

ELECTRON SPIN RESONANCE

OBJECTIVES

- * To learn some properties of a simple microwave reflection spectrometer.
- * To calibrate the magnetic field using DPPH.
- * To measure the g factor, nuclear spin, and hyperfine coupling constant of the $^{55}\text{Mn}^{2+}$ ion.

REFERENCES

- * A. Melissinos, *Experiments in Modern Physics*
- * Alger, *Electron Paramagnetic Resonance*
- * Poole, *Electron Spin Resonance*
- * Wertz & Bolton, *Electron Spin Resonance, Elementary Theory and Applications*

Assignment:

Measure cavity Q, f_0 /F.W.H.M. Calibrate the magnetic field with the DPPH. Try the MgC_2 next. Understand g factor, the hyperfine interaction, a magnetic dipole transition, a Faraday isolator, an attenuator, and Q as used here.

INTRODUCTION

ESR (also known as EPR -- Electron Paramagnetic Resonance) is to electron spins as NMR (nuclear magnetic resonance) is to nuclear spins. In the case of ESR, transitions between energy levels of electronic magnetic moments in a magnetic field are induced by an externally applied radio frequency electromagnetic field. Since electronic magnetic moments are much greater in magnitude than nuclear moments, their energy levels in a given magnetic field are much more widely split. Correspondingly, the energy of the RF quanta which induce transitions are much higher, so that while the RF frequencies involved in NMR work are one the order of 20 MHz, the frequencies used in ESR work are in the microwave range: in our case, 9.5 to 10.5 GHz, corresponding to wavelengths of about 3 cm.

THE REFLECTION SPECTROMETER: Fig. 1

The system used in our lab for ESR work, called a reflection spectrometer, is diagrammed on the following page. The sample to be investigated is placed in a glass tube within a microwave cavity between the pole faces of an electromagnet. Microwave power is directed from an oscillator to an outside wall of the cavity, where a portion of the power enters through a hole called the iris. The extents of the waveguide cavity are defined at one end by the iris, and at the other by a screw driven plunger. A fraction of the incident RF power is reflected, and this reflected power is monitored by the indicated detector. The resonant frequency of the cavity (which is determined by physical dimensions and is independent of magnetic field) is adjusted to correspond to the frequency of the oscillator, and the phase of the incident microwave is adjusted to give a maximum power transfer into the cavity with minimum reflection.

While keeping the microwave frequency fixed, the magnetic field is varied until spin resonance occurs. At resonance, microwave power is absorbed by the sample, resulting in a net change in the characteristics of the cavity, with a consequential increase in the amount of reflected power. The variation in the reflected power as a function of magnetic field strength is the signal which will be measured in this experiment.

The microwave system uses so-called X-band components (designed for use in a frequency range of 8-12 GHz). You should learn the function and principle of operation of these devices, including the Faraday isolator, wavemeter, directional coupler, slotted line tuner, iris coupler, resonant cavity, and diode detector (lots of good physics here!).

MICROWAVE SOURCE

There are a variety of microwave RF sources than can be used in this experiment. Among them are the klystron, the H-P BWO sweep oscillator, the Gunn diode oscillator, and the phase locked transistor oscillator.

The first two are tube type oscillators and are somewhat noisy and/or unstable. The latter two are solid state oscillators, and are quiet, stable and easy to use. For this experiment we will use the most stable phase locked bipolar transistor oscillator.

SOLID STATE MICROWAVE RF OSCILLATORS

The solid state oscillator is the preferred RF source for the ESR/EPR experiment. However, these devices are somewhat delicate. Extreme care must be used when connecting these devices to their DC power supply. Excessive voltage (or current) and/or reversed polarity can destroy these devices).

Solid state oscillators are powered by a single, variable voltage, regulated DC power supply capable of producing 20 volts DC at 1 amp. Our Power Designs TP340 works nicely for this.

DETECTOR

Since microwave frequencies are too high to observe and measure directly with conventional means, a microwave mixer diode is used. The diode rectifies the AC RF signal, and produces a DC voltage that is proportional to the RF amplitude, much like an AM radio detector.

PROCEDURE

Turn on the power supply for the microwave oscillator. It is best to check the operating voltage first, before connecting it to the oscillator. The recommended operating voltage is -20 volts. Every effort must be taken not exceed this voltage. It is probably to set the supply to 0 volts, then bring it up to 20. Also please note the polarity.

You can verify that it is operating by measuring the current at the detector on the waveguide near the oscillator using the oscilloscope.

Your first measurement should be to find the frequency of your oscillator. Slowly adjust the wavemeter through the range of 9 to 11 GHz. Look for a dip in the output detector voltage on the oscilloscope. Take the reading between two red lines on the wavemeter. Record this value for your calculations, and compare it with the frequency printed on the oscillator.

Insert your sample* into the waveguide cavity between the poles of the magnet. The axis of the waveguide should be at exactly 90^0 to the field, and the sample should be centered in the field.

