Experiment 2: Electron Paramagnetic Resonance

1. Principles of electron paramagnetic resonance

The purpose of this lab is to understand the principles of electron paramagnetic resonance (EPR), and learn the techniques used in operating an EPR spectrometer. As a practice we will measure the $g$-factor and the hyperfine splitting constant for the V$^{2+}$ ions in a MgO crystal.

*Electron paramagnetic resonance* is a technique of measuring the absorption spectrum of materials with unpaired electron spins at the presence of an external magnetic field. The absorption is due to the excitation between electron spin states whose energies depend on the external magnetic field, and is in the microwave region of the electromagnetic waves. It is therefore also called *electron spin resonance*. EPR was first observed by the former Soviet physicist Yevgeny Zavoisky in Kazan State University in 1944. The applications of EPR have been extended into various research areas in physics, chemistry and biological sciences. Today EPR has grown from an experimental technique into a established research subject in science. For reference books on the principles and applications of EPR, I recommend you Weil and Bolten’s *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications* in general, and Abragam and Bleaney’s *Electron Paramagnetic Resonance of Transition Ions* for more advanced topics.

When two electrons share the same atomic or molecular orbital, their spin quantum numbers must be different, e.g., one spins up and the other spins down. If all electrons in an atom are paired, the total spin of the atom will be zero, and the atom is said to be *diamagnetic*. In contrast, if an atom contains one or more electrons with unpaired spins, it is called *paramagnetic*. Paramagnetic atoms realign themselves in an external magnetic field, which results in the splitting of energy levels due to Zeeman effect. In EPR spectroscopy the materials are required to be paramagnetic, which makes it suitable in studying the following types of materials: 1) atoms or ions with incomplete inner shells, e.g., transition metal atoms, rare earth atoms and actinides, 2) atoms, molecules and lattice defects with odd numbers of electrons, e.g. free sodium atoms, organic radicals, and 3) metals.

Although we are interested in the 3$d$ transition metal ions in this lab, the principles of paramagnetic resonance can be easily illustrated by considering a system where each molecule has only one free electron. Considering a free electron with *spin quantum number* $s=1/2$, its *spin angular momentum* $S$ has an amplitude of
\[ S = \sqrt{s(s+1)}\hbar = \sqrt{\frac{1}{2} \left( \frac{1}{2} + 1 \right)}\hbar = \frac{\sqrt{3}}{2}\hbar. \]  

(1)

The corresponding magnetic moment due to electron spin is

\[ \mu_s = -g_e \frac{e}{2m} S = -g_e \frac{S}{\hbar}\mu_B. \]  

(2)

Here \(-e\) is the charge of the electron, and \(m\) is the mass of the electron. \(\mu_B = \frac{e\hbar}{2m} = 9.274 \times 10^{-21}\) erg/Gauss is the Bohr magneton, which is a nature unit for measuring the magnetic moment of an electron due to its orbital or spin angular momentum. The value of \(g_e\) is called the \(g\)-factor, which is a dimensionless number that measures the proportionality between the observed magnetic moment of a system and its angular momentum. This is more evident when the above equation is written as \(\mu_s = -g_e \frac{S}{\hbar}\mu_B\). For a free electron the electron spin \(g\)-factor is \(g_e=2.00232\). This magic number comes from calculations in quantum electrodynamics. Please note due to historic reasons and the antique apparatus we currently use, CGS units (centimeter-gram-second) are used in our experiment. You may need to remember 1 erg=10^{-7} J (Joule) and 1 Gauss (G) = 10^{-4} T (Tesla).

