H}}_{KH} = \hat{\mathcal{H}}_K + \hat{\mathcal{H}}_H + \hat{\mathcal{H}}_{\Gamma}, \qquad (1.4)$$

Evidence for a Kitaev QSL have been observed in materials with honeycomb planes in their crystal lattices. These materials contain S = 1/2 late transition metal ions in an octahedral environment with strong spin-orbit coupling  $\lambda$ , such as the Ir<sup>4+</sup> in Na<sub>2</sub>IrO<sub>3</sub> [7], and Ru<sup>4+</sup> in  $\alpha$ -RuCl<sub>3</sub> [8].

Experiments on Na<sub>2</sub>IrO<sub>3</sub> have established that it undergoes antiferromagnetic ordering at a Néel temperature of  $T_N \approx 15 \text{K}$  [9]. However, the behaviour of its bulk magnetic susceptibility  $\chi$  in its paramagnetic state suggests a much higher Curie-Weiss temperature  $\Theta_{CW}$  of -125 K [10], which is a signature of the strong frustration of spin liquids.



FIGURE 1.4: Phase diagram showing the possible ordering of spins in a Kitaev-Heisenberg system arising from  $J_K$  and  $J_H$ .  $\psi$  is defined such that  $J_H = \cos(\psi)$  and  $|J_K^{\gamma}| = \sin(\psi)$ . Figure from [11]

In the Kitaev-Heisenberg model, the existence of ordering in Kitaev QSL candidates is dependent on the magnitude of the Ising and exchange energies  $J_K$  and  $J_H$ , as the bonddependent Ising interactions favour a spin liquid state while the Heisenberg exchange interaction favours antiferromagnetic or ferromagnetic ordering depending on its sign. A phase diagram of the Kitaev-Heisenberg model is shown in figure (1.4). More complex orders such as zig-zag can be explained by effect of the off-diagonal exchange term  $\Gamma$  [6].

Distortions in the lattice which deviate from the ideal Kitaev geometry as well as further neighbor interactions will introduce additional terms into the Kitaev-Heisenberg Hamiltonian, but their effects remain unaddressed for now [6].

#### **1.3** Copper Iridate $(Cu_2IrO_3)$

In this study, our focus is on the Kitaev QSL candidate  $Cu_2IrO_3$ , which has a very similar layered honeycomb structure as its parent compound Na<sub>2</sub>IrO<sub>3</sub>. Our Cu<sub>2</sub>IrO<sub>3</sub> sample was synthesized at Boston College by Abramchuk *et al.*. This was done by replacing the Na<sup>+</sup> ions in Na<sub>2</sub>IrO<sub>3</sub> with Cu<sup>+</sup> via metathesis with CuCl [12]. The crystal structure of Cu<sub>2</sub>IrO<sub>3</sub> is shown in figure (1.5) and a perpendicular view of its honeycomb planes is shown in figure (1.6).



FIGURE 1.5: Crystal structure of  $Cu_2IrO_3$  viewed along the a-axis. This material consists of layers of  $Ir_{2/3}Cu_{1/3}O_6$  honeycomb planes. The  $Ir^{4+}$  ions are bonded to each other via two  $O^{2-}$  ligands

 $Cu_2IrO_3$  has two different types of Cu sites. Cu ions within the honeycomb planes are labeled as Cu(H) while interlayer Cu are labeled as Cu(I). Due to the stacking faults, there are 2 distinct Cu(I) lattice sites labeled  $Cu(I_1)$  and  $Cu(I_2)$ , with  $Cu(I_1)$  occupying twice as many lattice sites as  $Cu(I_2)$ .

Cu<sub>2</sub>IrO<sub>3</sub> possesses Ir-Ir-Ir (122.5° to 118.7°) and Ir-O-Ir (98.1° to 95.0°) bonds angles closer to the ideal Kitaev geometry (120° and 90°) [13] than Na<sub>2</sub>IrO<sub>3</sub>, which has 114.9° to 124.2° Ir-Ir-Ir and 98° to 99.4° Ir-O-Ir bond angles. This is important, as deviation from the ideal geometry tends to increase the Heisenberg exchange term  $J_H$ .



FIGURE 1.6: Honeycomb lattice of  $Ir^{4+}$  ions viewed along the c'-axis with Cu(H) sites at the center of the hexagonal cells. The bond-dependent Ising interactions  $J_K^{\gamma}$  are superimposed onto the Ir-Ir bonds.

Heat capacity measurements of Cu<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> conducted by Abramchuk *et al.* is shown in figure (1.7). Since the Cu<sub>2</sub>IrO<sub>3</sub> data does not display a sharp peak within the observed temperature range, there is no evidence for its magnetic ordering. This is unlike Na<sub>2</sub>IrO<sub>3</sub>, which clearly has a peak at its Néel temperature [12], indicating an antiferromagnetic transition.  $\alpha$ -RuCl<sub>3</sub> has also been shown to exhibit such a peak in its heat capacity at  $T_N \approx 6.2$  K [14].



FIGURE 1.7: Heat capacity of  $Cu_2IrO_3$  and  $Na_2IrO_3$  vs temperature. Figure from [12]

Bulk susceptibility measurements of Cu<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> were done by Abramchuk *et al.* and the results are shown in figure (1.8). Effective magnetic moment  $\mu_{eff}$  and  $\Theta_{CW}$  were determined by fitting  $\chi$  to the Curie-Weiss model

$$\chi = \frac{C}{T - \Theta_{CW}}, \quad \text{where} \quad C = \frac{g\mu_B)^2 J(J+1)}{3k_B}, \quad (1.5)$$

 $N_A$  is Avogadro's number,  $\mu_B$  is the Bhor magneton, g is the Landé g-factor, J is the angular momentum quantum number, and  $k_B$  is the Boltzmann constant. It is apparent that Cu<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> exhibit similar behaviour of  $\chi$  down to ~ 50 K. Below this temperature, the  $\chi$  of Cu<sub>2</sub>IrO<sub>3</sub> exhibits an extreme upturn while the  $\chi$  of Na<sub>2</sub>IrO<sub>3</sub> peaks at T = 15 K, both deviating from the Curie-Weiss model.