Use a rubber o-ring around the sample tube to help keep it positioned. A tiny change in position will affect the null of the spectrometer.

Connect the detector output to the oscilloscope. Adjust the micrometer on the slide screw tuner so that the probe tip does not extend into the waveguide (counter clock-wise 1/2"), and monitor the DC detector output on the scope. Do not unscrew the probe completely.

Match the resonant frequency of the cavity to the oscillator by tuning the cavity termination adjustment for a dip (or null) in the reflected RF at the detector output. Carefully adjust the cavity for a minimum, then use the micrometer probe insertion adjustment of the slide screw tuner to improve the null (further reduce power reflected from the cavity.)

Use thumb wheel knob to position the probe at the proper phase in the RF field, and further improve the null. This should reduce the reflected signal at the detector to just a few tenths of a millivolt.

You may begin a search for resonance by applying the magnetic field. The main B field is supplied by the 9" Varian magnet and its power supply. Before turning on the power supply, open the chilled water lines, return line first then supply line -- (close in the reverse order).

Slowly sweep the power supply manually through the range between 50 and 60 amps. You should make a calculation to determine more precisely the magnetic field at which resonance will occur. Use the magnet calibration curve (taped to the magnet) to convert from field in KGauss to current in amps. Use the oscilloscope to look for a "jump" in the detector output as you cross resonance. Use the sweep motor to produce a slow, repetitive sweep when you are ready to take data.

Then one piece at a time begin connecting and testing the pre-amp, the H-P sinewave oscillator, and ultimately the lock-in amplifier.

*(DPPH, a black crystalline power, is a very good calibration sample.) See paper by David Papas for Mn^{2+} sample preparation.

PAR 113 Pre-Amplifier

The Princeton Applied Research pre-amplifier serves a dual function: 1.) to increase the amplitude of the signal from the detector, and 2.) to limit the bandwidth of the signal coming from the detector.

The gain needs normally to be set to either 10 or 100 as the signal in many cases will be "reasonably" large. A more important function is to limit the amount of noise coming from the detector, and to improve the signal to noise ratio. To properly set the band limits, one must consider the frequency characteristics of the signal, as well as the characteristics of the filter itself. For the high frequency cut-off, make sure the filter is set ABOVE the modulating frequency. Note that if the filter is set too close to the modulating frequency, it will attenuate your signal as well as the noise because it's roll-off slope is on the order of 6dB per octave. On the low frequency end, consider that the low frequency roll-off should be correspondingly lower than the modulating frequency.

GAUSSMETER

You will use a gaussmeter to make the actual measurements of your magnetic field. The sensitive area of the hall probe is approximately .1 inches from the end. The plane of the

probe must be precisely normal to the magnetic field. It should be placed as close to the sample as possible for an accurate measurement of the field near the sample.

Your data can be plotted on the XY Plotter as; lockin amplifier output as a function of magnetic field. The ratiometric output of the gaussmeter is used to drive the X axis of the XY plotter. However most of the time you will be measuring changes of only a few hundred gauss in a field of a few kilogauss. The gauss meter has a unique feature which makes it particularly well suited to this experiment, by allowing you to make incremental measurements. By adjusting the zero offset controls, you can null the magnetic field at resonance to zero, allowing you to plot only the change in field during a field sweep.

H-P Sinewave Oscillator

This oscillator is used to drive the helmholtz coils, which are mounted on the pole pieces of the 9" Varian magnet. With these coils you can modulate the net magnetic field surrounding your sample. You should use a frequency which is harmonically unrelated to 60 Hz, as there is an abundance of line noise in the environment of the lab.

Also, make an attempt to measure the amplitude of the modulating field, and it's relation to the voltage output from the sine oscillator. This information will be crucial in determining the appropriate amplitude for the modulating field compared with the width of the resonance peak(s). (The amplitude of the modulating field should be smaller than the width of the peak(s), again refer to Fig. 2.)

Lock-In Amplifier

The most sensitive way to record data in this experiment is with the lock-in amplifier. It has the ability to detect extremely small signals in the presence vast amounts of noise.

The lock-in requires two input signals. One is a reference signal. For the reference we use the AC voltage used to modulate the effect we are looking for. In this case we modulate the magnetic field using Helmholtz coils driven by a Hewlett-Packard audio oscillator. The lock-in makes it's frequency and phase measurements relative to this signal.

The other requisite signal is the one from your detector (vis a vis the PAR 113 pre-amplifier). The lock-in "looks" for a signal at the reference frequency, to the exclusion of all other frequencies, and measures its amplitude and relative phase. The lock-in amplifier thus produces as it's output, a derivative of the resonance peak as illustrated by the transfer characteristic in Figure 2. Success in this experiment will depend to a large extent upon how well you can adjust the frequency and amplitude of the modulating field, and how well you can match the filtering and phase of the lock-in to the modulating field. Please refer to the manuals for more information on lock-in amplifiers.