Building a Loop-Gap Resonator for X-Band EPR Spectroscopy

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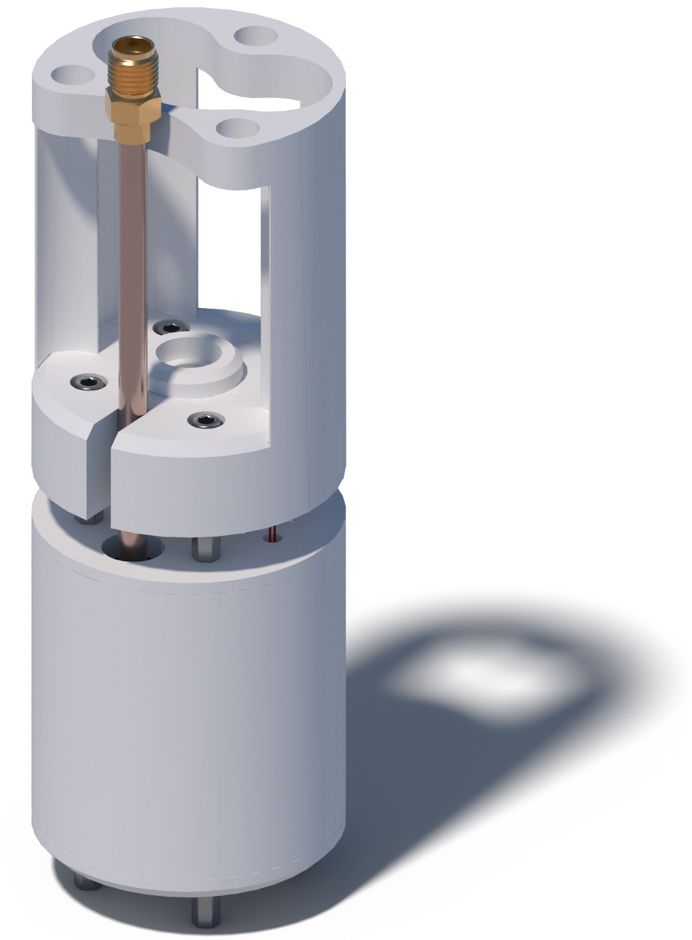

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1 Introduction

In the 1980s the loop-gap resonator (LGR) was introduced to EPR (electron paramagnetic resonance) spectroscopy by Hyde et Al as an alternative to the widely used rectangular TE_{102} or the cylindrical TM_{110} EPR cavity [1]. This new type of resonator was progressively improved to include the concepts of multiloop, multigap resonators [2]. In recent years, there has been a growing interest in developing low-cost and portable EPR spectroscopy systems for a wide range of applications, including in Physics, Chemistry, Biology, and medicine. One promising approach to achieving this goal is the use of a loop-gap resonator, which is a type of resonant circuit that can be used to generate and detect EPR signals. LGRs are particularly attractive for pulsed EPR spectroscopy due to their large filling factor, low quality factor, and low cost of fabrication. In this paper, recent advances in the use of LGRs for EPR spectroscopy will be discussed, including the design and characterization of LGRs, the optimization of EPR measurements using LGRs, and the application of LGR-based EPR spectroscopy in various fields. The construction of a loop-gap resonator based on Bridge12's design will be detailed and areas where further research is needed will be identified.

1.1 Theoretical background

As the name suggests, EPR spectroscopy applies to paramagnetic materials, i.e. materials that have unpaired electrons, e.g. biological enzymes or semiconductors. Electrons have an intrinsic magnetic moment property called spin which can be thought of as the particle "spinning" around its own axis. The associated spin quantum number S has magnetic components $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$. When subjected to a magnetic field B_0, the electron's magnetic moment aligns itself to the field either parallel ($m_s = \frac{1}{2}$) or anti-parallel ($m_s = -\frac{1}{2}$). Due to Zeeman splitting, their respective energies can be expressed as follows:

$$E = m_s g_e \mu_B B_0 \tag{1}$$

where:

g_e = is the electron's g-factor,
μ_B = is the bohr magneton ($= 9.274 \times 10^{-24}$ J·T^{-1}).

The g-factor, sometimes called the g-value, is a dimensionless quantity that characterizes the magnetic moment and angular momentum of a particle, an atom or the nucleus. For a free electron, $g = 2,0023$. The separation of energy level

$$\Delta E = g_e \mu_B B_0 \tag{2}$$

implies that the splitting is directly proportional to B_0, see on Figure 1.

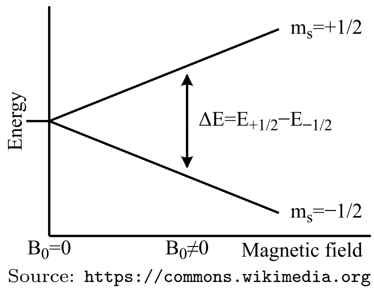

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Figure 1: EPR splitting

An unpaired electron can absorb or emit a photon of energy $h\nu$. This will change its energy according to the resonance condition $h\nu = \Delta E$. From Equation 2, the fundamental equation of EPR spectroscopy is found to be:

$$h\nu = m_s g_e \mu_B B_0 \ . \tag{3}$$

During an EPR spectrometer spectra measurement, electromagnetic radiation (photons) is blasted at the sample while a magnetic field is applied. Both the frequency of the electromagnetic radiation and the strength of the magnetic field can be varied, although in practise the frequency is usually kept constant and the field strength is swept. The frequency is most often found to be in the X-band region ($9-10$GHz) with fields of about 3500G.

When the sample is exposed to fixed frequency electromagnetic waves, the magnetic field is increased until the energy gap between the two spin states ($m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$) matches the energy of the microwave radiation. At this point the unpaired electrons can move between the two states and since there are typically more electrons in the lower state due to the Maxwell-Boltzmann distribution, a net absorption of energy is observed. The Maxwell-Boltzmann distribution expresses the ratio of upper and lower energy states as:

$$\frac{\eta_{upper}}{\eta_{lower}} = \exp\left(-\frac{h\nu}{kT}\right) \tag{4}$$

where:

η_{upper} = is the number of paramagnetic centers in the upper energy state,
η_{lower} = is the number of paramagnetic centers in the lower energy state,
k = is the Boltzmann constant ($= 1.381 \times 10^{-23}$ J·K^{-1}),
T = is the temperature.

At $T = 298$ K and $\nu = 9,75$ GHz, $\eta_{upper}/\eta_{lower} \approx 0,998$ so there are a few more paramagnetic centers in the upper energy level than in the lower one. Note that lower the temperature has an immediate effect of lowering that ratio, thus increasing the microwave absorption and improving the sensitivity of the measurement. Note that a high spectrometer frequency is also desirable to minimize the minimal number of detectable spins. The first derivative of the absorption is usually taken and displayed as spectra as it tends to be sharper and more refined, making it easier to identify and quantify the individual spectral components. It also has the added benefit of eliminating baseline distortion or noise. In continuous wave (CW) EPR, meaning when using continuous microwave radiation at a fixed frequency, modulation coils are used together with a lock-in amplifier to increase the signal to noise ratio,. The Helmholtz coil produces a small additional magnetic field parallel to the static B_0 typically at 100 kHz. Note that modulation coils are not used for pulsed EPR, which as its name implies pulses microwave radiation through the sample.

From a hardware standpoint, EPR spectrometers are composed of a few key components, see Figure 2. The console houses the signal processing and control electronics. The Bridge houses the microwave source and the detector. The basic operation of the bridge is laid out in the block diagram on Figure 3. Once the microwave is generated at A, it passes through the attenuator at B to precisely control the microwave power which the sample sees. Since the desire is to only measure the microwave radiation reflected back from the resonator, the microwave needs to go through a circulator at C. This device filters the incoming wave from port 1 and sends it through port 2 whereas the reflected wave is sent into port 3 towards the detector. What is referred to as the cavity is the resonator, responsible for amplifying the weak signals from the sample. There are multiple types of resonators. Cavity-based resonators act like a simple metal box which resonates with microwaves just like an organ pipe resonates with sound waves. At the resonance frequency, no microwaves will be bounced back, instead being trapped inside the cavity.