If we now apply an external static magnetic field with strength \(B\) to our system, the energy levels of the free electron are then

\[ E = -\mu_s \cdot B = g_e \frac{\mu_B}{\hbar} S \cdot B. \]  

(3)

Let the magnetic field \(B = |B|\) be in the \(z\) direction. Because the eigenvalues of the \(z\) component of the electron spin is \(S_z = m_s\hbar = \pm \frac{\hbar}{2}\), where \(m_s = \pm \frac{1}{2}\) is the spin magnetic quantum number, we then have

\[ E = g_e \mu_B m_s B = \pm \frac{1}{2} g_e \mu_B B. \]  

(4)

This means that in a magnetic field a free electron has two energy levels corresponding to \(m_s = \pm \frac{1}{2}\), as shown in Fig. 1. This is the electron Raman effect. The energy difference between the two levels is

\[ \Delta E = g_e \mu_B B = \hbar \nu. \]  

(5)

Here \(\nu\) is the resonant frequency between the two levels. If we place this electron in an electromagnetic wave that has exactly the resonant frequency, the electron may absorb a photon.
from the electromagnetic wave and move from the ground state $E_1$ to the excited state $E_2$. This transition can be detected by measuring the decrease of the power of the electromagnetic wave. In EPR spectroscopy the absorbed photon is in the microwave region, whose frequency is actually kept constant. Instead of varying the frequency of the microwave, the static magnetic field $B$ is scanned in a certain range so that the resonance condition Eq. 5 is satisfied. This means that briefly speaking in an EPR spectrum we measure the absorption of a microwave at a certain frequency by the material sample as a function of a scanning magnetic field.

![Energy levels of a free electron in an external magnetic field](image)

Fig. 1 Energy levels of a free electron in an external magnetic field

At thermal equilibrium the ground state $E_1$ has slightly more population than the excited state $E_2$, and the system has net absorption until the two levels have the same population. This does not occur in general because of a process called \textit{spin-lattice relaxation}, which couples the spin system and the crystal lattice. Spin-lattice relaxation is a non-radiative process that provides a path for the electron at the excited state to move back to the ground state by the emission of a \textit{phonon} with the energy $h\nu$. This process happens at a rate of $\frac{1}{T}$, where $T$ is called the \textit{spin-lattice relaxation time}, which causes line broadening in the EPR spectrum. Like in any other spectroscopic methods, line broadening may contain certain interesting points, but at the same time it prevents us from exploring the detailed structure of the spectrum of the system we are studying. The EPR linewidth can be estimated by using the uncertainty law $\Delta E\Delta t = h$, which gives

$$\Delta v = \frac{g_s \mu_B}{h} \Delta B \approx \frac{1}{T}.$$  \hspace{1cm} (6)

As shown in Eq. 6, in an EPR spectrum the resonance linewidths are measured in terms of the width of the magnetic field $B$. There exist other line broadening mechanisms, such as the spin-spin interaction. This can be reduced by diluting the paramagnetic ions in a diamagnetic salt so that the spins have an increased distance between each other.
2. EPR spectrum of $V^{2+}$

One of the most widely used applications of EPR spectroscopy is to study the paramagnetic ions in solids, especially in various crystals. Ions with an unpaired electron spin, such as the iron group vanadium, chromium, manganese, iron, cobalt, nickel and copper, each has a characteristic spectrum depending upon their valence state, as well as a characteristic hyperfine structure depending upon their nuclear spin. EPR spectroscopy can be used to identify these ions as impurities in a crystal, and very often valuable information about the environment around the ions can be obtained.

The degeneracies of the electron states in an ion can be broken by the static electric field produced by the surrounding charge distribution in the crystal, which is called crystal field splitting. The symmetry of the site occupied by the ion is thus very important. Obviously these are complex effects. Therefore we have picked a fairly simple yet representative case, $V^{2+}$, whose paramagnetism arises from the partially filled $3d^3$ atomic shell. We will observe the spectrum of dilute $V^{2+}$ ions that have substituted the Mg$^{2+}$ ions in a MgO crystal. In general, the $g$-factor in the expression for the transition energy, as in Eq. 4, is a second-rank tensor represented by a $3\times3$ matrix. MgO has the cubic structure like NaCl, therefore a highly symmetric octahedral symmetry presents at the cation site, and the $g$-factor is isotropic in this case. In addition, our sample also contains a small amount of Cr$^{3+}$, which has the same $3d^3$ electron configuration.