FIGURE 1.8: Bulk molar susceptibility  $\chi$  vs temperature of Cu<sub>2</sub>IrO<sub>3</sub> (Red) and Na<sub>2</sub>IrO<sub>3</sub> (Blue) measured at an external field of  $|\mathbf{B}| = 1$  T. Figure from [12]

In this thesis, a spectroscopic technique known as nuclear magnetic resonance (NMR) is used to investigate the intrinsic behaviour of  $\chi$ , free of defects, and to better understand the local magnetic structure of Cu<sub>2</sub>IrO<sub>3</sub>.

### Chapter 2

# **Fundamentals of NMR**

#### 2.1 Energy Levels of Nuclear Spin

In the presence of a static magnetic field, the energy level of a nucleus splits due to the Zeeman interactions between its magnetic moment  $\mu$  and the external field  $\mathbf{B}_0$  according to the Hamiltonian [15]

$$\hat{\mathcal{H}} = -\boldsymbol{\mu} \cdot \mathbf{B}_0 = -\gamma_N \hbar \mathbf{B}_0 I_z, \qquad (2.1)$$

where  $\boldsymbol{\mu} = \gamma_N \hbar \boldsymbol{I}$  is the magnetic moment of the nucleus and the z-axis is defined parallel to  $\mathbf{B}_0$ .  $I_z$  is the z-component of the nuclear angular momentum, and  $\gamma_N$  is the nuclear gyromagnetic ratio. This results in energy levels of

$$E = -\gamma_N \hbar B_0 m$$
, where  $m = -I, -I+1, \dots, I-1, I$ , (2.2)

as shown schematically in the left column of figure (2.1). In addition to the Zeenman interaction, the nuclear spin Hamiltonian is dependent on other local effects such as the hyperfine and quadrupole interactions, as discussed in sections (2.5) and (2.7) respectively.

Transitions between these energy levels can be induced by applying an alternating magnetic field at the resonant frequency  $\nu = \Delta E/h = (E_{m-1} - E_m)/h = \gamma_N \mathbf{B}_0/2\pi$ .



FIGURE 2.1: Visualization of energy level splitting of a spin 3/2 nucleus. The horizontal blue lines in each column represent the 4 energy levels each corresponding to a value of  $I_z$ . The light blue regions in the right column represent a continuum of possible energy levels which depend on the relative angle between the crystal and the applied field.

#### 2.2 Classical Motion of Spin

For a particle with magnetic moment  $\mu$  in a field  $\mathbf{B}_0$ , the field exerts a torque  $\tau$  on the particle

$$\tau = \boldsymbol{\mu} \times \mathbf{B}_0. \tag{2.3}$$

The equation of motion of  $\mu$  is therefore

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \gamma_N \frac{\mathrm{d}\boldsymbol{I}}{\mathrm{d}t} = \boldsymbol{\mu} \times \gamma_N \mathbf{B}_0. \tag{2.4}$$

In a rotating reference frame of angular velocity  $\Omega$ , it can be shown via change of coordinates that equation (2.4) becomes

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \boldsymbol{\mu} \times (\gamma_N \mathbf{B}_0 + \boldsymbol{\Omega}). \tag{2.5}$$

By choosing  $\Omega = -\gamma_N \mathbf{B}_0$ , we see that  $\boldsymbol{\mu}$  is static in the rotating reference frame and is thus precessing about  $\mathbf{B}_0$  at the Larmor frequency  $\omega_L = -\gamma_N \mathbf{B}_0$  in the laboratory frame.

If an additional rotating magnetic field  $\mathbf{B}_1$  is applied perpendicular to  $\mathbf{B}_0$  such that

$$\mathbf{B}_0 = \mathbf{B}_0 \hat{\boldsymbol{z}}, \qquad \mathbf{B}_1 = \mathbf{B}_1 (\hat{\boldsymbol{x}} cos(\omega_L t) + \hat{\boldsymbol{y}} sin(\omega_L t)), \qquad (2.6)$$

then, in the  $\mathbf{\Omega} = -\gamma_N \mathbf{B}_0$  rotating reference frame

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \boldsymbol{\mu} \times (\gamma_N \mathbf{B}_0 + \boldsymbol{\Omega} + \gamma_N \mathbf{B}_1 \hat{\boldsymbol{x}}) = \boldsymbol{\mu} \times \gamma_N \mathbf{B}_1 \hat{\boldsymbol{x}}, \qquad (2.7)$$

 $\mu$  will then precess about the rotating frame x-axis at an angular velocity of

$$\boldsymbol{\omega} = \gamma_N \mathbf{B}_1. \tag{2.8}$$

In reality, this allows us to control the orientation of the spins within the sample relative to  $\mathbf{B}_0$ . By placing the sample inside a solenoid, a radio frequency (RF) alternating current can be used to generate  $\mathbf{B}_1$  (the details of which are outlined in appendix (A)). Starting from thermal equilibrium, the total spin is in the direction of  $\mathbf{B}_0$ . According to equation (2.8), for a spin I = 1/2 nucleus, turning on  $\mathbf{B}_1$  for a duration of  $t_{90} = \pi/2\gamma_N |\mathbf{B}_1|$ rotates the spins by 90° about the rotating frame x-axis, while turning it on for a duration of  $t_{180} = \pi/\gamma_N |\mathbf{B}_1|$  rotates the spins by 180°, as shown in figure (2.2).



FIGURE 2.2: (a) Coil with sample in thermal equilibrium, spins are parallel to  $\mathbf{B}_0$ . (b) Spins are perpendicular to  $\mathbf{B}_0$  after  $t_{90}$  pulse. (c) Spins are flipped from (b) after  $t_{180}$  pulse, and remain perpendicular to  $\mathbf{B}_0$ . Image from [15]

For nuclei with spin I > 1/2, quadrupole interactions cause the energies of  $I_z = m \leftrightarrow m+1$  transitions to be different for each set of I and m values. This causes the precession rates about  $\mathbf{B}_1$  in the rotating frame to be faster compared to I = 1/2 nuclei with the same  $\gamma_N$  and  $|\mathbf{B}_1|$  [16]. The rate of precession is proportional to the parameter  $A = \sqrt{I(I+1) - m(m+1)}$ . For example, in our sample Cu<sub>2</sub>IrO<sub>3</sub> with spin 3/2 Cu nuclei,  $t_{90} = \pi/2\sqrt{3}\gamma_N|\mathbf{B}_1|$  and  $t_{90} = \pi/4\gamma_N|\mathbf{B}_1|$  for  $I_z = \pm 3/2 \leftrightarrow \pm 1/2$  and  $I_z = \pm 1/2 \leftrightarrow \pm 1/2$  transitions respectively [17]. A full table of transition rates for given I and m can be found on pages 110-111 of [17].

