

# ELECTRON SPIN RESONANCE

v2.2

Last revision: C. Schroeder, 4-2003

## I. INTRODUCTION

In this experiment, you will use Electron Spin Resonance (ESR) to characterize the local environment of the unpaired electrons in two copper salts and a series of aqueous solutions of Manganese ions. Before beginning, read pp. 340-344 and 374-389 in Melissinos, Experiments in Modern Physics, the handout "Hyperfine Splitting," and the attached appendix. Answer the following questions in your lab notebook. The physics discussed in these questions forms the basis you will need to understand and report on your results.

1. What is  $g$  in terms of the basic properties of a free, isolated electron?
2. Why should  $g$  depend on the local "chemical" environment of an unpaired electron, *i.e.* how the other electrons and nuclei are positioned around the unpaired electron?
3. Describe the electronic structure and give the spectroscopic notation for  $\text{Cu}^{+2}$  and  $\text{Mn}^{+2}$ .
4. How big is the magnetic field of a proton at a distance equal to a typical atomic radius? How does it compare to the  $\sim 3\text{KG}$  you will be applying to the samples? Why and how should the magnetic field of the nucleus affect the ESR signal of the unpaired electron surrounding that nucleus, *i.e.* what is the origin of the hyperfine splitting?
5. How big is the magnetic field of an electron at a distance equal to a typical inter-ion distance in a 1M solution? What is the characteristic distance dependence of the field? How does it compare to the  $\sim 3\text{KG}$  you will be applying to the samples? Considering this field, why might the ESR signal be affected if two unpaired electrons come near each other?

## II. THE APPARATUS

These notes are intended primarily to describe the minor differences between our spectrometer and that described in Melissinos. In these notes, all references to Melissinos will be designated by "M", e.g. "Fig. 8.21 M."

Our apparatus is similar to that of Fig. 8.21 M, but differs in the method of power division. In Fig. 8.21M, the "magic T" has the property that power incident in arm A divides equally between arms B and C. The power in arm C is absorbed in the dummy load, while that in arm B

is incident on the cavity containing the sample. The interesting power is that reflected from the sample cavity, which changes when magnetic resonance absorption occurs. This reflected power is again divided equally by the “magic T,” half going to the detector in arm D, half returning via arm A to the oscillator where it is lost. This scheme wastes half the power available from the oscillator, and half of the signal power reflected from the cavity. Our spectrometer replaces the “magic T” by a 15 db coupler, as shown in Fig. 1.

Power incident on the directional coupler from the klystron oscillator goes primarily to the absorbing load. A small amount, about 3%, of the incident power is coupled to the cavity arm, i.e. the coupled power is 15 db less than the incident power. However, when power is reflected from the cavity it goes primarily (97%) to the detector, and only a small amount is lost. This technique is wasteful of input power, but makes efficient use of the signal power. We can afford to waste input power, because our klystron puts out more power than we need. In some cases it is necessary to reduce the input power still further by means of the variable attenuator following the klystron. With no attenuation, the power incident on the cavity is 3-5 milliwatts.

Our cavity is fixed-tuned, and oscillates in the TE<sub>102</sub> mode, which means that it contains 2 half wavelengths of the TE<sub>10</sub> mode. For the field configurations in this mode see Fig. 8.26M. Remember that the fields in the cavity are standing waves, but that in the waveguide they are traveling waves.

### Tuning the Klystron to The Resonance Frequency of the Cavity

The klystron must be tuned to the resonant frequency of the sample cavity. To do this the klystron frequency must be varied by modulating the reflector voltage with a 60 Hz sine wave. The modulating voltage is injected into the klystron power supply from the modulating panel. Fig. 8.24M shows the typical power output versus reflector voltage for the klystron. Each bell-shaped curve is called a “klystron mode.” The maximum modulating voltage is sufficient to sweep the klystron over an entire mode, and the particular mode is determined by the DC value of the reflector voltage set with the reflector voltage control. The power reflected from the cavity is monitored by observing the voltage across the microwave crystal detector. When the cavity and the klystron are not tuned to the same frequency, the mode pattern should appear as in Fig. 2a. When the modulated klystron is being swept through the cavity frequency the reflected power appears as in Fig. 2b. The dip in Fig. 2b is due to the absorption of power by the cavity. It is the microwave case of a system (cavity) with a natural resonant frequency being able to absorb power from a driving force when the driving frequency matches the natural frequency. Once the mode pattern of Fig. 2b is obtained, the modulation voltage on the reflector should be reduced slowly to zero, keeping the klystron tuned to the cavity by adjusting the DC reflector voltage so as to minimize the power reflected from the cavity.