We now consider the energy levels of $V^{2+}$ in MgO. We first consider the ground state of the $3d^3$ electron configuration, and then the splitting of these ground state energy levels by the octahedral crystal field. All three electrons in the $d$ shell have orbital quantum numbers $l = 2$, and spin magnetic quantum numbers $m_s = \pm 1/2$. They are equivalent electrons. For a multi-electron atom, the angular momentum quantum numbers are represented by term symbols. In the Russel-Saunders or L-S coupling scheme the electrons are coupled together to form a system with total orbital quantum number $L$ and total spin quantum number $S$. The total angular momentum quantum number $J$ is then obtained by vectorial addition of $L$ and $S$. For our equivalent $d^3$ configuration, the possible resultant term symbols are $^2P$, $^2D$ (twice), $^2F$, $^2G$, $^2H$, $^4P$, and $^4F$. These symbols are written in the form of $^{2S+1}L_J$. For the method of determining term symbols for a given electron configuration, please refer to any atomic physics textbook. My favorites are Donald McQuarrie’s *Quantum Chemistry* at beginning level, and Ira Levine’s *Quantum Chemistry* at advanced level. For a physics student both your eyes and your mind will be expanded and enlightened when you discover that the electron structure in molecules can be accurately calculated after reading these classical textbooks. In calculating electronic energies, the Coulomb and exchange interactions between electrons slightly modify the atomic shell
energies. Among the various possible terms the one with the lowest energy is given by \textit{Hund's rules}, which is the term we are interested in. According to Hund's rules, the lowest energy term is that having 1) maximum total spin, and then 2) maximum total orbital momentum. Thus the lowest energy term for \( V^{2+} \) is \(^4F\), which has the \textit{total electron spin quantum number} \( S=3/2 \) and \textit{total orbital quantum number} \( L=3 \), and a degeneracy of \((2S+1) \times (2L+1)=4 \times 7=28\). The spin degeneracy is specified by the \textit{total electron spin magnetic quantum number} \( M_S = -3/2, -1/2, 1/2, \) and \( 3/2 \).

The \( V^{2+} \) ion is then placed in an octahedral crystal field produced by the MgO crystal. The orbital degeneracy is split into a singlet \(^4A_2\) and two triplets \(^4T_1\) and \(^4T_2\), as shown in Fig. 2. Please refer to Orton, \textit{Electron Paramagnetic Resonance: An Introduction to Transition Group Ions in Crystals}. Actually, the singlet state \(^4A_2\) is the lowest by a considerable amount (~10^4 cm\(^{-1}\)) of energy. At ordinary temperature only this singlet level is occupied, where the magnetism arises from electron spin only. The four fold spin degeneracy is unaffected by the cubic crystal field.

We then place the \( V^{2+} \) substituted MgO crystal in an external field \( B \) which is in the \( z \) direction. There are small second order spin-orbit effects, which influence the magnetic properties of the ion. As a result the actual magnetic field strength at the electron is slightly different from the external field \( B \). This can be taken into account by introducing an \textit{effective g-factor}, usually in the range of values \( g = 1.97 \) to \( 1.99 \), in the expression for the energy levels of the system. Eq. 4 now is modified into

\[
E = g \frac{\mu_B}{\hbar} \mathbf{S} \cdot \mathbf{B} = g \frac{\mu_B}{\hbar} S_z B = M_S g \mu_B B. \tag{7}
\]

The splitting of the energy levels by the crystal field and the external magnetic field is illustrated in Fig. 2. In the magnetic field the system takes four energy levels at \( E = M_S g \mu_B B \) with \( M_S = -3/2, -1/2, 1/2, \) and \( 3/2 \).