Following a  $t_{90}$  pulse, the spins, and hence the net nuclear magnetization of the sample, precess about the z-axis in the stationary frame. This induces a current in the solenoid oscillating at the resonant frequency and is known as free induction decay (FID). The amplitude of the current can then be measured using our equipment.

#### 2.3 Spin Echo Pulse Sequence

Measurements of the FID signal are partially obscured by unwanted currents in the solenoid and detection equipment. Random noise can be minimized by repeating the experiment and averaging the signal over many iterations [17]. This increases the signal to noise ratio by a factor of  $\sqrt{N}$  where N is the number of iterations.



FIGURE 2.3: Spin echo pulse sequence

However, a transient noise known as ringdown persists after the RF pulse and may greatly obscure the FID signal. Ringdown is caused by the dissipation of standing waves within the solenoid and nearby conductors, which were built up by the high-energy RF pulse. Since it is coherent with the RF pulse, signal averaging does not reduce ringdown. Thus it requires more sophisticated techniques to be eliminated. One method of mitigating ringdown is by employing a spin echo sequence. Instead of measuring the FID signal, an additional  $t_{180}$  pulse is applied to the sample after time  $\tau$ , as shown in figure (2.3).



 $t = t_{90} + \tau$   $t = t_{90} + \tau + t_{180}$   $t = t_{90} + 2\tau + t_{180}$ 

FIGURE 2.4: Behaviour of nuclear spins within sample during spin echo sequence.  $\hat{x}'$  and  $\hat{y}'$  are  $\hat{x}$  and  $\hat{y}$  in the  $\mathbf{\Omega} = -\gamma_N \mathbf{B}_0$  reference frame. a) The sample is in thermal equilibrium and magnetization is parallel with  $\mathbf{B}_0$ . b)  $t_{90}$  pulse rotates the spins perpendicular to  $\mathbf{B}_0$ . c) Spins are dephased over time  $\tau$ . d)  $t_{180}$  pulse flips the spins. e) Spins realign after time  $\tau$ .

Due to the inherent inhomogeneity of the applied magnetic field  $\Delta \mathbf{B}_0$ , the spins precess at different rates after the  $t_{90}$  pulse, drifting apart from each other at an angular velocity of approximately  $\gamma \Delta \mathbf{B}_0$ . Thus, they dephase over time, causing the FID signal to decay. Since the  $t_{180}$  pulse flips each of the dephased spins about the y-z plane, the spins refocus at time  $2\tau$ , generating a second signal known as a spin echo. Since ringdown dies out approximately 2  $\mu$ s to 50  $\mu$ s after the end of the  $t_{90}$  and  $t_{180}$  pulses, it can be separated from the spin echo signal by a sufficiently long  $\tau$ .

Another technique used to cancel out ringdown is known as phase cycling. The phase of the  $t_{90}$  and  $t_{180}$  pulses, as well as the sign of the observed spin echo are changed for every sequence such that the ringdown is canceled out in the sum of the resulting signals, as its phase is also dependent on the phase of the RF pulses. In our spin echo experiments, a set of 4 spin echo sequences is used [18]:

Sequence 1:  $t_{90}$  about +x' axis,  $t_{180}$  about +x', spin echo is added.

Sequence 1:  $t_{90}$  about -x' axis,  $t_{180}$  about +x', spin echo is subtracted.

Sequence 1:  $t_{90}$  about -x' axis,  $t_{180}$  about +y', spin echo is added.

Sequence 1:  $t_{90}$  about +x' axis,  $t_{180}$  about +y', spin echo is subtracted.

Since only RF pulses near the resonant frequency  $\nu$  will generate a spin echo, the  $\nu$  of certain isotopes in a material (in our case <sup>63</sup>Cu and <sup>65</sup>Cu) can be determined by performing spin echo sequences at varying frequencies and using a phase sensitive detector to observe the signal intensity, which should peak at  $\nu$ , as seen in figure (2.5).



FIGURE 2.5: Theoretical NMR spectrum for resonant frequency  $\nu$ . The width of the resonance peak depends on a variety of factors such as nuclear dipole-dipole interactions, distribution of Knight shift, and quadrupole interaction.

#### 2.4 NMR Electronics

A block diagram of the equipment used in our experiments can be seen in figure (2.6). The RF frequency source generates a continuous RF current of a set frequency. The RF current is then converted into the desired  $t_{90}$  and  $t_{180}$  pulses via TTL gating signals from the Aries, which are then amplified by a factor of 60 dB (i.e. 1000 times) through the power amplifier.

These high voltage pulses from the amplifier are then sent to an RLC circuit inside the NMR probe through a pair of antiparallel series of diodes. Since the diodes each have a well-defined threshold voltage, they are able to eliminate low-voltage noise created by the power amplifier while allowing the intended high voltage RF pulses to pass through. This is especially important during the data-acquisition phase of the pulse sequence as the RF pulses have low voltage tails [17].



FIGURE 2.6: Schematic of NMR spectrometer at Imai labs [18]

The NMR probe which includes the sample and RLC circuit is inserted into a cryostat and sometimes immersed in liquid N<sub>2</sub> or He cryogen. The sample is fitted into the inductor of the RLC circuit. The segment of the cryostat containing the sample is placed in the center of a  $|\mathbf{B}_0| = 9 \text{ T}$  magnet.

To prevent the high-voltage pulses going into the RLC circuit from reflecting back to the power amplifier, the capacitance of the matching and tuning capacitors ( $C_m$  and  $C_t$  respectively) must be changed such that the resonant frequency of the RLC circuit equals that of the RF pulses [17]

$$\omega_0 \approx \frac{1}{\sqrt{L(C_m + C_t)}},\tag{2.9}$$

where  $\omega_0$  is the RF pulse frequency and L is the inductance of the solenoid. Additionally, to maximize the power transfer to the RLC circuit, its impedance must match the characteristic impedance of 50  $\Omega$  of the transmission cable such that

$$\frac{\omega^2 L^2 [1 + C_m/C_t]^2}{r} = 50 \,\Omega,\tag{2.10}$$

where r is the small but non-zero resistance of the solenoid. This gives us 2 degrees of freedom,  $C_t$  and  $C_m$ , to satisfy the 2 conditions (2.9) and (2.10). In our experiments, adjustment of  $C_t$  and  $C_m$  is done manually by connecting the input of the RLC circuit to a network analyzer and tuning the values of  $C_t$  and  $C_m$  until the maximum amount of power is absorbed by the RLC circuit.

