

Magnetic ordering of quantum magnets: Locating Chlorine resonance in organic quantum magnets using nuclear quadrupole resonance spectroscopy and testing newly designed spectrometer.

Estefania Perez del Solar
University of Florida

Mentored by Dr. Neil Sullivan
University of Florida

Abstract

Chlorine's magnetic structure within a crystal makes an ideal place to use nuclear quadrupole resonance techniques in order to understand the magnetic structure of a whole organic magnet. NQR measurements were done on the chlorine sites of two known crystals and one unknown quantum magnet in order to study the magnetic structure. A superheterodyne NMR spectrometer was built and tested to conduct to the study.

Introduction

The focus of this experiment was to study the magnetic ordering and critical fields of organic quantum magnets by using nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) techniques. The magnet used in this particular experiment was $\text{NiCl}_2 \cdot 4\text{SC}(\text{NH}_2)_2$ - which goes by the name of DTN. Bose-Einstein condensation (BEC) was found in these crystals and it is a potential candidate to locate the never before seen behavior of Bose-Glass (BG). The ultimate goal of this experiment was to find Bose-Glass behavior in DTN crystals. This was accomplished by studying the magnetic structure of the crystal when placed inside a high magnetic field and low temperature environment. The transition between BEC to BG in bosons is the analog of the metal-to-insulator transition in fermions.

DTN has high symmetry at the chlorine sites and because of this it has a smaller number of inequivalent symmetries at the Cl sites, making it an optimum area for finding clear signals that resolve the fine structure of DTN. In order to do this it is necessary to first find the unknown NQR absorption frequency for Cl. This frequency could be anywhere in the range of 25 to 40 MHz. This is where my work comes in; I conducted the search for this NQR resonance in Cl using a newly built spectrometer designed to be used not only specifically for this experiment but also for future NQR experiments. I first attempted to observe the NQR frequency in a zero-field, room temperature setting before observing it in a high field, low temperature environment.

The first part of the project was to learn how the spectrometer works in order to do some tests on it to make sure it was working properly. Two samples with known resonances were used, Sodium Chlorate and para-Dichlorobenzene, to test the spectrometer and the labview program that was written to control it. The details of the tests will be explained later. A few of the components for the circuit were also made. The second part involved placing the actual DTN crystals in the spectrometer to find the NQR frequency. Since only a range of where the resonance frequency might be found is known, a frequency sweep using increments of 20 KHz was done in order insure that the resonance was not missed.

Details of new spectrometer

As mentioned previously, a superheterodyne NMR spectrometer was built for this experiment. Although the lab is already equipped with one that works fine, it is not very user friendly and is bulky and a little out dated. This new spectrometer was designed to be used by people who have limited background knowledge on NMR so it can be used for a wider variety of experiments. The spectrometer itself also has several innovative and unique features, making it the only one of its kind. For example, it has a broad band of several hundred MHz, which makes it ideal for searching for and measuring broad NMR spectrum lines in systems that have strong local magnetic fields. This feature also allows for studying structures with unknown resonances. Secondly, the

superhet is that it also has a built-in phase shifter that allows the user to change the phase between its outputs.

The primary goal of this experiment was to find the resonance frequency of the Chlorine atoms within the lattice of the DTN crystal.

This is done by placing the sample crystal in an NQR spectrometer. The ability of this spectrometer to measure the frequency comes from being able to apply RF (radio frequency) pulses on this sample that is placed within a copper coil. The RF pulses knock the spins of the nucleus out of stability, and then the signal created by the precession of the nucleus back into stability is measured by an oscilloscope so the signal can be observed. This signal is called Free Induction Decay (FID). By measuring the FID, the magnetic structure of the crystal can be determined.

NMR and NQR

The technique used for this experiment is Nuclear Quadrupole Resonance. To understand it, it is better to first explain what NMR is. Nuclear magnetic resonance uses the fact that the nucleuses of certain atoms behave like magnetic dipoles, and due to their spin they have an intrinsic angular momentum. Samples that want to be studied are placed with a high enough magnetic field that it aligns the nucleuses of the atoms with it. Then these samples are pulsed with RF pulses at particular intervals and this throws the spin out of alignment, like mentioned above, and the observed precession

signal back into equilibrium is the information used to determine the structure or composition of a sample.

In NQR, it is not necessary to place a sample in a magnetic field in order to study its structure. Since the nucleuses are aligned into quadrupoles, the rotations caused by precession in a magnetic field are far more complicated to keep track of. Instead if the magnetic structure is stable enough, when pulsed with the right RF, it shakes the crystal lattice, it starts to vibrate, and eventually reaches equilibrium again. This creates a measurable FID signal. This does not mean that the sample can not be placed in a magnetic field. Further along in this experiment, the DTN crystal will be placed in a high magnetic field and low temperature environment. NQR deals with solid crystal, whereas NMR deals mostly with gases and liquids.