To turn on and tune the klystron use the following steps:

1. Place a sample (e.g., DPPH) in the cavity. Make sure the sample is in place, *i.e.*, that its bottom comes through the hole on the bottom of the cavity.
2. Turn on the oscilloscope and the amplifier (above oscilloscope). Set the amplifier GAIN (knob in the back) to 200. Both X and Y on the oscilloscope should be DC-coupled. X should be the phase-shifted output from the modulation panel, while Y should be the output from the amplifier.

Recommended scope settings at this point are **Ch1**: .5 V, **Ch2**: 2 V, and **Time**: XY.

3. On the klystron Panel, set BEAM VOLTAGE to 370 V and REFLECTOR VOLTAGE to 0 V. Flip the klystron power supply switch to FIL. Wait a minute. Then flip it to H.V. & FIL.

4. Turn on the modulation panel. Set the MODULATION FUNCTION switch to EXT and connect ATTENUATED OUTPUT on the modulation panel to MOD.IN on the klystron power supply. Set MODULATION AMPLITUDE to 50.

5. Increase REFLECTOR VOLTAGE from 0 to 4 V, while watching the oscilloscope. You should see four pairs of peaks slide across the scope display. The second lowest of these, at a reflector voltage of about 1.1 V, produces the sharpest mode pattern. Adjust the klystron tuning-screw to make the pattern as symmetric as possible (see Fig. 2b), disregarding any difference in peak heights.

6. Turn down MODULATION AMPLITUDE while adjusting REFLECTOR VOLTAGE to keep the klystron tuned to the cavity frequency, i.e. keep the dip in the mode pattern centered on the scope. As you reduce the modulation, increase the sensitivity of the Y-axis of the scope. The vertical position of the signal can be adjusted with the FINE REFERENCE control of the amplifier (note: decreasing the FINE REFERENCE causes the signal to rise on the scope.).

7. After reducing the modulation to zero, disconnect the ATTENUATED OUTPUT from MOD.IN. The scope now displays a horizontal line, whose level indicates the power reflected from the cavity with microwave frequency determined by the reflector voltage setting. Carefully adjust the reflector voltage to minimize the D.C. level of the signal. Now the power absorbed by the cavity is maximized; the klystron is tuned to the resonant frequency of the cavity.

8. The frequency meter has its own adjustable cavity, connected to a large, calibrated cylindrical dial. When the frequency of the cavity matches that of the klystron, the cavity absorbs energy and the signal level on the scope goes to a minimum. Adjust the frequency meter dial until the DC level on the scope dips sharply. When the level is minimized, you can read the frequency from the dial. Then give the dial a few turns to move it away from resonance, so that it doesn't interfere with the sample's signal. You are now ready to observe electron spin resonance.

The klystron frequency may drift slowly, resulting in increased noise. For best results, tune the klystron frequency immediately before each recorded ESR sweep. Turn on the Current Regulated Power Supply for the DC magnetic field, and slowly turn up the current. When the field reaches a resonance, the sample absorbs a maximum of power, and the reflected power detected at the scope goes through a minimum.

### Displaying and Recording of ESR Signals

For a simple oscilloscope display, we use sinusoidal modulation of the magnetic field. This is provided by a set of auxiliary coils wound on the magnet poles and driven at 60 Hz by a step-down transformer fed by a variac. By adjusting the variac control, we can set the amplitude of the 60 Hz field modulation about the DC field set by the magnet power supply. When the field crosses a resonance of the sample, the reflected power which drives the scope's Y-axis decreases. The X-axis is driven by the 60 Hz phase-shifted output of the modulation panel. If the

phase of this signal does not match that of the field modulation, each resonance will appear as two dips on the scope (why?). Adjust the phase so that the two dips coincide.