Inside the preamplifier box, the quarter-wavelength  $(\lambda/4)$  cable and grounded diodes are used to isolate the sensitive detection equipment from the remains of the RF pulses not absorbed by the RLC circuit. Another pair of antiparallel diodes, similar to those connected to the amplifier, is grounded and used to divert the high voltage RF from the detection equipment while not affecting the low-voltage spin echo signal. Since a standing wave is formed between the output of the power amplifier diodes and the grounded diodes, its amplitude at the grounded diodes can be minimized using the  $\lambda/4$ cable [18]. Additionally, since electrical propagation in the cable is different than in a vacuum, the length of the  $\lambda/4$  cable we use in our experiments is related to the RF frequency by the equation l = 45m/f where l is the length of the cable and f is the RF frequency in MHz [17].

The spin echo signal is collected in the same solenoid containing the sample and is sent back to Aries via the RF preamplifier box. The entire process is controlled using a computer program called MacNMR.

#### 2.5 The Knight Shift

Due to couplings between the spin of magnetic cations (Ir<sup>4+</sup> in our case) and the magnetic moment of nearby electrons, the local magnetic field at the nucleus differs from the applied field  $\mathbf{B}_0$ . Thus, the resonant frequency  $\nu$  is shifted from the Lamor frequency by a factor of (1 + K)

$$\nu = \frac{\gamma_N \mathbf{B}_0}{2\pi} (1+K), \qquad (2.11)$$

where K is known as the Knight shift. The Knight shift comprises of two components, the chemical shift  $K_{chem}$  and the electron spin shift  $K_{spin}$ , such that  $K = K_{spin} + K_{chem}$ . The chemical shift is due to the orbital magnetic moment of the electrons and is dependent on the diamagentic and Van Vleck susceptibility of the orbital electrons, evaluated respectively as [19]

$$\chi_{dia} = -\frac{e^2}{4mc^2} < 0|\sum_i (x_i^2 + y_i^2)|0>, \qquad (2.12)$$

$$\chi_{V.V.} = 2\mu_B^2 \sum_n \frac{|\langle 0|L_z|n \rangle|^2}{E_n - E_0},$$
(2.13)

where  $|n\rangle$  are the excitation states of the orbital electrons.  $x_i$  and  $y_i$  are coordinate operators for the i-th electron, and  $L_z$  is the z-component of the angular momentum operator. Since  $E_n - E_0$  is on the order of  $10^4$  K,  $\chi_{dia}$  and  $\chi_{V.V.}$  (and consequently  $K_{dia}$ and  $K_{V.V.}$ ) are essentially temperature independent when it comes to NMR experiments (unless another orbital level energy  $E_n$  is close to  $E_0$ ).

In contrast, the spin contribution to the Knight shift is temperature dependent and is proportional to the electron spin susceptibility  $\chi_{spin}(T)$  and the spin hyperfine coupling constant A [18] [20]. Thus, the Knight shift is evaluated

$$K = K_{spin} + K_{dia} + K_{V.V.} = (\gamma_e \gamma_n \hbar^2)^{-1} [A \chi_{spin}(T) + A_{orb} \chi_{V.V.}] + K_{dia}, \qquad (2.14)$$

The orbital hyperfine coupling constant is theoretically estimated to be

$$A_{orb} = 2\gamma_e \gamma_n \hbar^2 < (\sum_i r_i)^{-3} >, \qquad (2.15)$$

where  $\langle (\sum_i r_i)^{-3} \rangle$  is the average cubic inverse of the radial distance of the orbital electrons, while  $\gamma_e$  and  $\gamma_n$  are the gyromagnetic ratios of the electron and nucleus respectively. Note that, in our representation, the unit of  $A_{orb}$  is [erg] (omitting a factor of  $\mu_0$ ). The value of A is discussed in the next section. By plotting the experimental data of the Knight shift K against spin susceptibility  $\chi_{spin}$  for a range of temperatures, the hyperfine coupling constant and chemical shift can be determined from the slope and intercept of the linear relation, respectively.

#### 2.6 The Hyperfine Coupling Constant

The spin hyperfine coupling constant is composed of 5 components [20]

$$A = A_{contact} + A_{cp} + A_{dipolar} + A_{spin-orbit} + B_{transfer},$$
(2.16)

where  $A_{contact}$  arises from the Fermi contact interaction between the nucleus and selectron spins.  $A_{cp}$  is from core polarization, where outer electron spins polarize the s-electrons.  $A_{dipolar}$  comes from the dipolar interaction between electron spins and the nucleus.  $A_{spin-orbit}$  is due to the polarization of electron orbits by electron spins [18]. Lastly, the transferred term  $B_{transfer}$  is due to the mixing of states between the selectrons and the electrons of neighboring atoms [20]. In our material Cu<sub>2</sub>IrO<sub>3</sub>, the transferred hyperfine field from neighboring magnetic Ir<sup>4+</sup> ions is the dominant component of the Knight Shift. We define  $A_{hf}$  as the hyperfine coupling strength from one of the neighboring Ir<sup>4+</sup> ions such that

$$A_{hf} = \frac{B_{transfer}}{N_{n.n.}\gamma_N\hbar},\tag{2.17}$$

where  $N_{n.n.}$  is the number of Ir<sup>4+</sup> nearest neighbors and the factor of  $\gamma_N \hbar$  is used to convert the hyperfine coupling constant from units of energy into units of  $[Oe/\mu_B]$ . Thus, to calculate  $A_{hf}$  we use the slope of the K vs  $\chi$  plot in the equation

$$A_{hf} = \frac{\Delta K}{\Delta \chi} \frac{N_A \gamma_e \gamma_N \hbar^2}{N_{n.n.} \gamma_N \hbar} = \frac{N_A \mu_B}{N_{n.n.}} \frac{\Delta K}{\Delta \chi},$$
(2.18)

where  $\chi$  is in units of [emu/mol].