Setting up the circuit and apparatus

In order to actually measure the FID signal, the sample must be placed inside a copper coil that will serve as both the receiver and transmitter coil. Figure 1 shows the two coils made for two different samples that were used to test the spectrometer.



Figure 1: Right, sodium chlorate coil. Left, para-Dichlorobenzene coil.

The amount of turns the coil has is proportional to the inductance of the coil, an important value to know because this coil will be connected to a tuning capacitor box that will allow the reduction of the noise between the coil and the frequency produced by the signal generator. The relationship between the three is

$$\omega^2 * C * L \sim 1, \quad (1)$$

where ω is the resonance frequency, C is the capacitance, and L is the inductance of the coil. A suitable tuning capacitor box was also built that allowed for both fine and coarse tuning for maximum precision. The general structure for a capacitor box consists of two capacitors in series and two in parallel inside the box with the knobs and/or screws to adjust them outside the box. I first built one that had too little capacitance and the screws were too fine, so tuning was difficult. Consequently, the job was sent to the electronic shop where a larger box with two coarse capacitors and two fine capacitors was built. This one had three actual knobs instead of screws and one screw-in capacitor, which made it far easier to tune. Although the shop made the box itself, I properly soldered the capacitors together. The receiver coil was connected to one side of the capacitor box, and the other side was connected to a hybrid tee.

In order to find the resonance of the coil, the hybrid tee was connected to both the signal generator and the oscilloscope. The frequency output of the signal generator depends on the sample placed within the coil. To test it I made a six turn coil of .75 in. in diameter and 1 in. in height with an inductance of $L = .5 \mu\text{H}$. A glass tube with sodium

chlorate was placed within the coil. The tube was sealed to prevent humidity from ruining the sample. The reason sodium chlorate was chosen as a good testing sample is because extensive NQR studies have shown the crystal to have a nice symmetric structure that provides strong and clear signals at the known resonance frequency of $\omega=29.93$ MHz [1].

After carefully adjusting the capacitance, it was possible to lower the signal on the oscilloscope to just noise. The less interference between the coil and the resonance frequency the better, because when an RF pulse hits the sample, the signal to noise ratio will lower and it will be easier to observe the free induction decay. The noise level was reduced to about 5 mV.

From the hybrid tee, the connection to the signal generator was removed and connected to the RF power amplifier. Then, the connection to the oscilloscope was replaced by a fast recovery broadband amplifier that led the signal to the spectrometer.

After everything was properly connected, the superhet and the power amplifier were turned on. The oscilloscope was set to trigger externally by the superhet and also to signal average in order to see a clearer signal and reduce the noise. Using a labview program that was written to control the pulses created by the superhet, an RF pulse of $T_a=40\mu s$ was applied to the coil. The signal generator was then connected directly to the spectrometer where a National Instrument Time Card added 20 MHz to the pulse. Consequently, the signal generator needed to compensate for this addition. In the case

of sodium chlorate, $f_0 = 29.93$ MHz, so the signal generators needs to read $f=49.93$ MHz. If the RF is at the right frequency, this pulse knocks the Cl quadrupole out of stability.

Finding the FID signal for known test sample

Both Sodium Chlorate (NaCl_3) and para-Dichlorobenzene (DCB) were used as test samples. NaCl_3 was used first. A clear signal was found at $f=29.93221$ MHz. In Figure 2, the Free Induction Decay for this sample can be seen. The next step was to see how far off resonance is it possible to see the FID. It was determined that it has to be within 100 kHz of the resonance frequency in order to see appreciable amplitude of the FID. Knowing this is helpful because it shows that when trying to find the FID of the unknown DTN, increments of at least 100 kHz intervals must be taken to make sure that the resonance is not skipped over.

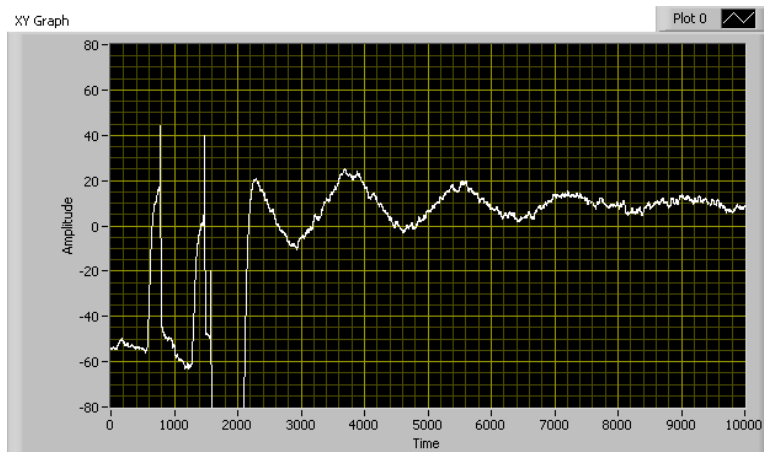


Figure 2: $T_a = 50\mu\text{s}$ pulse, $f = 49.93221$ MHz, $\text{avg} = 700$ count.