In our EPR experiment, electron transitions occur between the four energy levels according to the selection rule \( \Delta M_S = \pm 1 \), as shown in Fig. 2. This is because the absorbed or emitted photon has a spin of \( s=1 \). Here in the absence of hyperfine splitting, the three allowed transitions \((M_S = -3/2 \rightarrow -1/2, -1/2 \rightarrow 1/2 \) and \( 1/2 \rightarrow 3/2\)) are coincident in energy, which results in one resonance line in the spectrum.

Vanadium ion has actually a strong \textit{hyperfine splitting} due to the interaction between the electronic magnetic moment, resulted from its total electron spin quantum number \( S = 3/2 \), and the magnetic moment of its nucleus, resulted from its \textit{total nucleus spin quantum number} \( I = 7/2 \). The strong dipole-dipole interaction between the two magnetic moments causes the splitting of the ground state levels. The energy in Eq. 7 has to be modified to include the effects of \textit{nuclear spin angular momentum} \( I \),
\[ E = g \frac{\mu_B}{\hbar} \mathbf{S} \cdot \mathbf{B} + A \frac{\mathbf{I}}{\hbar} \cdot \frac{\mathbf{S}}{\hbar} + g_n \frac{\mu_n}{\hbar} \mathbf{I} \cdot \mathbf{B}. \]  

(8)

Here the second term represents the dipole-dipole interaction between the electron and nuclear magnetic moments, which will lead to the hyperfine splitting of the spectral line. \( A \) is called the **hyperfine splitting constant**. The third term, which takes similar form as the first term, is the energy of the nucleus in the external magnetic field. Here \( g_n \) is the gyromagnetic ratio of the nucleus, which is the ratio between its magnetic dipole moment and its angular momentum. The value \( \mu_N = 5.051 \times 10^{-24} \text{erg/Gauss} \) is the **nuclear magneton**. It turns out that the last term can be neglected relative to the other two terms, mainly because \( \mu_n \) is much smaller than \( \mu_B \).

Fig. 2 Energy levels of \( \text{V}^{2+} \) in the crystal field and the external magnetic field

The eigenvalues of \( I_z \), the \( z \) component of the nuclear spin angular momentum, is

\[ I_z = M_I \hbar = \left( -\frac{7}{2}, -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2} \right) \hbar, \]

where \( M_I \) is the **total nuclear spin magnetic quantum number**. The eigenvalues of \( S_z \), the \( z \) component of the electron spin angular momentum, is

\[ S_z = M_S \hbar = \left( -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2} \right) \hbar. \]

Consequently Eq. 8 is now reduced to

\[ E(M_S, M_I) = g \mu_B M_S B + A M_S M_I, \]  

(9)
The energy levels of our system are now specified by the quantum numbers $M_s$ and $M_I$. Due to hyperfine splitting each energy level in Fig. 2, specified by $M_s$, is split into eight hyperfine levels specified by $M_I$. Fig. 3 shows just two of the energy levels of the system, $M_s = \pm 1/2$, plotted against increasing magnetic field. Please note the inversion of the sequence of the energy levels with respect to $M_I$ when $M_s$ changes its sign, which is in accordance to Eq. 9.

The selection rules for a transition in our system is $\Delta M_s = \pm 1$ and $\Delta M_I = 0$ when a photon is absorbed or emitted. The possible transitions are then $(M_s, M_I) \rightarrow (M_s + 1, M_I)$ with energy differences of

$$h\nu(M_s, M_I) = E(M_s + 1, M_I) - E(M_s, M_I) = g\mu_B B + AM_I. \quad (10)$$

Therefore the three coincident spectral lines in Fig. 2 are split into eight separate lines, which can be specified by the common quantum number $M_I$ of the lower and upper levels. Each separate spectral line still contains three overlapped lines, specified by the $M_s$ value of the lower energy level involved. Fig. 3 shows the transitions between $M_s = -1/2$ and $M_s = 1/2$. The two other sets of spectral lines, namely between $M_s = 1/2$ and $M_s = 3/2$, and between $M_s = -3/2$ and $M_s = -1/2$, produce eight spectral lines at exactly the same positions. The unusual shape of the spectral line will be explained later.