In transition metals, the spin contribution to the Knight shift mainly depends on Fermi contact and core polarization from itinerant s-band and d-band electrons. The Fermi contact contribution from s-electrons is [21]

$$K_s = \frac{8\pi}{3} < |\Psi(0)|^2 >_{\rm F} \chi_p^s, \tag{2.19}$$

where  $\langle |\Psi(0)|^2 \rangle_F$  is the average over the Fermi surface of the probability density of itinerant s-electrons at the nucleus, and  $\chi_p^s$  is the Pauli spin susceptibility of itinerant s-electrons. Similarly, the Knight shift due to core polarization of s-electrons by d-electrons is

$$K_d = -\frac{8\pi}{3} < |\Phi_{cp}(0)|^2 > \chi_p^d(T), \qquad (2.20)$$

where  $\langle |\Phi_{cp}(0)|^2 \rangle$  is defined in [21] and is representative of an admixture of s-electrons due to polarization by itinerant d-electrons, and  $\chi_p^d(T)$  is the temperature-dependent Pauli spin susceptibility of itinerant d-electrons.

#### 2.7 Quadrupole Interaction

An additional interaction affecting the resonant frequency is the energy associated with the electric quadrupole moment of the nucleus and the electric field gradient (EFG) exerted on it by external charges. This results in a quadrupole term in the Hamiltonian [15]

$$\hat{\mathcal{H}}_Q = \frac{1}{6} \sum_{\alpha,\beta} V_{\alpha\beta} Q_{\alpha\beta}^{(\text{op})}, \qquad (2.21)$$

where  $V_{\alpha,\beta}$  is the EFG tensor at the site of the nucleus and  $Q_{\alpha,\beta}^{(\text{op})}$  is the quadrupole operator [15]

$$Q_{\alpha,\beta}^{(\text{op})} = e \sum_{\text{protons}} (x_{\alpha k} x_{\beta k} - \delta_{\alpha \beta} r_k^2), \qquad (2.22)$$

where k is the index for each proton. Since the electric quadrupole operator is dependent on the spin state, the quadrupole Hamiltonian can be written as [16]

$$\hat{\mathcal{H}}_Q = \frac{e^2 q Q}{4I(2I-1)} [3I_Z^2 - I(I+1) + \frac{1}{2}\eta (I_+^2 + I_-^2)].$$
(2.23)

Equation (2.23) is defined in the axis X, Y, Z, which are the principle axis of the EFG tensor  $V_{\alpha\beta}$  such that

$$|V_{ZZ}| \ge |V_{YY}| \ge |V_{XX}|, \qquad eq = V_{ZZ}, \qquad \eta = |\frac{V_{XX} - V_{YY}}{V_{ZZ}}|, \qquad 1 \ge \eta \ge 0.$$
 (2.24)

eq is therefore the EFG along the principal axis of the EFG tensor,  $\eta$  is known as the asymmetry parameter, and eQ is defined as the electric quadrupole moment of the nucleus

$$eQ = \frac{1}{2} \int (3z^2 - r^2)\rho(\mathbf{r})d^3x. \qquad (2.25)$$

In high magnetic fields where the Zeeman interaction is much stronger than the quadrupole interaction the effect the quadrupole interaction has on the energy levels can be calculated using perturbation theory to second order. In the case of an axially symmetric EFG tensor with  $\eta = 0$ , one can show that [16]

$$E_m^{(1)} = \frac{1}{4}h\nu_Q(3\mu^2 - 1)(m^2 - \frac{1}{3}a), \qquad (2.26)$$

$$E_m^{(2)} = -h \frac{\nu_Q^2}{12\nu_L} m [\frac{3}{2}\mu^2 (1-\mu^2)(8m^2-4a+1) + \frac{3}{8}(1-\mu^2)^2 (-2m^2+2a-1)], \quad (2.27)$$

where

$$a = I(I+1), \qquad \mu = \cos \theta, \qquad \nu_L = \frac{\gamma H}{2\pi}, \qquad \text{and} \qquad \nu_Q = \frac{3(eq)(eQ)}{h2I(2I-1)}.$$
 (2.28)

We see that for  $I = 1/2 \leftrightarrow I = -1/2$  transitions (central transitions), the first order energy shift is zero. While for other transitions (satellite transitions), the first order energy shift is the dominant term since  $\nu_L >> \nu_Q$ .

The effect the quadrupole interaction has on the spin state energies thus depends on the relative angle of the crystal to  $\mathbf{B}_0$ . For powder samples with uniform angular distribution of grains, quadrupole effects results in multiple broadened peaks for each transition, as seen in figure (2.7).

#### 2.8 Powder Alignment

To minimize the angle distribution  $\theta$ , the sample can be converted into a uniaxially aligned powder by being suspended in STYCAST 1266 and cured in a strong magnetic field, as shown in figure (2.8). Due to the anisotropy of magnetic susceptibility, the crystals rotate until their easy axis (the direction with the highest magnetic susceptibility) aligns with  $\mathbf{B}_0$ , as this is the most energetically favourable configuration. This was done on our Cu<sub>2</sub>IrO<sub>3</sub> sample. Considering the anisotropic magnetic susceptibilities of Na<sub>2</sub>IrO<sub>3</sub> [7], we expect the crystal c-axis of Cu<sub>2</sub>IrO<sub>3</sub> to align with  $\mathbf{B}_0$ .



FIGURE 2.7: Simulated high-field NMR spectrum of spin  $^{3/2}$  powder sample with large  $\nu_Q$  and  $\eta=0.1.~\nu_Q$ 



FIGURE 2.8: Diagram outlining process of creating a uniaxially aligned powder sample.

### Chapter 3

### **Results and Analysis**

#### 3.1 NMR Lineshapes

Spin Echo experiments were conducted on ~220 mg of Cu<sub>2</sub>IrO<sub>3</sub> powder in an applied field of  $\mathbf{B}_0 = 9 \,\mathrm{T}$ . The RF frequency f is swept through intervals between 75 and 135 MHz for a variety of temperatures ranging between 4.2 K and 298 K, in order to probe the spectrum of transition energies of <sup>63</sup>Cu and <sup>65</sup>Cu with nuclear spin <sup>3</sup>/<sub>2</sub>.