Next, para-Dichlorobenzene was used to double check that the apparatus worked properly. A six turn coil of 1.25 in. diameter and 1 in. in length was made to hold the glass vial. The inductance of such a coil is $L \approx 1.2 \mu\text{H}$ [2]. The Q for the coil was very high (~ 814), making it a little difficult to find the resonance. A couple of the turns of the coil were removed and resistance of $R = 17.86 \text{ k}\Omega$ was added to the tuning box to reduce the Q. $Q = f/\Delta f$, where f is the resonance frequency and Δf is frequency at which sample still resonates outside of f (HWHH). With the added resistance, $Q = 513$. It is known that $f = 34.25 \text{ MHz}$ for DCB at $T = 300\text{K}$ [3]. After connecting the sample to the spectrometer, a frequency sweep of .01 MHz intervals was done between 34.20 and 34.31 MHz. Figure 3 shows that a sharp and clear FID signal was found at $f = 34.26471 \text{ MHz}$ with a room temperature of $T \sim 290\text{K}$.

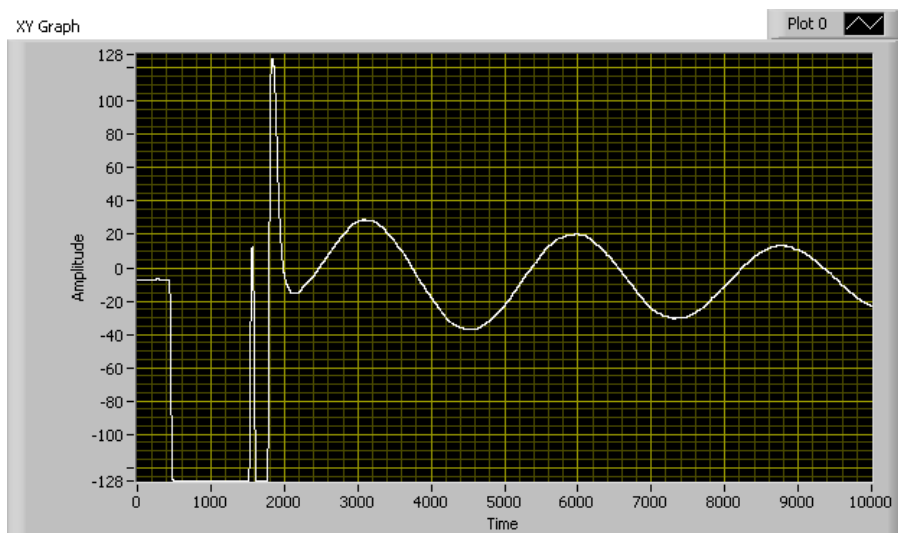


Figure 3: $T_a = 40 \mu\text{s}$ pulse, $f = 34.26471 \text{ MHz}$, 1000 count avg.

The next step was to immerse the sample in liquid nitrogen to see if it reduced the signal to noise ratio being picked up by the coil. In order to do this, a 4 in. coaxial

cable was added to the sample end in order to submerge it into LN2 bath within a styrofoam container. It was estimated that the approximate resonance frequency at $T=77K$ is $f \sim 34.8125$ [3]. Tuned coil to this frequency. Placing the sample within nitrogen increased the sensitivity tuning capacitor box. I connected the sample to the spectrometer and began a frequency sweep around this area and found a crisp signal at $f = 34.81251$ MHz. Figure 4 shows a graph of this signal, which has a clearer signal than the other two previous ones.