In an EPR experiment the microwave frequency $\nu$ is fixed and the magnetic field $B$ is scanned. It is evident from Eq. 10 now that the important $g$-factor can be evaluated by first measuring the position of the center-of-gravity of the eight spectral lines, $B_c$, and then use

$$g = \frac{h\nu}{\mu_B B_c}. \quad (11)$$

After plugging in the constants one finds

$$g = 714.48 \times \frac{\nu / \text{GHz}}{B_c / \text{G}}. \quad (12)$$

As shown in Eq. 12, here the microwave frequency is measured in GHz, and the magnetic field is measured in Gauss. It can be shown from Eq. 10 that the hyperfine splitting constant $A$ is measured by the separation between adjacent hyperfine spectral lines, $\Delta B$, as

$$A = g\mu_B \Delta B. \quad (13)$$

The line separation $\Delta B$ can be precisely measured. Provided that the effective $g$-factor is well known, the hyperfine splitting constant can be determined accurately. For $V^{2+}$ the value is in the range of 5 to $10 \times 10^{-3}$ cm$^{-1}$. Here 1 cm$^{-1} = 1.986 \times 10^{-16}$ erg.

The much less abundant Cr$^{3+}$ impurity ion in our sample has a very small hyperfine splitting. As a result it gives a weak spectral line at the center of the spectrum.
Fig. 3 Hyperfine splitting of the energy levels of $\text{V}^{2+}$ and the resultant EPR spectrum

3. Experimental apparatus

Our experimental apparatus for the EPR lab was obtained as a gift from the Department of Physics in the University of Illinois at Urbana-Champaign in summer 2015. Thanks to Jack Boparai, a WIU Physics alumnus and currently a lab manager in UIUC, for thinking of us and arranging the transfer of the equipment. Thanks to Dr. Mark Boley for transporting the heavy equipment by his truck together with me. I spent fall 2015 semester to set up and troubleshoot the instruments. Also this lab manual is written mostly based on the one that had been used in UIUC for about twenty years. This EPR apparatus is a modified Varian E4 model. The modification was done by the former Micro-Now Instrument Company in Chicago led by scientist Clarence Arnow. Fortunately the EPR apparatus works very well now at our place. The recorded spectra are of textbook quality. I encourage every student to study the principles of EPR and take the most advantage of this apparatus. At the same time all students are required to
follow the instructions carefully when doing the experiment. Whenever you have a question, I am beside you and ready to help you.

The EPR spectrometer is currently located in Currens Hall 109, and is shown in Fig. 4. The spectrometer mainly consists of a microwave bridge, a magnet, and the receiving system. In the figure you can see the microwave bridge and its controller, the magnet and its power supply, the magnetic field controller, the modulation controller, an oscilloscope and an x-y chart recorder. In Fig. 5 we show the front panels of the microwave bridge controller, the magnetic field controller, the modulation controller, and the chart recorder controller.

![Fig. 4 EPR spectrometer](image)

The microwave bridge serves the function of generating microwaves and detecting the EPR signal. A klystron oscillator generates the microwave energy in the frequency range tunable from 8.8 to 9.6 GHz for the excitation of the sample. The klystron frequency can be tuned by the FREQUENCY knob on the front panel. The klystron output is fed to an attenuator to adjust the microwave power. The attenuator is controlled by the ATTENUATOR/POWER knob on the front panel, which indicates the microwave power incident upon the sample cavity located in the center of the magnet. Power attenuation is indicated in dB, and 0 dB has a maximum power of 200 mW. The DETECTOR CURRENT meter indicates the microwave crystal detector bias current in μA. At the resonant frequency of the sample cavity, the microwave energy is stored in the cavity and there is little energy reflected back to the crystal detector. When the sample absorbs the microwave energy, the impedance of the cavity is changed and a signal is reflected to the detector, which results in the EPR signal.
For each sample the cavity resonance frequency must be tuned separately. This is done in the TUNE mode of the klystron, after the ATTENUATION/POWER is set to about 25 dB. Once tuned, in the OPERATION mode an automatic frequency control (AFC) locks the klystron frequency to the sample cavity resonant frequency.