Throughout our experiments, the value of  $\tau$  ranges from  $7 \,\mu s$  to  $30 \,\mu s$  depending on the relative strength of ringdown. Due to the decrease of signal to noise ratio at higher temperatures, up to 15000 scans were needed per data point. The NMR signal intensity I was integrated over the entire duration of the spin echo (approximately  $20 - 30 \,\mu s$ ) and normalized by a factor of

$$\frac{1}{N \times exp(-hf/k_BT) \times f} \sim \frac{T}{Nf^2},\tag{3.1}$$

where  $exp(-hf/k_BT)$  is the Boltzmann factor of the energy splitting and N is the number of scans. The Boltzmann factor accounts for the population difference between spin states at equilibrium, which is proportional to the magnitude of the precessing magnetic moment. We approximate the Boltzmann factor to T/f since  $hf << k_BT$  for the temperatures in our experiments. The additional factor of f is due to the amplitude of the signal being proportional to the precession rate of the sample magnetic moment, which is proportional to f. The result of the frequency sweep for T = 125 K is shown in figure (3.1) for unaligned powder.



FIGURE 3.1:  $^{63}$ Cu and  $^{65}$ Cu full line shape at 125K and  $\mathbf{B}_0 = 9$ T.

We see that due to the large  $\nu_Q$  of Cu(I) (measured to be 26 MHz), the NMR spectra of  ${}^{63}$ Cu and  ${}^{65}$ Cu overlap. It is also apparent that the ratio of the integrated intensity of the  ${}^{63}$ Cu and  ${}^{65}$ Cu central transitions is approximately the natural abundance of the two isotopes, 69% to 31%. As predicted by equation (2.27), the central transitions each contain 2 peaks corresponding to portions of the powder where crystal c-axis is perpendicular to  $\mathbf{B}_0$  (90°) and at a 41° angle to  $\mathbf{B}_0$ . The steep drop in the middle of the central transition corresponds to the c-axis being parallel with  $\mathbf{B}_0$  (0°). We can also see the upper and lower satellite peaks of  ${}^{63}$ Cu in accordance with equation (2.26). The value of  $\nu_Q$  for the Cu(I) and Cu(H) sites were determined by Takahashi *et al.* [22]. Nuclear Quadrupole Resonance (NQR) was conducted on Cu<sub>2</sub>IrO<sub>3</sub> in order to determine the value of  $\nu_{NQR}$  for each Cu site, where

$$\nu_{NQR} = \nu_Q \sqrt{1 + \eta^2}.\tag{3.2}$$



FIGURE 3.2: Measurements of the  $\nu_{NQR}$  of  $^{63}$ Cu and  $^{65}$ Cu H-site and I-sites. Figure acquired from [22].

As temperature decreases, defect spins polarized by  $\mathbf{B}_0$  increasingly broaden the NMR peaks. It was observed by Kenny *et al.* [23] that a fraction of the Cu(H) sites were occupied by spin 1/2 Cu<sup>2+</sup> ions instead of Cu<sup>1+</sup>. Charge conservation thus implies that some of the spin 1/2 Ir<sup>4+</sup> sites are occupied by spinless Ir<sup>3+</sup> atoms. Though the temperature dependence of the broadening is reminiscent of RKKY spin oscillations, the effect of defect spins on Cu<sub>2</sub>IrO<sub>3</sub> and other Iridates has not yet been fully understood in current theoretical condensed matter research. The Knight shift can be observed qualitatively as the 41° and 90° peaks shift towards higher frequencies as temperature decreases. However, since the width of the 90° and 41° peaks exceed the scale of the Knight shift, it is difficult to deduce the Knight shift using an unaligned powder sample. In order to accurately quantify the Knight shift, we aligned the sample powder using the process described in section (2.8). NMR frequency sweeps were done for a set of temperatures on the uniaxially aligned sample with the crystal c-axis mounted both parallel and perpendicular to  $\mathbf{B}_0$ . The resulting lineshapes are shown in figure (3.3) in comparison to the unaligned powder results.



FIGURE 3.3: Side by side  $\mathbf{B}_0 = 9T$  NMR lineshapes at various temperatures. The lineshapes for each temperature are cascaded over one another in order to emphasize the movement of the peaks. The 3 plots are categorized as a) c-axis mounted perpendicular to  $\mathbf{B}_0$ , b) c-axis mounted parallel to  $\mathbf{B}_0$ , and c) unaligned powder. The blue, red, and green arrows indicate the Cu(I) 90° peak, Cu(I) 0° peak, and Cu(H) 0° peak respectively. The vertical black line in each plot represents the Larmor frequency for bare nuclear spins with no shifts.

We immediately notice that the Knight shift can be more accurately determined from the aligned powder lineshapes. However, residual Cu peaks can be seen in aligned powder lineshapes since a fraction of the powder failed to align. The small peaks near 101.7 MHz and 101.3 MHz are likely from Cu metal and Na respectively, as the probe itself is partially composed of Cu metal, and the process of synthesizing  $Cu_2IrO_3$  leaves Na impurities at the Cu lattice sites. Due to its proximity, the Cu metal signal slightly shifts the apex of the Cu(I) 0° peak, leading to a higher range of error.

Cu(H) only has 1/3 times the occupancy of Cu(I). Moreover a twice larger  $\nu_Q$  of approximately 52 MHz decreases the peak intensity of its central transition by an additional factor of 4 via broadening. Therefore, Cu(H) peaks in the NMR lineshape are much smaller and broader than that of Cu(I). Due to its high quadrupole shift, the  $^{63}$ Cu(H) 90° central peak is likely overshadowed by the  $^{65}$ Cu(I) central transition in the c  $\perp$  **B**<sub>0</sub> lineshapes. However, in the c  $\parallel$  **B**<sub>0</sub> lineshapes, there appears to be small bumps between 102MHz to 103MHz at 100 K and below, while above 100 K, they become hidden by the Cu(I) 0° peak. We attribute these bumps to be the 0° signal from Cu(H) sites. The Knight shift of these peaks are thus tracked for the rest of the experiment.

#### 3.2 Quadrupole Correction

To isolate the Knight shift from the temperature independent quadrupole shift, NMR lineshapes were measured at the peak frequencies of Cu(I) 90°, Cu(I) 0°, and Cu(H) 0° with T = 295 K and varying the external field **B**<sub>0</sub> to values between 6.8 T and 9.0 T.