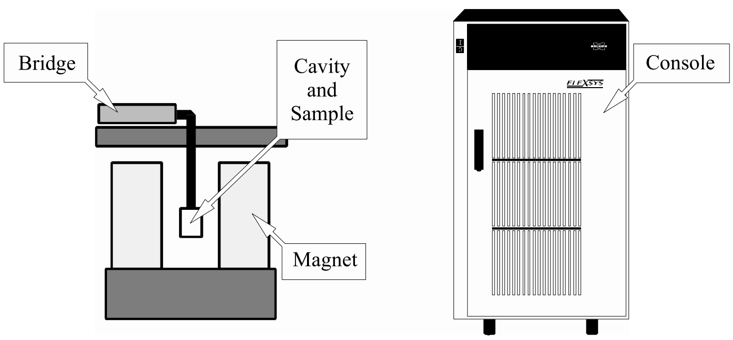


Figure 2: General outlay of an EPR spectrometer [3]

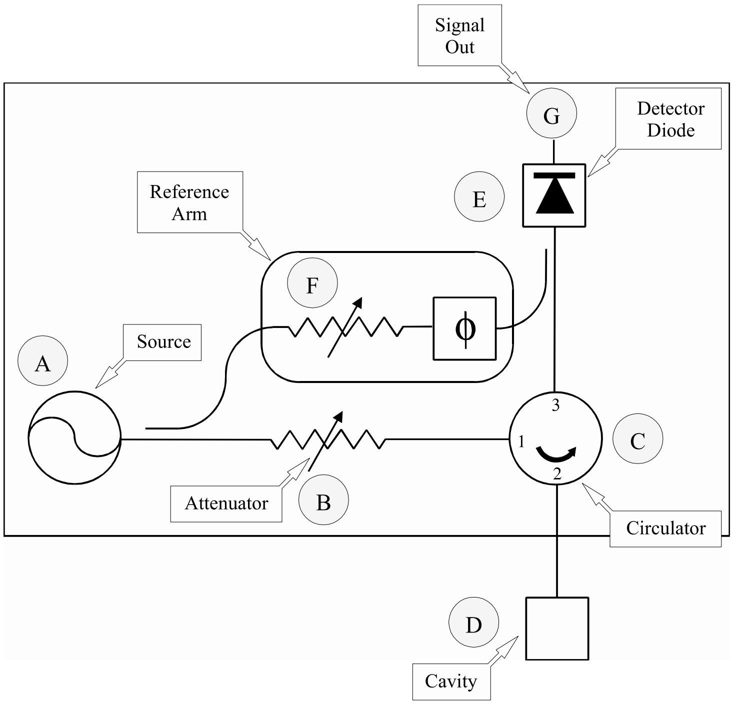
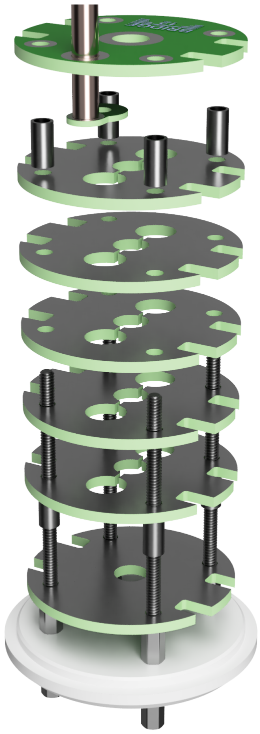
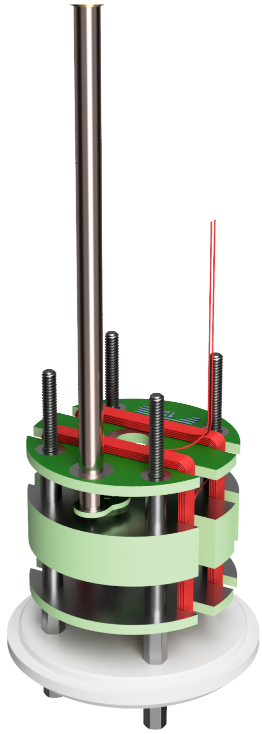


Figure 3: Block diagram of a microwave bridge [3]

Another major type of resonator and the one that is most relevant to this study is the loop-gap resonator. To explain its inner workings, see Figure 4 as this is the resonator that will be built in this project. These resonators are said to be lumped element resonators, meaning they can be modelled using capacitors and inductors. The loops act as inductive elements whereas the gaps act as capacitive elements, see Figure 5a. As shown on Figure 5b, the magnetic field is concentrated in the loops whereas the electric field are located at the gaps. This is desirable because most samples have non-resonant absorption of the microwaves via the electric field. Instead it is the magnetic field that drives the absorption in EPR. Placing the sample in the electric field minimum and magnetic field maximum produces the biggest signal and highest sensitivity. Also notice the addition of the modulation coils as well as copper shielding around the resonator. The shielding is to prevent the microwaves to be perturbed by the displacement of nearby metallic objects.

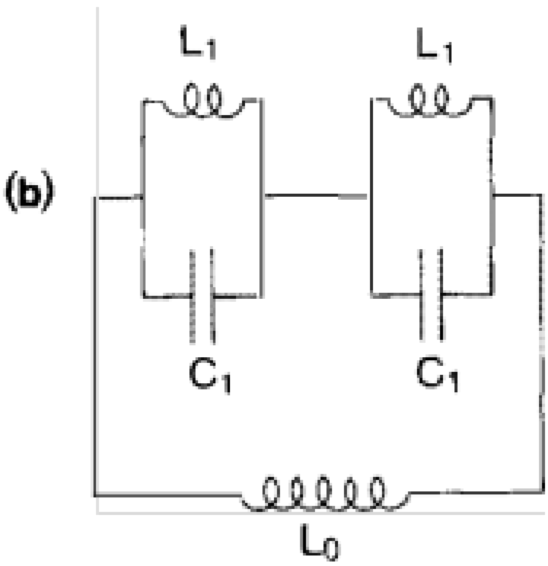


(a) Exploded resonator

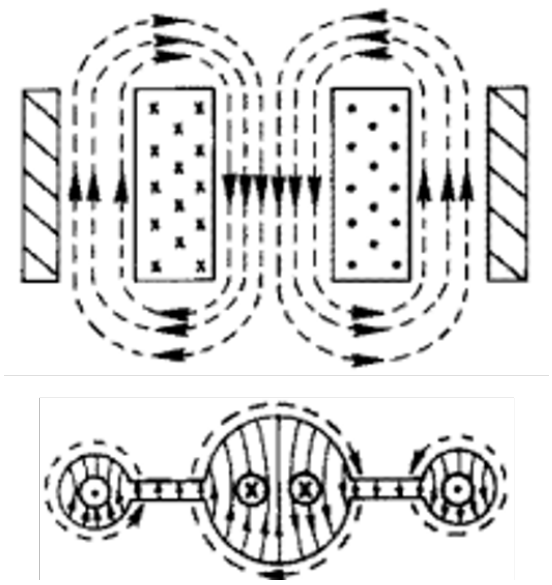


(b) Partially assembled resonator

Figure 4: A view of the PCB-based construction of the resonator



(a) Corresponding circuit



(b) Path of B field (dotted), E field (continous)

Figure 5: Lumped-element construction[2]

Electron Spin - Electron spin refers to the intrinsic angular momentum of an electron. In the context of electron paramagnetic resonance (EPR) spectroscopy, electron spin refers to the magnetic moment generated by the angular momentum of electrons in a paramagnetic species in a sample. Electrons have a property called spin angular momentum, which is similar to the rotation of a planet around its axis. Electrons also have a magnetic moment associated with their spin, which is proportional to their angular momentum. In a sample containing paramagnetic species, the magnetic moments of the electrons are randomly oriented, but when a magnetic field is applied, the magnetic moments align with the field, resulting in a net magnetic moment for the sample. In EPR spectroscopy, the magnetic moment of the electrons in a paramagnetic species is used to obtain information about the magnetic properties of the sample. The magnetic moment of the electrons generates a signal that can be detected and measured, providing important information about the electron spin, magnetic moment, magnetic anisotropy, and magnetic susceptibility of the sample. This information is critical for understanding a wide range of scientific and technological applications, including chemical reactions, biological processes, and materials science. Overall, electron spin is an important aspect of EPR spectroscopy, as it provides a means of measuring the magnetic properties of paramagnetic species in a sample. By detecting and measuring the magnetic moments of electrons in a sample, researchers can obtain important information about the electronic and magnetic structure of the sample, which is critical for understanding a wide range of scientific and technological applications.

Zeeman effect - The Zeeman effect refers to the change in energy levels of electrons in a magnetic field. In the context of electron paramagnetic resonance (EPR) spectroscopy, the Zeeman effect is a fundamental aspect of the measurement of the magnetic properties of paramagnetic species in a sample. In EPR spectroscopy, a strong magnetic field is applied to the sample, causing the electrons in the sample to align with the magnetic field. The application of an alternating radio frequency (RF) signal to the sample then results in a change in the energy levels of the electrons, which can be measured as changes in the RF signal. The energy difference between the spin-up and spin-down states of the electrons, which is related to the magnetic field strength, is known as the Zeeman splitting. The Zeeman effect is an important tool for understanding the magnetic properties of electrons in a sample, as it provides information about the magnetic moment, electron spin, and magnetic anisotropy of the electrons. This information is useful for studying the electronic and magnetic structure of paramagnetic species, such as radicals, transition metal ions, and coordination complexes. The Zeeman effect also plays a critical role in EPR spectroscopy, as it provides a means of detecting and measuring the magnetic properties of paramagnetic species in a sample, which is critical for understanding chemical reactions, biological processes, and materials science.