As we have mentioned, in an EPR measurement the microwave frequency is kept constant and the external magnetic field strength is scanned. The scan is provided by a saw tooth generator and the magnetic field is simultaneously monitored by a Hall probe. This is easier than to scan the microwave frequency since most microwave components have a fairly narrow band performance. The center of the magnetic field scan range is set by the FIELD SET control on the
console panel, and the width of the scan range is set by the SCAN RANGE knob. The scan is symmetric about the center field indicated by the FIELD SET control. For example, if the FIELD SET reads 3200 G and the SCAN RANGE is set to 100 G, the actually scanned magnetic field will be from 3150 G to 3250 G. The magnetic field is recorded by the x-axis of the chart-recorder.

In order to better amplify and record the EPR signal, one usually superimposes a high frequency magnetic field, which is fixed at 100 kHz in our setup, on top of the slowly scanned magnetic field. This modulation is done by means of small coils mounted outside of the cavity walls. The modulation magnetic field amplitude is kept smaller than the resonance spectral linewidth. Under these circumstances the detected signal at the modulation frequency is proportional to the slope of the absorption curve while the steady field is scanned through the resonance. The generated signal is called the first derivative EPR signal, often briefly referred simply as the EPR signal, as shown in Fig. 6. The phase and amplitude of the output signal of this modulation depend on the value of the magnetic field relative to the resonance line. They also depend on the line shape of the resonance. A phase-sensitive detection is employed to take care of the sign of the slope, which gives a true differential of the absorption line shape, as shown at the bottom of Fig. 6. Our system actually records the negative of the first derivative signal.

It is evident now that the magnetic field at the exact resonant position of an EPR spectral line is given by the position of the zero value in the first derivative signal. The linewidth of the resonance can also be estimated by using the first derivative signal. In practice, the distance between the positions of the positive and negative peaks in the first derivative signal are used to specify the linewidth of EPR, which is the distance between the maximum and minimum slopes of the original absorption curve, and is thus called the full inclination width. For simplicity let us consider a Gaussian line shape of $y = \exp(-x^2/2a^2)$. This line has a full-width-at-half-maximum of 2.35a, which means that at $x = \pm(2.35a)/2$ the absorption drops to one half of its peak value. The full inclination width is given by the difference between the two solutions of the equation $y''(x) = 0$, which happens to be 2a. We therefore conclude that the convenient full inclination linewidth is not far from the full-width-at-half-maximum linewidth.
The first derivative EPR signal is then amplified. The amplification is controlled by the RECEIVER GAIN step switches, which controls two multipliers. The overall gain is obtained by multiplying one switch setting by the other. The amplified signal output is then fed to the y-axis of the chart recorder. The signal is also shown on the DETECTOR LEVEL meter on the front panel, but we found that it is only useful at high gains.

The modulation amplitude of the 100 kHz magnetic field is controlled by the MODULATION AMPLITUDE step switch on the front panel. If the modulation amplitude is infinitely small, a true first derivative curve will result, but then the signal level will be very small. Therefore in actual measurement the modulation amplitude has to be increased somehow. However, too large modulation amplitude will broaden the linewidth of the EPR signal. As a rough rule a modulation amplitude of about 1/10 of the signal linewidth is usually adequate.

4. Experiments
4.1 Startup

Please first open the coolant water valve until the currently labeled mark on the valve is pointing straight upward. The system needs several minutes to cool down. During this period we can do other preparations.