FIGURE 3.4: Lineshapes of <sup>63</sup>Cu at select values of  $|\mathbf{B}_0|$ . The lineshapes are zoomed in on a) the Cu(I) 0° peak, b) the Cu(I) 90° peak, and c) the Cu(H) 0° peak. The x-axis is scaled by  $1/\gamma_N \mathbf{B}_0$  for each value of  $|\mathbf{B}_0|$  so that the apparent Knight shift is clearly observable.

We plot the apparent Knight shift of the peak  $\nu$  from the Larmor frequency  $\nu_L = \gamma_N |\mathbf{B}_0|/2\pi$ , defined as  $K_{apparent} = (\nu - \nu_L)/\nu_L$ , in figure (3.5) as a function of  $1/\nu_L^2 \propto 1/|\mathbf{B}_0|^2$ . We can linearly extrapolate  $K_{apparent}$  to  $1/\nu_L^2 \to 0$  to calculate the true Knight shift K. This is because second order quadrupole approximation of  $\nu$  can be rearranged into the form of

$$\nu = \gamma_N |\mathbf{B}_0| (1+K) + \frac{D}{\gamma_N |\mathbf{B}_0| (1+K)}$$

$$\implies \frac{\nu - \gamma_N |\mathbf{B}_0|}{\gamma_N |\mathbf{B}_0|} = K_{apparent} \approx K + \frac{D}{\gamma_N |\mathbf{B}_0|^2},$$
(3.3)

where D is constant with respect to  $|\mathbf{B}_0|$ , and can be calculated using equations from section (2.7). The straight lines in figure (3.5) shows the results of the linear extrapolation.



FIGURE 3.5: Plot of  ${}^{63}K_{apparent}$  vs  ${}^{1}/(\gamma_{N}\mathbf{B}_{0})^{2}$  used to isolate the Knight shift from the quadrupole shift for Cu(I) 0°, Cu(I) 90°, and Cu(H) 0°.

It can be seen that there is almost no quadrupole shift for the Cu(I) 0° and Cu(H) 0° peaks, which implies that the  $\eta$  of the EFG tensor at the Cu(I) and Cu(H) sites are close to 0. This is consistent with the axial symmetry of these Cu sites about the c-axis. Using the slope of the 90° data, we calculate that for an external field of  $|\mathbf{B}_0| = 9$  T, a quadrupole correction of -1.086% must be applied to the apparent Knight shift of Cu(I) 90° to get its true Knight shift.

#### 3.3 Temperature Dependence of Knight Shift

After correcting for quadrupole effects, the Knight shift of Cu(I) 0°, Cu(I) 90°, and Cu(H) 0° are plotted against temperature alongside the spin susceptibility  $\chi_{spin}$  of Cu<sub>2</sub>IrO<sub>3</sub>, as shown in figure (3.6).



FIGURE 3.6: Temperature dependence of Knight shift of Cu(I) 0°, Cu(I) 90°, and Cu(H) 0°. The Knight shift  ${}^{63}K$  is superimposed onto the spin susceptibility  $\chi_{spin}$  of Cu<sub>2</sub>IrO<sub>3</sub>.

Since the paramagnetism of Cu<sub>2</sub>IrO<sub>3</sub> comes mainly from the magnetic Ir<sup>4+</sup> ions, we find the spin susceptibility  $\chi_{spin}$  by subtracting the Van-Vleck and diamagnetic susceptibility of Ir<sup>4+</sup> and Cu<sub>2</sub>IrO<sub>3</sub> respectively (both of which are constant over our temperature range) from the bulk susceptibility  $\chi$  of Cu<sub>2</sub>IrO<sub>3</sub>, such that

$$\chi_{spin} = \chi - \chi_{dia} - \chi_{V.V.}, \qquad (3.4)$$

where the  $\chi_{dia}$  of Cu<sub>2</sub>IrO<sub>3</sub> is estimated to be  $-0.089 \times 10^{-3} emu/mol$  (using the  $\chi_{dia}$  of individual ions from [24]) and  $\chi_{V.V.}$  is reported to be  $0.16 \times 10^{-3} emu/mol$  by [10]. The temperature dependence data of  $\chi$  comes from [12].

We see that the behaviour of the Knight shift follows that of  $\chi$  down to approximately 50 K. Since the Knight shift is influenced only by the intrinsic spin susceptibility, the upturn of bulk susceptibility  $\chi$  below 20 K in Cu<sub>2</sub>IrO<sub>3</sub> is likely due to the susceptibility of defect spins.

The difference in the  $0^{\circ}$  and  $90^{\circ}$  Knight shift of Cu(I) indicates that the hyperfine coupling between Cu(I) and  $Ir^{4+}$  is anisotropic and stronger along the ab-plane. We also see that along the c-axis, Cu(H) has stronger hyperfine coupling than Cu(I) due to its geometric proximity to the Ir atoms.



FIGURE 3.7: Temperature dependence of Knight shift of honeycomb and interlayer sites of <sup>23</sup>Na in Na<sub>2</sub>IrO<sub>3</sub>.  $T_N$  represents the Néel temperature of Na<sub>2</sub>IrO<sub>3</sub>. This data is from [22].

The temperature dependence of the Knight shift of  $^{63}$ Cu in Cu<sub>2</sub>IrO<sub>3</sub> is qualitatively similar to that of  $^{23}$ Na in Na<sub>2</sub>IrO<sub>3</sub>, shown in figure (3.7). The ratios between the Knight shift of the honeycomb and interlayer sites,  $\approx 2.5$ , are close for  $^{63}$ Cu and  $^{23}$ Na. This supports the hypothesis that the small peaks in figure (3.3) (B) are indeed Cu(H).

Thus, we have successfully used NMR to determine the intrinsic spin susceptibility of Cu<sub>2</sub>IrO<sub>3</sub>. Additionally, Cu<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> are similar in terms of  $\chi_{spin}$ , while greatly differing in the behaviour of spin relaxation rate  $1/T_1$  [22].

#### 3.4 Knight Shift vs Bulk Susceptibility

According to equation (2.14),  $\chi_{spin}$  is proportional to the spin shift  $K_{spin}$  of both Cu (I) and Cu (H) sites in the absence of a chemical shift. Thus, to get the hyperfine coupling constant  $A_{hf}$ , we create a K vs  $\chi_{spin}$  plot using the data from figure (3.6). The result is shown in figure (3.8).