Hyperfine Interaction - Hyperfine interaction refers to the interaction between the magnetic field generated by the electrons in an atom and the magnetic field generated by the nucleus of the atom. In the context of EPR spectroscopy, hyperfine interactions can play a role in the magnetic properties of paramagnetic species in a sample and can affect the magnetic field experienced by the electrons. The hyperfine interaction can lead to a splitting of the electron spin energy levels, which can be detected and measured in EPR spectroscopy. By studying the hyperfine interaction, researchers can obtain information about the electronic structure and magnetic properties of the atoms in a sample, which is useful in fields such as materials science, biology, and chemistry. The measurement of hyperfine interactions is particularly important in EPR spectroscopy because it provides information about the atomic and molecular structure of a sample, which is critical for understanding the underlying mechanisms of chemical reactions and biological processes.

g-factor - The g-factor, also known as the g-value or the Landé g-factor, is a dimensionless quantity that describes the magnetic moment of an electron in a magnetic field. In the context of electron paramagnetic resonance (EPR) spectroscopy, the g-factor is used to describe the strength of the magnetic moment of an electron in a paramagnetic species in a sample. The g-factor is related to the Zeeman effect, which describes the energy splitting of electron spin levels in a magnetic field. The g-factor is determined experimentally by measuring the energy difference between the spin-up and spin-down states of an electron in a magnetic field. This energy difference is related to the magnetic moment of the electron, which is proportional to the g-factor. The g-factor is a fundamental property of an electron, and it provides important information about the electronic structure and magnetic properties of paramagnetic species in a sample. In EPR spectroscopy, the g-factor is used to obtain information about the magnetic anisotropy of a sample, which is critical for understanding the underlying mechanisms of chemical reactions and biological processes. The g-factor is also used to obtain information about the magnetic moment, electron spin, and magnetic susceptibility of paramagnetic species in a sample, which is useful in fields such as materials science, biology, and chemistry. Overall, the g-factor is an important tool for understanding the magnetic properties of paramagnetic species in a sample and is widely used in EPR spectroscopy.

Larmor precession - Larmor precession refers to the rotational motion of a magnetic moment in a magnetic field. In the context of electron paramagnetic resonance (EPR) spectroscopy, Larmor precession refers to the rotational motion of the magnetic moment of an electron in a sample in response to an applied magnetic field. When an electron in a sample is exposed to a magnetic field, it aligns with the field, generating a magnetic moment. If the magnetic field is then oscillated at a specific frequency, the electron's magnetic moment will start to precess, or rotate, around the magnetic field direction. This precession is referred to as Larmor precession, and it results in a change in the energy levels of the electron, which can be detected and measured in EPR spectroscopy. The frequency of Larmor precession is related to the strength of the magnetic field and the magnetic moment of the electron, and it is a fundamental aspect of EPR spectroscopy. By measuring the frequency of Larmor precession, researchers can obtain information about the magnetic properties of paramagnetic species in a sample, including the magnetic moment, electron spin, and magnetic anisotropy. This information is critical for understanding the underlying mechanisms of chemical reactions, biological processes, and materials science. Overall, Larmor precession is a key component of EPR spectroscopy, as it provides a means of measuring the magnetic properties of paramagnetic species in a sample. By detecting and measuring the Larmor precession of electrons in a sample, researchers can obtain important information about the electronic and magnetic structure of the sample, which is critical for understanding a wide range of scientific and technological applications.

Resonators: Advantages of LGR: 1. a large filling factor 2. a large conversion factor 3. a low quality factor (Q) 4. can provide large uniform microwave fields across the sample

This is a 3 loop 2 gap resonator.

Q-factor - The Q-factor, also known as the quality factor, is a measure of the efficiency of an oscillating system, such as a resonator. In the context of electron paramagnetic resonance (EPR) spectroscopy, the Q-factor of a resonator refers to the efficiency with which the resonator can store and transfer energy to the sample being studied. The Q-factor is defined as the ratio of energy stored in a resonator to the energy lost per cycle. A high Q-factor indicates that a resonator is highly efficient at storing energy, while a low Q-factor indicates that a resonator is less efficient and loses energy more quickly. In EPR spectroscopy, the Q-factor of a resonator is an important parameter, as it affects the sensitivity and resolution of the spectrometer. A high Q-factor resonator will be more sensitive, as it can store and transfer more energy to the sample, resulting in stronger signals and better resolution. A low Q-factor resonator will be less sensitive, as it loses energy more quickly and generates weaker signals. The Q-factor of a resonator is determined by several factors, including the size and shape of the resonator, the quality of the material used to construct the resonator, and the environment in which the resonator is operated. By optimizing the Q-factor of a resonator, researchers can improve the sensitivity and resolution of their EPR spectrometer, providing more accurate and detailed information about the magnetic properties of the sample being studied. Overall, the Q-factor of a resonator is a critical parameter in EPR spectroscopy, as it affects the sensitivity and resolution of the spectrometer. By optimizing the Q-factor of a resonator, researchers can improve the accuracy and detail of their measurements, providing important information about the magnetic properties of paramagnetic species in a sample.

Paramagnetic materials - Paramagnetic materials are materials that contain unpaired electrons and exhibit a weak, positive magnetic susceptibility. These materials are attracted to magnetic fields, and the magnetic moments of their electrons are aligned with the magnetic field. Paramagnetic materials have a magnetic moment that is proportional to the magnetic field, and the magnetic susceptibility of these materials is proportional to the number of unpaired electrons. Paramagnetic materials include elements such as iron, cobalt, and nickel, as well as many metal oxides, metal salts, and some organic compounds. In electron paramagnetic resonance (EPR) spectroscopy, paramagnetic materials are used as samples to study their magnetic properties. EPR spectroscopy measures the magnetic moments of the electrons in a paramagnetic species in a sample, providing information about the electron spin, magnetic moment, magnetic anisotropy, and magnetic susceptibility of the sample. This information is critical for understanding a wide range of scientific and technological applications, including chemical reactions, biological processes, and materials science. Overall, paramagnetic materials are important in EPR spectroscopy, as they provide a means of measuring the magnetic properties of materials. By detecting and measuring the magnetic moments of electrons in paramagnetic species in a sample, researchers can obtain important information about the electronic and magnetic structure of the sample, which is critical for understanding a wide range of scientific and technological applications.

Continuous wave EPR - Continuous Wave (CW) Electron Paramagnetic Resonance (EPR) is a spectroscopic technique used to study the magnetic properties of paramagnetic materials. In this method, a continuous microwave frequency is applied to a sample, and the magnetic moment of the electrons in the sample is detected by measuring the absorption of the microwave radiation. In CW EPR, the microwave frequency is continuously scanned over a range of frequencies, and the absorption spectrum is recorded. The spectrum provides information about the magnetic properties of the sample, including the electron spin, magnetic moment, magnetic anisotropy, and magnetic susceptibility. CW EPR is widely used in a variety of applications, including chemical reactions, biological processes, materials science, and metallurgy. The advantages of CW EPR include its high sensitivity, which allows for the detection of low-concentration paramagnetic species, and its ability to provide detailed information about the magnetic properties of the sample. However, one of the disadvantages of CW EPR is its low resolution, which can make it difficult to distinguish between closely spaced electron spin transitions. To overcome this limitation, pulse EPR techniques have been developed, which use short, intense pulses of microwave radiation to obtain higher resolution spectra. Overall, Continuous Wave EPR is a valuable tool for studying the magnetic properties of paramagnetic materials. It provides high sensitivity and valuable information about the magnetic properties of the sample, but its low resolution can be a limitation in some cases. Nevertheless, CW EPR continues to be an important technique in the field of EPR spectroscopy, providing critical information about the magnetic properties of a wide range of materials.

Coupling -

Lock-in amplifier -

Microwave Bridge -

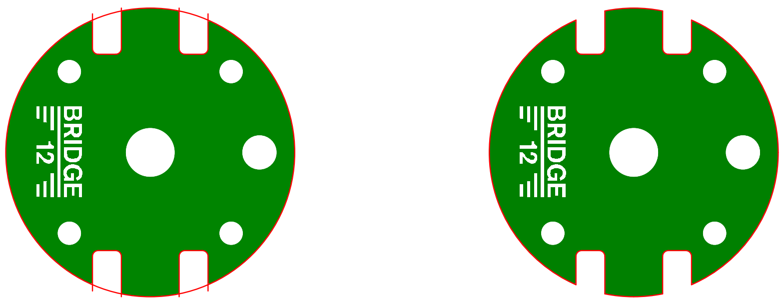
Advantages of Loop-gap resonators: 1. a large filling factor 2. a large conversion factor 3. a low quality factor (Q) 4. can provide large uniform microwave fields across the sample [2]. Find those in reference (textbook)

2 Methods

2.1 Modifying PCB files

The first task at hand was to go through all the files and resources that were provided by the Bridge 12 open source project, see Appendix B. It was quickly found that the PCB files needed fixing before they could be sent to a manufacturer to be built out.