Please place a sheet of calibrated chart paper on the recorder platen with the start line of the scan range exactly at the position of the pen tip of the recorder. In this way the reading of the magnetic field is most accurate and different scans can be compared directly. The paper is held in place by a vacuum mechanism in the base under the paper. The vacuum mechanism will work after the recorder is switched on. Before you actually record a spectrum, you may need to use a used paper at first for adjusting and optimizing the spectrometer. Of course you are not learning from me on how to save papers, but these EPR papers are special and are hard to find now. We do not have the original pens for the chart recorder, but any pen should work. In the experiment the height of the pen should be finely adjusted so that the curve is properly drawn during a scan, but no trace of curve should be drawn when the pen moves backward to the left. An equivalent way of doing this is to set the pen tip a little lower than normal, and at the end of each scan immediately pause the scan and remove the pen by detaching it from the magnetic pen holder.

On the microwave bridge control panel please set the bridge MODE to STANDBY. Set ATTENUATION/POWER to 25 dB. On the recorder control panel please set RECORDER/ON-OFF to OFF.

You can now switch on the main power switch of the spectrometer, which is located on the lower left corner of the main console.

4.2 Operations of the spectrometer

We here describe the general procedure of recording the EPR spectrum of a sample. In this lab you will record the EPR spectra of two samples, one is the DPPH (2,2-diphenyl-1-picrylhydrazyl), the other is the MgO:V$^{2+}$ crystal. The sample tubes are shown in Fig. 7. Our DPPH sample appears to be a dark brown powder, and the MgO:V$^{2+}$ crystal appears to be light green. Please note that control settings differ for different samples. The settings in this section are specially trimmed for the DPPH sample, which produces a relatively large signal to simplify the process of locating the spectral line. Each time when you change a sample, the procedure described here needs to be repeated.
4.2.1 Inserting the sample

Wipe the sample tube with a lint-free cloth. Insert the sample (DPPH) in the cavity to the black tape mark so that the active volume is centered in the cavity.

4.2.2 Bridge tuning

1) Set ATTENUATION/POWER at 25 dB and turn MODE switch to TUNE. The *klystron mode trace* will soon appear on the oscilloscope. A klystron mode trace shows the output microwave power as a function of microwave frequency. It is produced by monitoring the microwave power while scanning the reflector voltage of the klystron.

2) Adjust FREQUENCY control until cavity signal dip is centered at the highest point of the klystron mode trace, as shown in Fig. 8. When the frequency of the klystron matches that of the sample cavity, the microwave power is absorbed by the cavity and little reflection occurs, so that a dip appears on the klystron mode trace. This dip is then adjusted to the center of the klystron mode trace, as shown in Fig. 8 (c).
Fig. 8 Klystron mode traces. In (a) a klystron mode trace is shown. In (b) the cavity dip signal is introduced. In (c) the cavity dip is centered.

3) Adjust the cavity coupling iris by the white teflon screw to the point where maximum dip is obtained in Fig. 8 (c). The iris helps to match the impedance between the cavity and the waveguide so that the absorption of the microwave power by the sample cavity is maximized.

4) Turn MODE switch to OPERATE. The AFC is now on, and the klystron is locked to the cavity frequency. Verification of the AFC lock can be made by rotating the FREQUENCY control back and forth through a small excursion of the dial and checking that the AFC output follows these excursions. The DETECTOR CURRENT should now be about 75 µA.

5) Slowly rotate the ATTENUATOR/POWER control down to approximately 10 dB and simultaneously keep the DETECTOR CURRENT at about 300 µA. If the detector current is not sufficient the EPR signal may not be adequate. Adjust the iris screw if necessary.

6) If necessary adjust the FREQUENCY control on the bridge to a setting that yields the maximum detector current. At this point the AFC output should be nearly zero.

4.2.3 Modulation settings

1) Set the MODULATION AMPLITUDE to 4 Gauss (4×10^0).