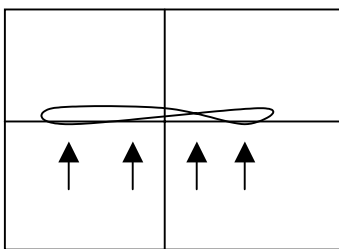


Figure 0a. Resonance, no modulation

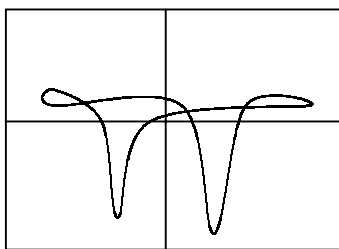


Figure 0b. Resonance, out of phase

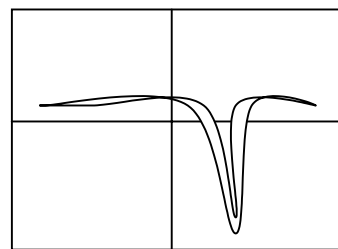


Figure 0c. Resonance, in phase

If the width of the ESR peak is small compared to the peak-to-peak modulation field, then the entire peak can be displayed on the oscilloscope; otherwise, only part of the peak can be displayed at any time. Using DPPH you should be able to estimate the maximum modulation field available from the auxiliary coils by decreasing the constant field away from a resonance until the peak is out of the range of the maximum modulation.

For capturing the peak(s) with the digital oscilloscope, the field sweep generator injects a current into the magnet power supply that can be used to vary the field above and below the value set by the current control on the Current Regulated Power Supply. The magnitude of the sweep output, and hence the range of the sweep, is set by the RANGE control. The field sweep generator has 3 modes: 0, MANUAL, and SWEEP. In the 0 position, the generator has no effect on the field. In MANUAL mode, the field can be varied by hand using the MANUAL potentiometer. In SWEEP mode, the field will increase or decrease as a linear function of time. The direction of the sweep may be selected, or the sweep stopped at any point, with the SWEEP DIRECTION control. The SWEEP TIME control selects the time to sweep over the complete range of sweep output current. The SWEEP OUTPUT meter monitors the sweep generator current, in both MANUAL and SWEEP modes.

Turn on the sweep generator and set the linear sweep mode to MANUAL. Then, adjust the MANUAL control so that the current output dial reads 0 mA. Next, slowly adjust the magnet current control on the main power supply until you see a resonance, indicated by the maximum deflection in the DC signal on the scope. The field is now centered at the resonance, and can be adjusted above or below it by turning the MANUAL potentiometer. Using the scope, adjust the sweep output range so that the entire resonance line (or lines) can be observed by manually varying the current from  $-100$  to  $+100$  mA. Reset the sweep current to 0 mA.

### Setting Up the Storage Scope:

1. Set Scope to x-y Storage Mode as follows
  - \* Press DISPLAY button (upper right of front panel)
  - \* X Y Display (bottom menu)
  - \* Triggered X Y (side menu)
  - \* Ch1 vs. Ch2 (side menu)
  - \* Ref 1 vs. off (side menu)
  
2. Set the Persist Time to  $\infty$  (infinity) as follows
  - \* Press Waveform Display (bottom menu)
  - \* Persist time (side menu)
  - \* Use the top right knob to adjust the persist time to  $\infty$  (infinity)
  
3. Adjust the axes and position of the display
  - \* Press the yellow Ch1 button
  - \* Use the first column of knobs to set scale to 1.00 V
  - \* Press the blue Ch2 button
  - \* (setting for Ch2 depends on the particular sample)

(Note: You will only see a signal after you hit Run/Stop. The screen should say “Roll” in the upper left.)