Indeed, the "edge.cuts" layer seemed to have been corrupted somehow. Opening the file on KiCad, an open-source suite for Electronic Design Automation (EDA), it appeared as if the outline of the PCB was not intersecting and would potentially lead to difficulties for the manufacturer. KiCad has limited tools to edit vector objects so instead the outline was exported as a .dxf file to Illustrator. There, the lines were intersected and the superfluous parts were removed. This updated file was then imported back into KiCad, ensuring a clean outline is present for the manufacturer. This was done for all 4 different PCB files. An example of before and after is given in Figure 6.



(a) Provided version (b) Updated version

Figure 6: Comparison of the provided and updated edge.cuts layers (in red)

2.2 Ordering parts

Next up the necessary parts were ordered. The PCB components were purchased on pcbway.com, all hardware including bolts, threaded rods and spacers on www.mcmaster.com. Later on brass threaded rods and magnet-wire were ordered from a local hardware store to complete the resonator holder.

Special attention was taken to select all the correct options in ordering the PCB components. They were also ordered in bulk as it was barely more expensive and spare parts give flexibility in case of a broken PCB or for building a second resonator. In the same fashion all hardware components were purchased at least in doubles.

Some of the components were readily available in the lab: the Coaxial cable and its SMA connector, as well as the top flange with both SMA connectors embedded in it. A bill of materials is available in Appendix B.

2.3 3D modelling

2.3.1 Modifying top hat

The resonator was to be used with the bruker 500 system present in the lab. It is equipped with a narrow and deep cryostatic chamber. It was thus necessary to integrate a way to hold the resonator from the top so that the whole assembly could be dropped into the cryostatic chamber. Previous experiments used a flange with three brass threaded rods to fasten the custom device to, see Figure 7. The setup is then fastened to the cryostatic chamber using a v-clamp.

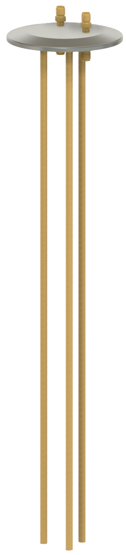
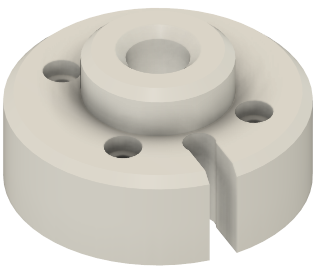
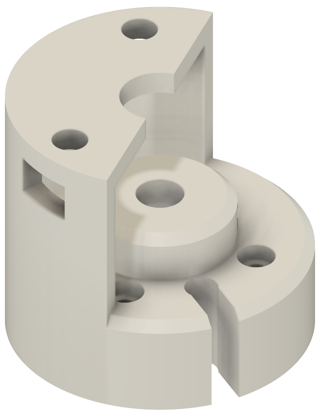


Figure 7: Flange and rods, base construction of the holder

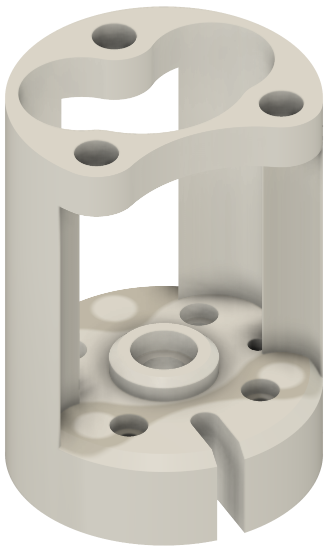
The 3D printing process forces some design restrictions. Most notably, the 3D printer is not able to print an overhang of more than a couple millimeters without support at best. For the final design, some supports were used in the bridge section near the top, see figure 8c.



(a) Starting point



(b) First iteration



(c) Final Design

Figure 8: History of iterative design of the top hat of the resonator

2.3.2 Rigidifier

One critical aspect for of the resonator is its modulation coils. These need to be aligned parallel with the magnetic field generated by the electromagnets of the bruker system. Without any reinforcement, the three rods allowed for torsion to occur, which would have rendered the alignment of the modulation coils difficult. It was thus necessary to develop a way the increase the rigidity of the resonator holder. For a shaft, the torsion is given by equation 5.

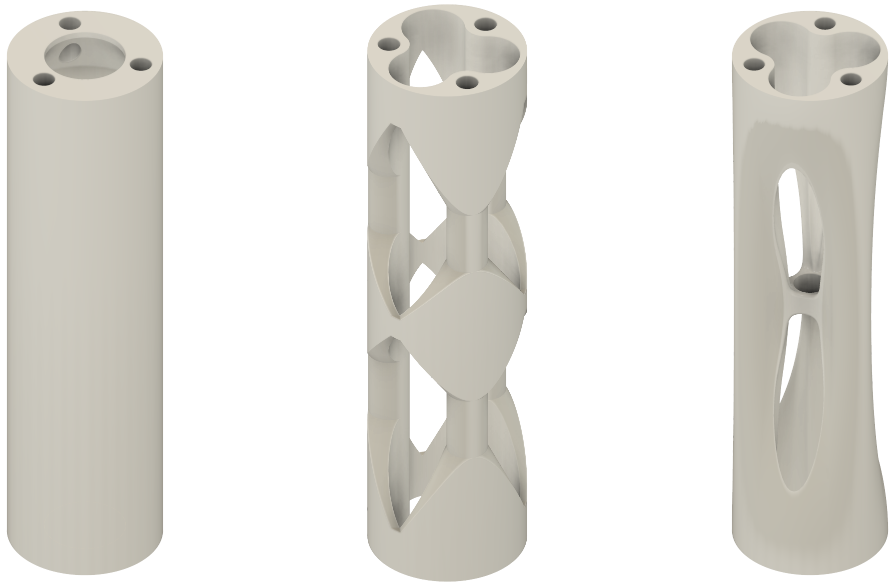
$$T = \frac{\tau J}{r} \tag{5}$$

where:

T = Torque (Nm)
τ = Shear stress (N/m^2)
J = Polar moment of inertia (m^4)
r = Radial distance of point from center of section (m)

The way to increase torsion rigidity is to increase the inertia along the rods' axis. The most basic approach is to simply have a cylinder with flanges on each end through which the rods would slide into. While functional, it is not elegant and prevents the user to see what is going on inside.

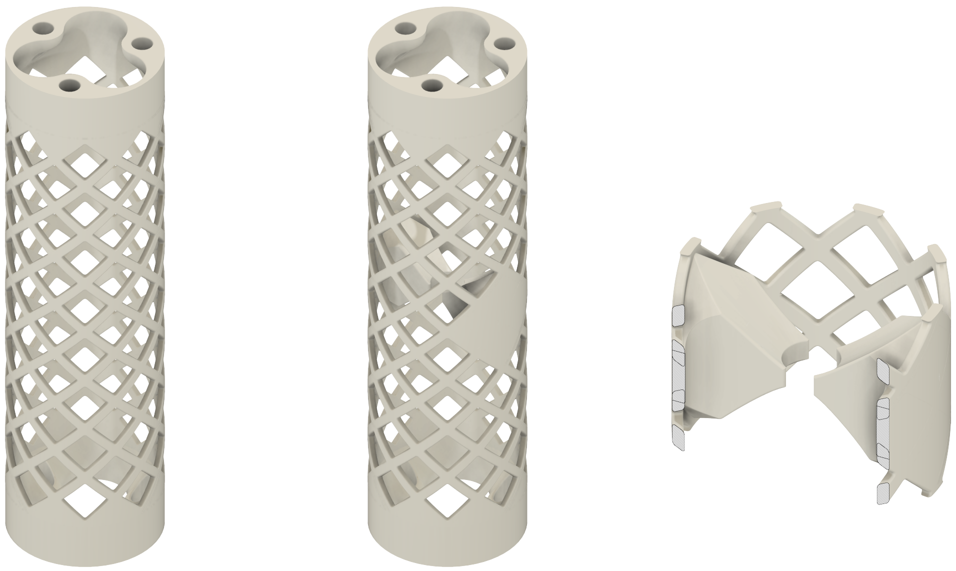
Another important constraints is the printing time. While tuning the 3D printer's parameters can mitigate some of this, the final print will always need to be of fine quality and with 100% infill. For prototypes, faster settings were used with hexagonal patterns as infill. The bulkier the design, the longer it will take to print. The printing capacity is limited in size to 150mm x 150mm. The rigidifier thus had to be printed in two parts.