FIGURE 3.8: <sup>63</sup>K vs  $\chi_{spin}$  plot for Cu(H) and Cu(I) sites. A linear fit with an assumed vertical intercept of 0 is used to calculate  $\Delta K/\Delta \chi$  for each of the 3 species. The defect-dominated region corresponds to temperatures below 50 K where the value of  $\chi$  is greatly altered by defect spins. Thus, only the data points above 50 K are considered in the linear fit.

Outside the defect-dominated region (color shaded light blue), the Knight shifts of all 3 species appear proportional to  $\chi_{spin}$  within their ranges of error. From figure (1.5), we know that Cu(I) sites have 4 Ir<sup>4+</sup> nearest neighbors while Cu(H) sites have 6 Ir<sup>4+</sup> nearest neighbors. Hence, the hyperfine coupling constant  $A_{hf}$  between each pair of Cu and Ir<sup>4+</sup> ions can now be calculated for the 3 types of Cu using the equation (2.18). The values of  $A_{hf}$  are reported in table (3.1).

	Cu(I)-c	Cu(I)-ab	Cu(H)-c
$A_{hf}[kOe/\mu_B]$	$2.3 \pm 0.1$	$7.6\pm0.1$	$4.4\pm0.2$

TABLE 3.1: Calculated values of  $A_{hf}$ 

In general  $Cu^{2+}$  ions have an additional Van-Vleck contribution to the Knight shift as large as ~ 1% due to the hole in their 3d orbitals [20]. The Cu(H) site we have observed, which has a vertical intercept of ~ 0%, cannot come from Cu<sup>2+</sup>. Thus, the Cu(H) sites observed in our NMR experiments are occupied by Cu<sup>1+</sup>.

Comparing our results to that of <sup>35</sup>Cl in  $\alpha$ -RuCl<sub>3</sub>, as shown in figure (3.9), we see that the Knight shift of <sup>35</sup>Cl is also anisotropic and linear to the bulk susceptibility at high temperatures. However, the saturation of K vs  $\chi$  in Cu<sub>2</sub>IrO<sub>3</sub> at low temperature is not present in the K vs  $\chi$  of  $\alpha$ -RuCl<sub>3</sub>, which instead has a slight upturn below 75K.



FIGURE 3.9: NMR shift of <sup>35</sup>Cl in  $\alpha$ -RuCl<sub>3</sub> with inset of K vs  $\chi$ , measured at  $|\mathbf{B}_0| = 15$  T by Baek *et al.*. The blue and red data represent the  $c' \parallel \mathbf{B}_0$  and  $c' \perp \mathbf{B}_0$  crystal orientations respectively. Figure from [14]

### Chapter 4

# Conclusion

#### 4.1 Summary

In this investigation, high field NMR techniques were used on a uniaxially aligned powder sample of Cu<sub>2</sub>IrO<sub>3</sub> to probe its intrisic spin excitations. It was determined that the temperature dependence of the Knight shift is linear to  $\chi$  down to 50 K, behaving as  $K \propto A_{hf}\chi_{spin}$ , and that the low temperature behaviour of  $\chi$  is likely due to defect spins in the lattice. Additionally, the similar Curie-Weiss temperature of Cu<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> observed by Abramchuk *et al.* was further supported by their nearly-identical behaviour of  $\chi_{spin}$  above 17 K. Finally, the hyperfine coupling constants of Ir<sup>4+</sup> to Cu sites were determined to be  $2.3 \pm 0.1[kOe/\mu_B]$ ,  $7.6 \pm 0.1[kOe/\mu_B]$ , and  $4.4 \pm 0.2[kOe/\mu_B]$ for Cu(I)-c, Cu(I)-ab, Cu(H)-c respectively.

### Appendix A

# Chapter 2 Supplement

Instead of a magnetic field rotating about the z-axis (parallel to  $\mathbf{B}_1$ ), a solenoid around the sample positioned perpendicular to the z-axis generates a linear oscillating field of the form

$$\mathbf{B} = 2B_1(\hat{\boldsymbol{x}}cos(\omega_L t))$$
  
=  $B_1(\hat{\boldsymbol{x}}cos(\omega_L t) + \hat{\boldsymbol{y}}sin(\omega_L t)) + B_1(\hat{\boldsymbol{x}}cos(\omega_L t) - \hat{\boldsymbol{y}}sin(\omega_L t))$  (A.1)  
=  $\mathbf{B}_1 + \mathbf{B}'_1$ ,

in the stationary reference frame, where

$$\mathbf{B}_{1}^{'} = \mathbf{B}_{1}(\hat{\boldsymbol{x}}cos(\omega_{L}t) - \hat{\boldsymbol{y}}sin(\omega_{L}t)), \qquad (A.2)$$

which, in the  $\mathbf{\Omega} = -\gamma_N \mathbf{B}_0$  rotating frame becomes

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \boldsymbol{\mu} \times \gamma_N \mathrm{B}_1 \boldsymbol{\hat{x}} + \boldsymbol{\mu} \times \gamma_N \mathrm{B}_1 (\boldsymbol{\hat{x}} \cos(2\omega_L t) - \boldsymbol{\hat{y}} \sin(2\omega_L t)).$$

$$\boldsymbol{\mu} \times \gamma_N \mathrm{B}_1 \boldsymbol{\hat{x}} + \boldsymbol{\mu} \times \gamma_N \mathbf{B}_1'.$$
(A.3)

Equation (A.3) is similar to that of equation (2.7) except  $\boldsymbol{\mu}$  undergoes an additional precession about a field rotating about the z-axis at an angular velocity  $2\omega_L$ . However, since  $2\omega_L >> \gamma_N B_1$ , precession of  $\boldsymbol{\mu}$  about  $\mathbf{B}_1$  is relatively static compared to its precession about  $\mathbf{B}'_1$ . Integrating over its period for a static and arbitrary  $\boldsymbol{\mu}_0$ 

$$\frac{\mathrm{d}\boldsymbol{\mu}}{\mathrm{d}t} = \boldsymbol{\mu}_0 \times \gamma_N \mathbf{B}_1',\tag{A.4}$$

we see that  $\boldsymbol{\mu}$  simply precesses about a fixed point with radius  $|\boldsymbol{\mu}_0|\gamma_N B_1/2\omega_L \ll |\boldsymbol{\mu}_0|$ , which is too fast and small compared to the precession about  $\mathbf{B}_1$  to alter its trajectory. Thus the behaviour of  $\boldsymbol{\mu}$  reduces to that of equation (2.7) when inside a linear oscillating field.

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