4. Acquire Data
  - \* Press Menu button (in Acquire column, far right)
  - \* Mode (bottom menu)
  - \* Sample (side menu)
  - \* Horizontal Resolution (bottom menu)
    - \* Normal (10k) (side menu) - **WARNING:** do not change Horizontal Delay or Autoset.
    - \* Adjust sampling rate with the time scale knob (bottom of middle column) so that the time given by the number of samples, 10k, divided by the sample rate, bottom right of screen after the Acquire menu button has been pressed (e.g., 250 Samples/second) is equal to or slightly greater than the sweep time. The slowest sampling rate is 100 Hz, so maximum sweep time is 100 s.

When you are ready to take data, start the ESR magnet current sweep and press the Single Seq button (upper right) on the scope.

## 5. Save Data to Disk

- \* Insert a 3.5" diskette into the slot below the scope screen.
- \* Press Save/Recall button (upper right)
  - \* Save Waveform (bottom menu)
  - \* File (side menu)
  - \* Use the upper left knob to display an existing file or, choose fdo: to save a new file. (The default name is TEK0000#.csv.) Use the yellow Ch1 and blue Ch2 buttons to be sure you **save both channels**.
  - \* Spreadsheet (side menu)
  - \* Save (side menu)

## III. THE EXPERIMENT

### A. Using DPPH:

- a. Measure the H of resonance in the apparatus and using the g factor in Melissinos find a calibration factor relating the H at the sample and the H measured by the Gauss probe mounted in the apparatus.
- b. Using careful traces of the resonance curve, measure the full width at half maximum of the resonance peak and compare it to the value given in Melissinos. This tells you the resolution of the instrument.

### B. For anhydrous and hydrated $\text{CuSO}_4$ powders:

Use the ESR line shape to determine if the local environments of the unpaired electrons in these two powders are the same or not.

### C. For the $\text{MnCl}_2$ solutions:

- a. Measure the ESR signal from several concentrations to observe the hyperfine splitting.
- b. Determine if the line widths and/or resonant fields of the separate lines are dependent on the average distance between  $\text{Mn}^{+2}$  ions. Finding the line width is challenging. Try crudely fitting the ESR traces to the correct number of overlapping Gaussian peaks. To save much agony in fitting, make the following simplifications: (i) fix the line positions using measurements directly from the traces, and (ii) set all the line widths to be equal.

**APPENDIX: HYPERFINE SPLITTING IN  $Mn^{+2}$** 

Figure 3 shows the energy level diagram for  $Mn^{+2}$ . The following notes will help you understand why there are only 6 lines the hyperfine energy spectrum.

Energy spacings are described by

$$\Delta E = \gamma B S_z + A I_z S_z$$

with dipole transitions allowed only for  $\Delta S_z = \pm 1$  and  $\Delta I_z = 0$ . Note for the electron angular momentum we need only the spin angular momentum since the ion is in the S state.

Then

$$\begin{aligned} E(S_z^i, I_z^i \rightarrow S_z^f, I_z^f) &= \gamma B (S_z^f - S_z^i) + A (I_z^f S_z^f - I_z^i S_z^i) \\ &= \gamma B (\pm 1) + A I_z (\pm 1) \\ &= \pm (\gamma B + A I_z) \\ |E(S_z^i, I_z^i \rightarrow S_z^f, I_z^f)| &= |\gamma B + A I_z| \end{aligned}$$

Therefore, all transitions with the same  $I_z$  are the same energy. Thus you have 6 distinct, 6-fold degenerate transitions.