(a) First iteration (b) Alternative design (c) Advanced alternative design

Figure 9: History of iterative design of the rigidifier

For printing duration times, another final design was chosen. It combines lightweight, elegance as well as optimal printing times with great rigidity. Note that two pieces are necessary due to printing size limitations. The bottom rigidifier has an added feature of holding the PTFE sample holder, see Figure 10c.



(a) Top rigidifier (b) Bottom rigidifier (c) Zoom on PTFE sample holder

Figure 10: Final design for the rigidifiers

2.3.3 Spool holder

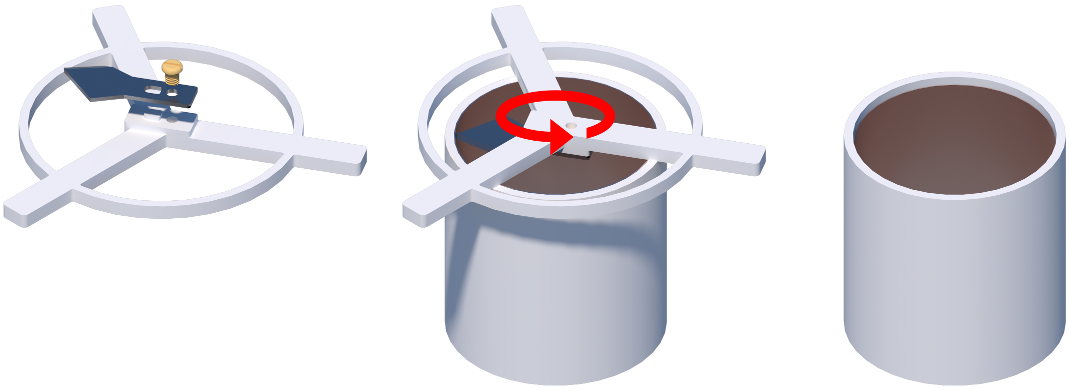
When building the resonator, one challenging aspect is to wind a magnet wire a total of 100 times around the PCB's. After a first awkward attempt, it was decided to design and print a small spool holder to help with the smooth unwind of the coil. As seen on Figure 11, the simple design includes a slanted cylinder with a flat foot that can be used to clamp the holder to the table using a C-clamp. Additionally a small riser was printed on the front to prevent the spool from binding. Tolerances were kept fairly loose as the spool is meant to rotate freely around the holder. The final print proved its usefulness and helped greatly in winding the coil correctly and efficiently. Being able to focus on the proper winding instead of having to deal with a temperamental spool ensures the correct amount of turns are being done one each side of the PCB's.

(a) (b)

Figure 11: Spool holder, with and without the spool

2.4 Copper foil slicing

The main body of the resonator has a snap fit with the caps on either side of it. The copper foil inside the main body would interfere with the snap fit so it needs to be cut 1.6mm from the edge. To get a clean cut, a small tool was designed and 3D printed. A razor blade was fastened in its center and by gliding the 3D printed surface on top of the main body, a 1.6mm strip of copper foil was cut out of the cylinder.



(a) Cutter design (b) Cutting action (c) Final result

Figure 12: Process of cutting a 1.6mm strip from the copper foil in the main body

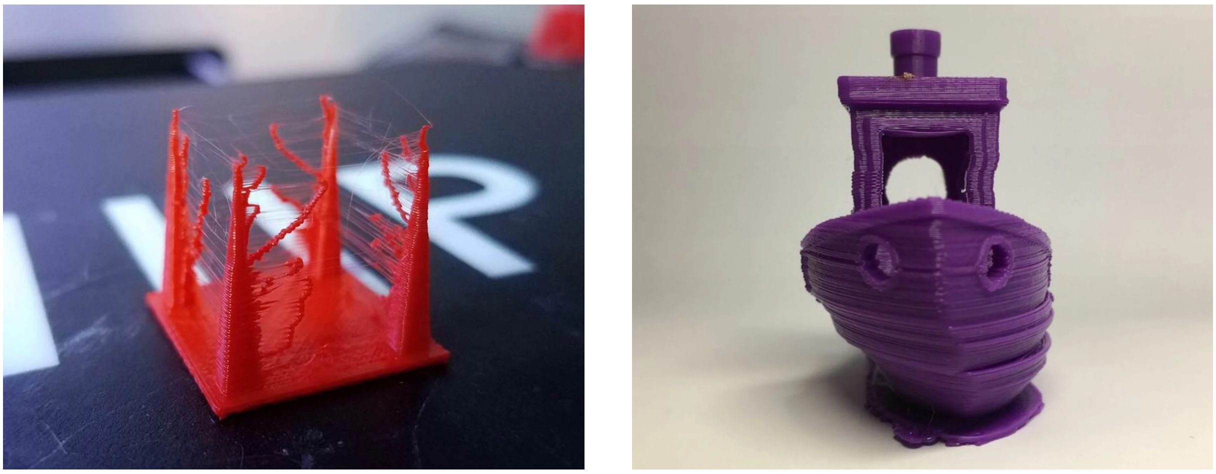
2.5 3D printer tuning

3D printers are powerful tools because they can create physical objects from digital designs. The UNSW lab is equipped with a Flashforge Adventurer 3. It was used for rapid prototyping along the development process but also to produce the final pieces.

Before any printing can be done, some maintenance and setting up was needed. The bed was first levelled using the built in calibration tool. After most prototyping was done and before printing the final design with 100% infill, a new nozzle was ordered and installed to improve the surface finish and printing of overhangs. For peace of mind, new filament was used for the final print as the filament used for prototyping was several months old and not stored in an adequate moisture-controlled container.

Two major printing defects came up while printing parts. One is stringing and happens when melted plastic leaks from the nozzle when it travels to the next point, see Figure 13a. It leaves thin strands of solidified plastic resembling a cobweb in the part. While it does not affect the structural rigidity of the part, it may present a problem later on when the part is slid inside the cryogenic chamber. One has to pay extra attention not to let any debris fall into it as cleaning it out would be hard to do. These strings of plastic are loosely held to the part and are difficult to clean up. One method to prevent this is to enable retraction of the filament on transition. When enabled, the filament is pulled back by the feeder when the extruder has to cross an empty space. Another method is to lightly blaze the part with a heat gun after printing. The strands of plastic may then melt and either reattach solidly to the body of the part or fall off. One then has to be careful as too much heat would deform the part. Another notable way to prevent stringing is to ensure that the PLA is moisture-free. Once moisture is present, it tends to boil up while printing and mix with the plastic. The filament used being in a temperature and moisture controlled laboratory, it is unlikely this was the main cause of stringing.

The second significant printing defect is layer shift. It affects both dimensional accuracy as well as visual appearance of the print. Since some of the parts of the resonator have a snap fit, it was important to mitigate this defect as much as possible. Moreover the cryogenic chamber has a fixed width of 40mm and so a significant deviation from the resonator may result in interference with the walls of the chamber. Layer shift happens every time a layer is printed with a horizontal offset from where it was intended, see Figure 13b. This defect can be caused by a variety of different things, but the first step is to calibrate the printer, including nozzle temperature, tightening relevant screws and bolts and levelling the print bed. Secondly one has to make sure the belts are tight. Loose belts are the leading cause of print shift in 3D prints. Then vibrations need to be minimized as much as possible. This can be achieved either by adding bump-absorbing rubber feet to the printer and by cleaning the printer. Sometimes small pieces of printed plastic can get loose and bind up one of the lead screws or into the print bed's path. This may cause jolting when changing direction, resulting in a small layer shift.



Source: https://all3dp.com/

(a) Stringing

Source: https://all3dp.com/

(b) Layer shift

Figure 13: 3D printer defects

2.6 Resonator assembly

The coaxial cable that was used already had a male SMA connector on each end. It was cut at a length of 7cm and then 5mm of the inner conductor was exposed using a tube cutter, see Figure 14a. Once soldered, the excess conductor can be filed down to 1mm of the PCB and the excess solder around the external conductor is filed down too so as not to interfere with the sliding movement of the coaxial cable. Excess solder might prevent proper coupling of the resonator.

Next up the Top PCB is slid into the coaxial cable through the appropriate hole, Figure 14b. The inner conductor of the coaxial cable was then soldered to the PCB loop and the outer conductor was soldered on the other side of the PCB, see Figure 14c, with the completed solder on Figure 14d

Leaving that assembly to the side, 4 threaded rods were screwed 3mm deep into threaded nuts. They were then passed through the 3D printed bottom cap and 4 spacers were added on top, see Figure 14e.

Then the bottom PCB was slid into place and 4 more spacers were added on top, see Figure 14f.