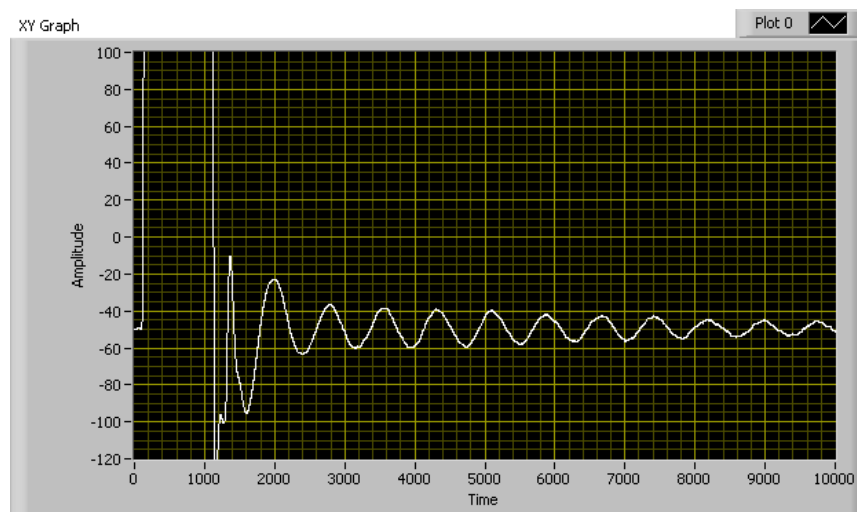


Figure 4: $T_a=40 \mu s$, $f=54.81251$ MHz, avg count=1000

Calculating the noise level for the sample at $T=292K$ and $T=77K$ using Eq. (2),

$$\langle v^2 \rangle^{1/2} = \sqrt{4K_b T \cdot R \cdot B}, \quad (2)$$

where T is temperature, R is the resistance, B is the bandwidth, and K_b is Boltzmann's constant, it was determined that having the sample submerged in liquid nitrogen reduced the noise level by 60%.

Testing DTN crystal for CI resonance

The DTN crystals used were $\sim 1/4$ in. long and $\sim 1/8$ in. thick. They were smaller than originally expected, so a smaller coil was made to accommodate this. A 15-turn coil with $L=2.3 \mu\text{H}$ was made. The resonance of the coil was found at $f=33.20531$ MHz. Since the only thing known about the resonance frequency of the CI quadrupole in DTN is that it may lie between 25-40 MHz range, a sweep between these frequencies was done using 20 kHz intervals, to make sure that it was not possible to skip over the resonance. Figure 5 is a photo of the DTN crystal used in the experiment.



Figure 5: DTN crystals used in the experiment. Diameter of $\sim 1/4$ in. long and $\sim 1/8$ in. thick.

In order to do this sweep, the coil needed to be tuned at a particular frequency first, for example $f=33.20$ MHz, before connecting it to the spectrometer. Afterwards, the sample coil was joined to the spectrometer, and using the signal generator, increments of 20 kHz were added until reaching 500 kHz above and below the tuned frequency. In this manner, covering 1 MHz at a time. Then the coil was disconnected from

spectrometer and retuned to 1 MHz above or below, reconnecting it to the spectrometer and doing a megahertz sweep again. In this way the range from 24.22794 to 40.72794 MHz was completed.

Conclusion

Unfortunately the resonance frequency of the Cl quadrupole in DTN was not found, possibly due to several reasons. First, the crystals were too small, which meant that the coil size had to decrease significantly in order to accommodate them. Reducing the size of the coil reduces its inductance and hence reducing the quality factor, making it harder to observe any signal. It probably would have been better if one larger crystal could be used as opposed to several small ones. Although the sample was not placed within a magnetic field, the different orientations of each individual crystal lattice could have somehow interfered with each, canceling out any potential signal. Placing the sample within liquid nitrogen might have helped, but it was impractical considering how long it took to sweep over 1 MHz and how fast liquid nitrogen boils off.

Even though the Cl resonance was not found at this stage of the experiment, possible improvements might allow success. Placing the sample in a high magnetic field is a possibility, although doing so complicates the whole ordeal because of the tensor nature of the quadrupole. However, placing the sample in a magnetic field might allow for measurements of the resonance. It is possible that the resonance can not be found, but hopefully future experiments will prove that otherwise. Although the ultimate goal of

the experiment is to find the critical fields and phase shift of an organic quantum magnet, like DTN, and observe the Glass-Bose behavior, this work is beyond the scope of this project.

Acknowledgments

The author wishes to acknowledge the summer REU program at the University of Florida for allowing this opportunity to do research, Dr. Hershfield for facilitating and running the program, and Dr. Sullivan for being a great adviser and allowing for this research to be done in his lab. Also, the author thanks the National Science Foundation for providing the funding for this program.

References

- [1] E.R. Andrew, *Nuclear Magnetic Resonance* (Cambridge University, London, England, 1969).
- [2] American Radio Relay League, *Radio Amateur's Hand Book* (Concord, New Hampshire, 1958).
- [3] S. Ganguly, J.R. Fernandes, D. Bahadur, and C.N.R. Rao, *J. Chem. Soc.* **75**, 923, (1979).