ESR

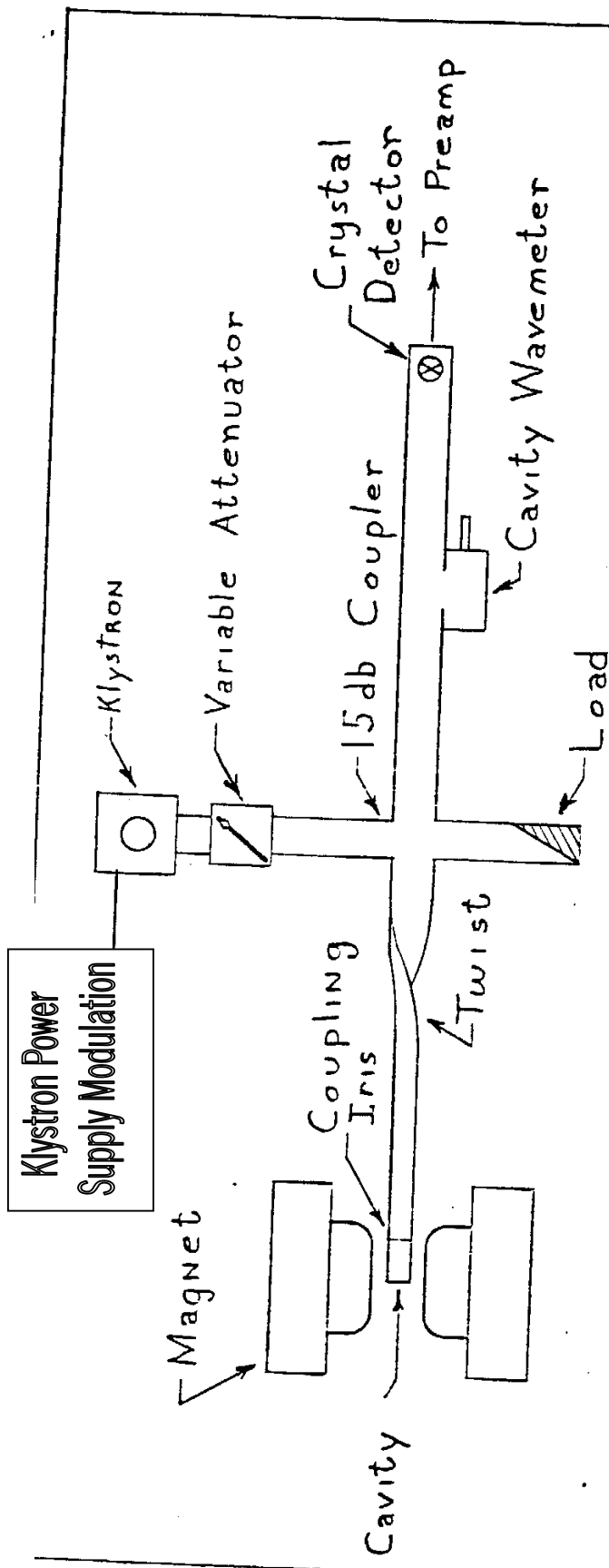


Fig. 1 ESR SPECTROMETER

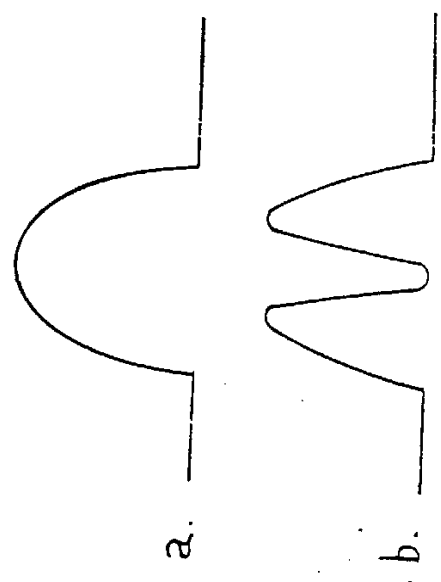
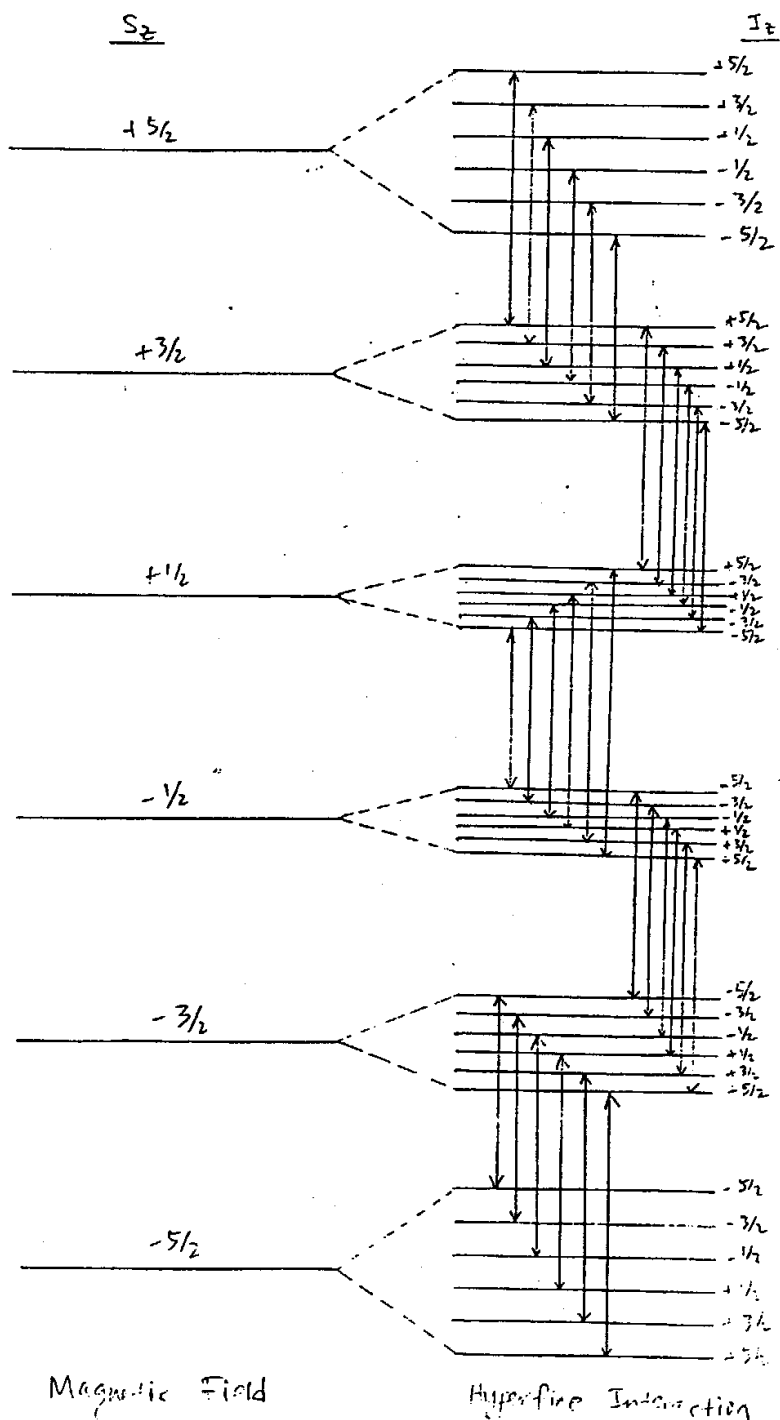


Fig. 2

Fig. 3. Energy level diagram for  $Mn^{2+}$

$Mn^{2+}$  ground state:  $6S_{5/2}$  with nuclear spin  $I = 5/2$

Hamiltonian  $\mathcal{H} = \gamma B S_z + A I_z S_z$



Allowed Transition

$$\Delta S_z = \pm 1$$

$$\Delta I_z = 0$$

$$\Delta E_1 = \gamma B + \frac{5A}{2}$$

$$\Delta E_2 = \gamma B + \frac{3A}{2}$$

$$\Delta E_3 = \gamma B + \frac{A}{2}$$

$$\Delta E_4 = \gamma B - \frac{A}{2}$$

$$\Delta E_5 = \gamma B - \frac{3A}{2}$$

$$\Delta E_6 = \gamma B - \frac{5A}{2}$$

$I_z$

$$\Delta E_1 \quad \frac{5}{2} \rightarrow \frac{5}{2}$$

$$\Delta E_2 \quad \frac{3}{2} \rightarrow \frac{3}{2}$$

$$\Delta E_3 \quad \frac{1}{2} \rightarrow \frac{1}{2}$$

$$\Delta E_4 \quad -\frac{1}{2} \rightarrow -\frac{1}{2}$$

$$\Delta E_5 \quad -\frac{3}{2} \rightarrow -\frac{3}{2}$$

$$\Delta E_6 \quad -\frac{5}{2} \rightarrow -\frac{5}{2}$$