The 5 central LGR PCB pieces could then be slid on top of that, with another set of 4 spacers added on top, see Figure 14g.

The coaxial cable assembly is then added on top, by sliding the top PCB into the threaded rods, and fastening the whole assembly with 4 threaded nuts, see Figure 14h. Finger tightening was plenty for this usecase.

Subsequently copper tape was wrapped tight around the spacers on either side of the 5 LGR PCB's. Note that the top copper tape was not wrapped around the side of the coaxial cable, see Figure 14i.

The magnet wire was then wound 50 times around the PCB's through the appropriate slots. Then that same wire was wound another 50 turns in the same direction around the other side. Finally both ends of the wire are brought up and cut 10cm above the Top PCB, see Figure 14j.

The 3D printed main body could then be lined with copper using the method described in Subsection 2.4. It was then slid on top and the 3D printed top cap was placed on top, making sure that the magnet wire is passed through the appropriate hole. 4 threaded nuts then tighten the entire assembly together, see Figure 14k.

Finally the 3D printed top body was added on top, aligning the coaxial cable in the appropriate slot and passing the magnet wire through yet another hole, see Figure 14l. The top hat was fastened with 4 screws.

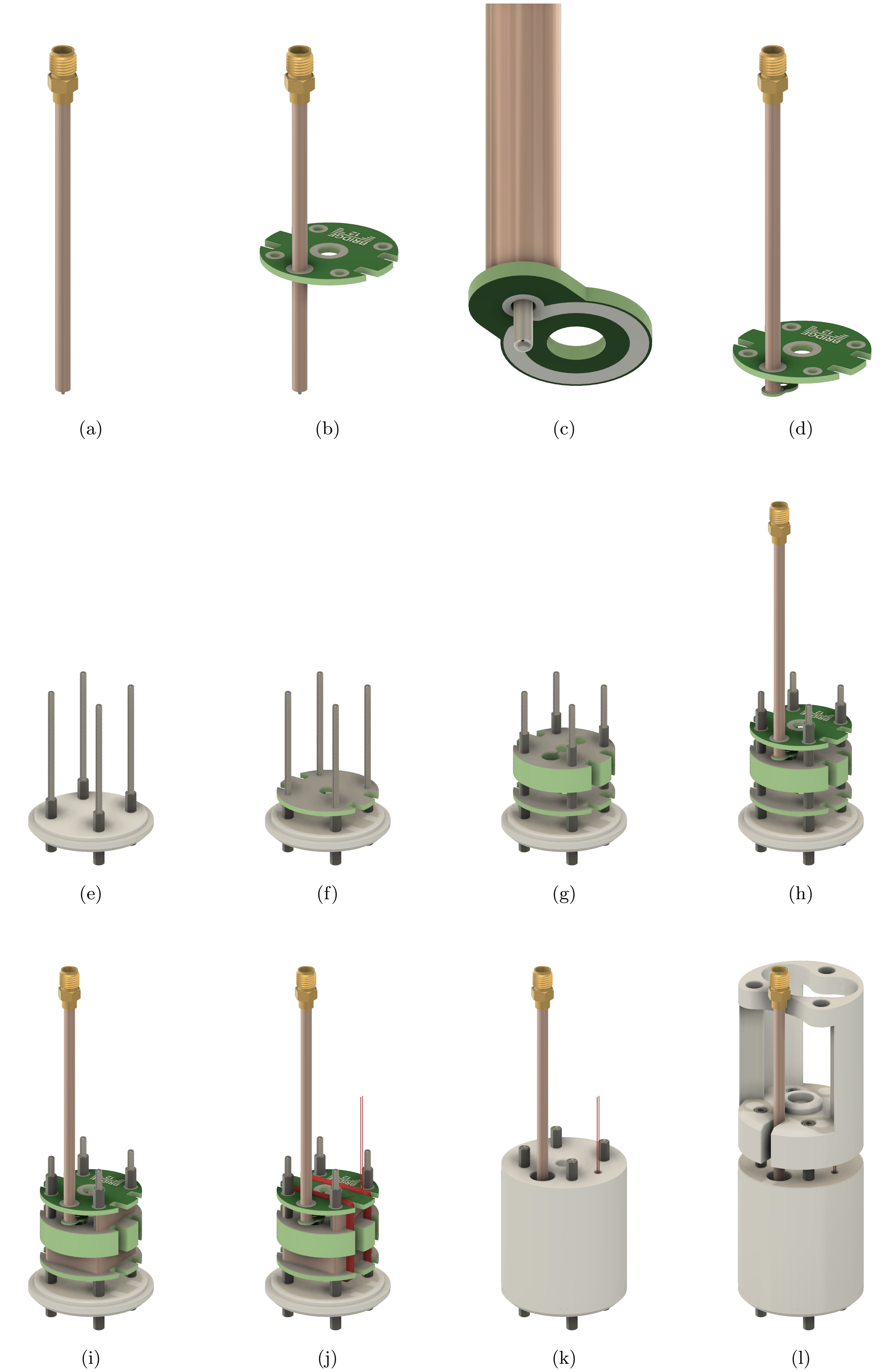


Figure 14: Steps for resonator assembly

Well well

2.7 FieldFox testing

The laboratory is equipped with a Keysight N9918A FieldFox handheld microwave analyzer, see Figure 15. It is a lightweight and durable cable and antenna analyzer, but also most relevant to this project it can analyze spectrum. It can operate at a maximum frequency of 26.5GHz which is more than adequate considering the bench top resonator operates in the vicinity of 10GHz.

It is equipped with 2 SMA ports on the top of the device, the "`Port 1 RF Output`" is used to connect to the coaxial cable of the resonator through a male to male coaxial extension cable. Once turned on, the mode button is pressed and "`NA`" for Network Analysis is selected. The NA application then opens by default in S11 mode, which is the correct mode for this analysis. If not, one can use "`measure`" to manually set the S11 mode. S11 is one of four scattering parameters and measures the reflection at port 1. The FieldFox automatically switches the internal source and receivers to make both forward and reverse measurements. Then under "`Freq/dist`", the center is set to 9GHz and the frequency span is set to 2GHz. A dip should now be visible around the center of the screen, representing a reflection of the signal back into the FieldFox. To measure that minimum, the button "`Mkr→/Tools`" is pressed, then "`Peak Search`" followed by "`Minimum`". The marker will then position itself at the correct position and the frequency can be read on the top right of the screen.

At this point a measurement can be taken. "`Run/Hold`" should be pressed, followed by "`Save/Recall`". It is recommended to select "`USB`" under "`Device`" and "`Data(CSV)`" under "`File Type`". Note that a png image can also be generated and may prove useful. Finally, "`Save`" is pressed and a filename is entered. The CSV file can then be opened into a data processing program like Excel.

Source: https://www.keysight.com/

Figure 15: Fieldfox N9918A

2.8 Bruker testing

The laboratory is equipped with the Bruker ELEXSYS-II E500, the basic components of which can be seen on 16. For this project it is set to Continuous Wave (CW) but it is also capable of performing a variety of other EPR methods including ENDOR (Electron nuclear double resonance) for pulsed EPR spectroscopy.

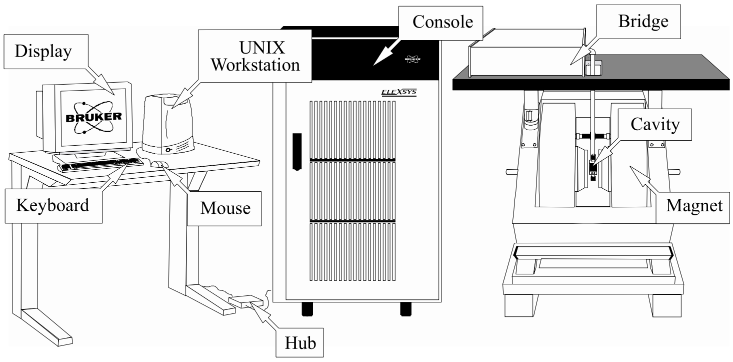


Figure 16: Bruker system [3]

The operation procedure of the Bruker is complex. Fortunately a step-by-step guide is available in Chapter 3 of the Bruker's instruction manual [3]. It guides the first time user from a completely shut down spectrometer to the acquisition of the absorption spectra. Note that the manual does not include the operation of the cryogenic chamber as this was added by the department later on and was not produced by Bruker itself. It is instead a custom solution by Cryogenic in the UK and has its own manual [4].

The basic operation for obtaining spectra can be condensed in the following steps. First the resonator has to be placed into the cryostat. To do so, the chamber has to be heated back up to around 100K, then the circuit is isolated from the rest of the circuit and an overpressure of Helium is applied before swapping the resonator and flushing the system by cycling overpressure and evacuation. The swap should take 1-1.5 hours. Secondly all the Bruker system components (console,power supply, heat exchanger) have to be turned on. It is then connected through the custom XEpr program on the computer. There, the Bridge has to be tuned and finally the spectra can be acquired.

3 Results

3.1 Tuning the coupling with the FieldFox

3.1.1 Effect of rotation of the coupling loop

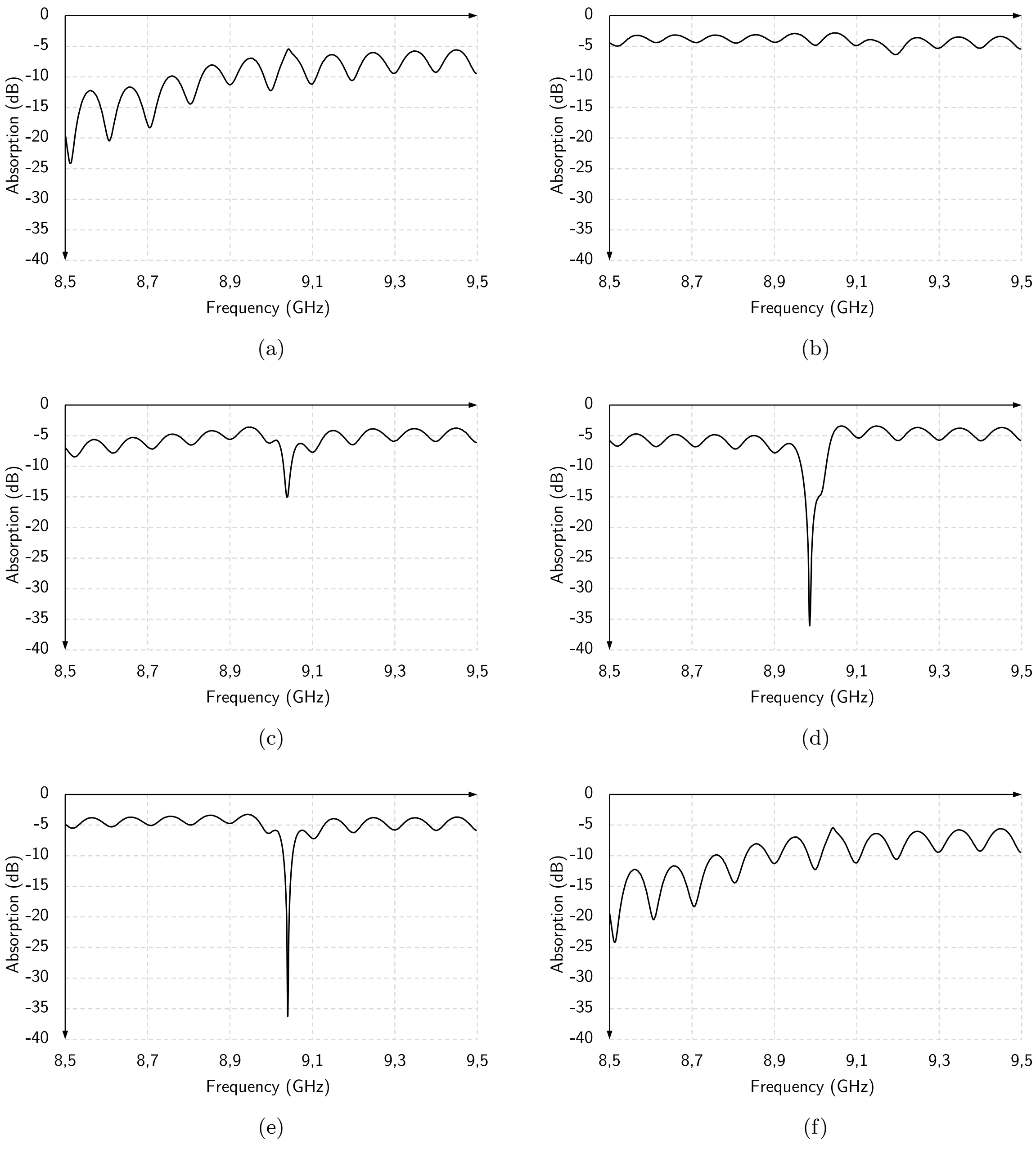
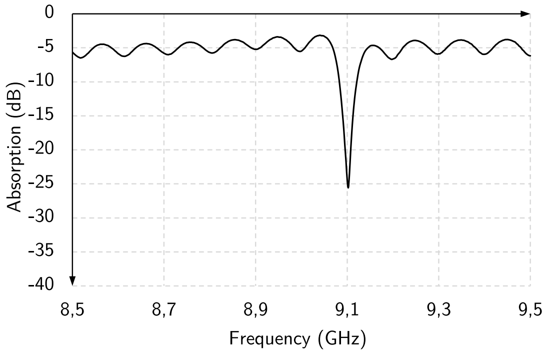
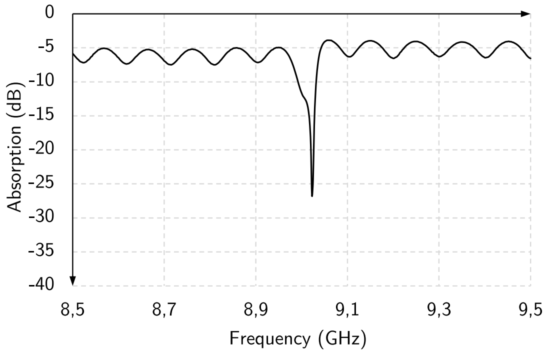


Figure 17: Effect of rotating the coaxial cable on the resonance frequency of the resonator.

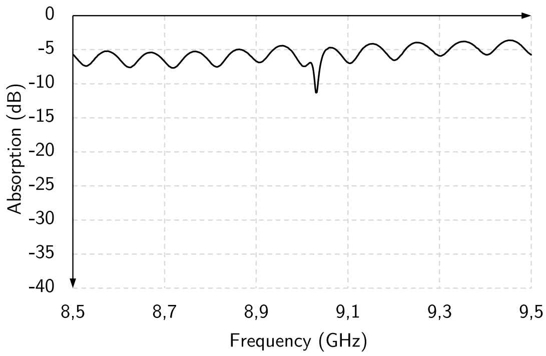
3.1.2 Effect of vertical spacing of the coupling loop



(a)



(b)



(c)

Figure 18: Effect of vertically displacing the coaxial cable on the resonance frequency of the resonator.

3.2 Testing in the Bruker system

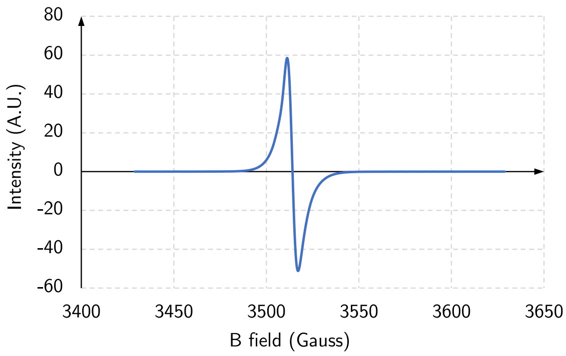


Figure 19: Absorption spectra of coal

4 Discussion

4.1 Interpretation of results

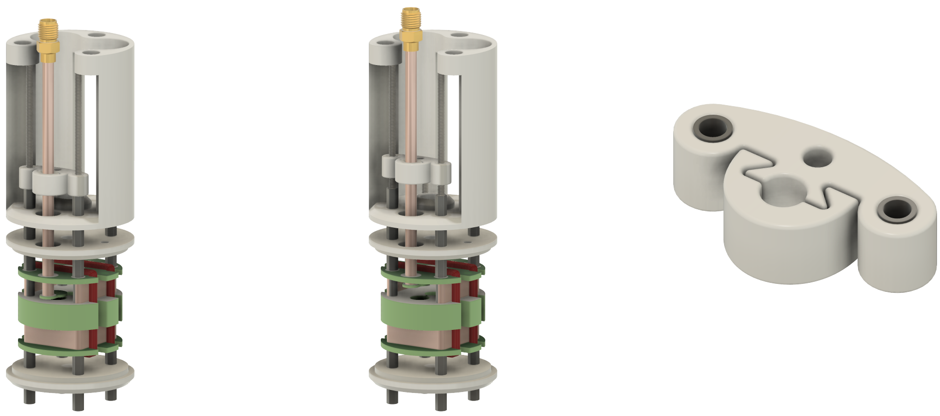
From the rotation graphs on Figure 17, it is clear that rotating the coaxial cable and thus the coupling loop affects the coupling in a significant way. Despite the approximate nature of the testing, the resonator is clearly displaying resonance at a frequency $f_r \approx 9,03GHz$ which is suitable for X-band spectroscopy. The vertical displacement of the coupling loop does show to affect the coupling as well, though to what extend is difficult to tell with the data. Figure 19 shows the spectra of a coal sample. It is as expected, with absorption shown to be taking place at around $G \approx 3514$ G.

4.2 Characterising the Resonator

With the chosen dimensions of the resonator, more specifically of the loops and gaps, it is possible to calculate with satisfactory precision the resonant frequencies or modes of the resonator.

4.3 Slider idea

One additional feature that was worked on but was not brought to completion is a slider to adjust the coupling of the resonator. It would have consisted of a 3D printed bracket that would clamp itself around the coaxial cable. Two metal spacers would be press fitted into it and would allow for a sliding movement around two of the same threaded rods that are already in use in the resonator. The main part that still needs figuring out is how to access this bracket from outside of the cryogenic chamber. Other resonators used in the Bruker can adjust the iris with a screw on the top hat. That would be a good source of design inspiration.



(a) Bottom slider limit (b) Top slider limit (c) Slider clamp

Figure 20: Illustrations of the slider's clamp and motion

4.4 Limitations

The major hurdle in acquiring spectra is the sensitivity of the coupling and the associated difficulty of adjusting it. The coaxial cable is a press fit in the 3D printed plastic. Friction is quite high to prevent unintentional detuning of the resonator as it is handled and inserted into the cryochamber. This renders the fine tuning harder as quite a lot of force is required to turn and move the coaxial cable. It also means the cable can en up slightly slanted in the slot, shifting the coupling loop off center.

4.5 Improvements on design

It was discovered that in Bridge12's original design, the coupling loop is not exactly aligned to the side-loop below. There is in fact a 0.9mm offset between the two, see Figure 21.

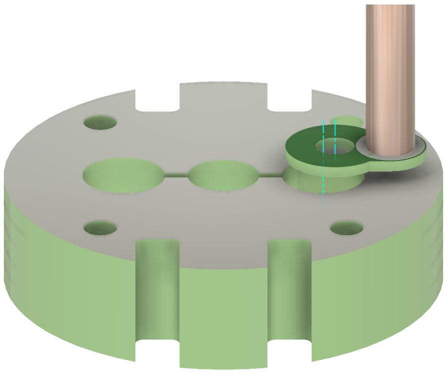


Figure 21: Coupling Loop offset

It is unclear whether this was a design mistake or whether it was on purpose. A simple way to test this would be to reprint a top body with the coaxial slot extended by 0.9mm and see whether the sensitivity of the resonator is improved.

4.6 Further research

Perhaps the most Pulsed EPR ODMR

4.7 Conclusion

5 Personal reflection

This project has been a great learning experience for me. It has exposed some of my strength and some of my weaknesses. First of all putting myself out there by searching for a BTR abroad, sending enquiries by emails to multiple different academics all over Australia was a major undertaking. This has proven successful and only serves to motivate me in further similar situations, to keep searching and applying without abandoning.

From a research perspective, I am mostly happy with my performance and behaviour during the project. I would be a fool to say I did everything I can. There is always more to be done, one can always work more. Designs can always be improved and written work can always better be phrased, go more in depth. I really struggled at first with the ordering of parts. It can feel daunting to a newcomer to spend someone else's money and risking misordering parts. The process of ordering was tedious, having to go through colleagues, ordering different parts on different websites, etc. There was an added difficulty of parts supply. Some were not available from the bill of materials provided by Bridge12, so suitable alternatives had to be found. This took a long time and delivery took weeks. I had do order the brass threaded rods comparatively late as I had not foreseen needing them but since it was the end of the fiscal year and with the holidays coming up, this had to be delayed as well. Finally an order concerning 3D printer parts was even cancelled due to a miscommunication. Either way it clearly stands out to me as a first order of business in my next projects. Part have to be ordered as soon as possible as it can completely hold a project to a standstill.

I had been meaning to learn CAD (Computer Aided Design) for years but never had a project to use it for. I had dipped my toes into Sketchup before and found it perfectly suitable for diy hobby projects like woodworking but I wanted to improve my skill by learning Fusion360. This project was a godsend in that regards, as I truly spent the time to learn Fusion360, and I can honestly say I got quite comfortable with it. I will look into Solidworks next. With the advent of quick prototyping through 3D printers, CAD design is a very valuable skill that I am sure I will use professionally in the future. If CAD is something I want to get into professionally, a more powerful computer would drastically increase my productivity. Especially if I start to work with more intricate designs, more graphical power would decrease the rendering time and smoothen the overall experience by a significant margin. Load simulations, which I have tinkered with for the rigidifier, would also benefit tremendously from upgraded PC hardware. For reference, I am using a 2018 HP Elitebook Spectre x360 1030G2 equipped with a dual core i7-7600U and Intel HD620 graphics. I also experimented with 3D rendering with v-ray for Sketchup although this was not exactly necessary for the project and ended up being more of a waste of time. I did still use a few of the v-ray renders in this report, most notably on the cover page, but most of the renders in the text are produced in Fusion360 directly. I will also look into blender for animating the design as it may prove useful for producing the video. How to teach Science is a hot topic and it seems obvious to me that attractive audio-visual content is key to attract the next generation.

I feel like I had the complete research experience. I had my own desk in the office surrounded by PhD students and post-docs. We exchanged on our respective projects regularly and I even participated in a week-long workshop involving multiple other Australian universities. My colleagues and friends told me about their experience doing research, during their PhD and beyond. I learned that it is important to find a supervisor that suits your working habits. Some researchers require a lot of feedback, direction whereas others strive by "doing their own thing". Though I doubt I will be pursuing the PhD route myself, I am grateful to have been given the opportunity to dip my toes in the field. I believe I now have a good understanding of what it takes to complete a PhD and what it entails. Perhaps the one thing I regret is not asking for more help and guidance to the PhD's and postdocs. I tend to think I will bother them by asking questions but all of them have been nothing but kind to me and would undoubtedly have gladly answered my questions. There is no need to feel intimidated, they are passionate about the subject and thus will most often gladly give some of their time for me. Everyone has its own very specific field of study so that teamwork was quite essential to some. They would ask colleagues to produce certain compounds or help with a problem that was more of someone else's domain. That is also why workshops are so important in the science community: not only do you through the presentations but exchanging with like-minded people from different backgrounds can be eye-opening. For me to participate in their biggest annual workshop was a highlight of the project and critically valuable for me.

My time management was not the best. I tended to procrastinate as I was very intimidated by the bruker system and CAD was just so fun and new. I tried correcting that by making a gantt chart, which helped somewhat in gaining perspective although I ultimately did not quite reach the goals. I also held a word counting excel sheet that would track my progress on writing the thesis. It also helped at first but it eventually became apparent that word counting is not the best metric in judging the state of the written thesis. A lot of rewording and shifting things around happen near the end reducing the graph's relevance. Another aspect that contributed to me procrastinating is the fear that it will not work.

I am frustrated with myself for not having tested the resonator in the Bruker spectrometer. I should have asked for help and faced the fear of operating such a physically big, complex and expensive instrument. Although I have performed all the steps of the acquiring changing the resonator and acquiring spectra, I would have still liked to do so with my own resonator. It would also have provided me with much more data for analysis. I realize my results and accompanying interpretation is somewhat lackluster.

This project also exposed some shortcomings of mine. I struggled with the literature review. I found it tedious and in this context it did not seem relevant to the work. I much preferred working towards solving problems, design constraints, going forward with the project rather than spending all this time reading and sorting through papers. I understand it is an indispensable part of every paper but I believe my skills are better served in other aspects of research. I am no theoretical scientist, I would much rather work on practical things. Perhaps the one exception to this is the formatting and production of figures for the paper. I do enjoy that and I am very particulate about it. I believe good figures and adequate formatting are fundamental to a good paper. I am simply not much of a writer it seems, though I am curious to find out what stance the scientific community is going to take on the use of AI tools such as ChatGPT in writing papers.

Finally I found it hard to find a good work-life balance. Being in Australia, the cost of living is very high here so I decided to live and work in a hostel afterhours. They were long hours usually in the evening and I missed having intimacy since I was sharing a room. It impacted my sleep and even with all that there was still a financial strain. I do not regret my decision to study abroad as it was an invaluable experience for me, however I will be happy to change the pace and find a different balance.

Appendices

A Cost breakdown

This is the cost appendix...

B Ressources

This is for all the files: CAD, etc.
Probably just a GitHub link.
Also link to original Bridge12 project.

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[1] W. Froncisz and James S. Hyde. "The loop-gap resonator: a new microwave lumped circuit ESR sample structure". In: *Journal of Magnetic Resonance (1969)* 47.3 (May 1982), pp. 515–521. ISSN: 0022-2364. DOI: 10.1016/0022-2364(82)90221-9.

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