2) Set the receiver GAIN to 2.5 (2.5×10^0).

4.2.4 Field control settings

1) Set SCAN RANGE to OFF and FIELD SET/THOUSANDS switch to 3 kiloGauss. Adjust the FIELD SET/Gauss to 300 Gauss.

2) Find the resonance by watching the DETECTOR LEVEL meter and slowly adjusting the FIELD SET/Gauss dial. In practice we found that this is only useful at high gains. We then instead find the resonance position by watching the motion of the pen after the chart recorder is switched on.

4.2.5 Recording a spectrum

Before you actually record a spectrum, you may need to use a used paper at first for optimizing the settings of the spectrometer. Especially the center of the resonance, the scan range, the modulation amplitude and the receiver gain need to be finely optimized.

1) On the recorder set the SCAN MODE to SINGLE.

2) Set the PEN MODE to AUTO.
3) Set the SCAN TIME to 1 min.
4) Turn on the RECORDER/ON-OFF switch.
5) If necessary press the recorder left FAST or NORMAL scan button. The pen carriage will move to the left side of the recorder.
6) Adjust the RECORDER PEN POSITION knob on the modulation controller to center the recorder pen on the y-axis of the chart.
7) Set the SCAN RANGE on the magnetic field controller to 40 GAUSS.
8) Set the SIGNAL FILTER on the modulation controller to 1.0 second. This is the integration time for the recorder to read the EPR signal. It can filter out the noise on the spectrum. It may also broaden the spectral linewidth.
9) Press the RIGHT scan switch. EPR signal recording is now started.

4.2.6 Changing the sample

**CAUTION:** Before removing sample from the cavity, always reduce the microwave power using the ATTENUATION/POWER control on the bridge, or excessive current may damage the detector crystal.

1) Turn the bridge ATTENUATION/POWER control to reduce the microwave power into approximately 25 dB.
2) Turn the bridge MODE to TUNE.
3) Remove the sample from cavity.

4.2.7 System Shutdown

**CAUTION:** To avoid damage to the crystal detector always turn off system power in the order given here.

1) Turn the RECORDER/ON-OFF switch to OFF.
2) Turn the bridge ATTENUATION/POWER control to about 25 dB.
3) Set the bridge MODE to STANDBY.
4) Turn off the main power switch.
5) Turn off the coolant water.

4.3 Calibration of the spectrometer with DPPH
As we mentioned above, measuring the $g$-factor of a sample is one of the major functions of an EPR spectrometer, which is given by Eq. 12, $g = 714.48 \times \frac{\nu}{U} / \frac{B}{G}$. However, rather than to measure the frequency of the microwave and the strength of the magnetic field to a great accuracy, in practice the measured $g$-factors are calibrated by comparing it with a sample that has a well-known $g$-factor. The organic free radical DPPH (Fig. 9) has been commonly accepted as a standard to calibrate EPR spectrometers. Due to a "free electron" associated with one of the nitrogen atoms, DPPH shows a very strong and narrow isotropic EPR spectral line. The $g$-factor of DPPH has been determined with a high accuracy of $2.0036 \pm 0.0003$. We therefore use DPPH as a standard and determine the calibrated $g$-factor of an unknown sample, $g_{\text{calibrated (sample)}}$, using the relation

$$g_{\text{calibrated (sample)}} = g_{\text{measured (sample)}} \times \frac{2.0036}{g_{\text{measured (DPPH)}}}.$$  (14)

Here the values of $g_{\text{measured}}$ are obtained from Eq. 12.

![Fig. 9 Molecular formula of DPPH radical](image)

Please record an EPR spectrum of DPPH. Please write down the settings you used on the head of the spectrum if you are using the chart recorder. A typical EPR spectrum measured by our spectrometer is shown in Fig. 10. The spectrometer settings in the figure can be used as initial references in your experiment. The spectrum paper can be minimized from A3 to Letter size using the copying machine in our department office. Please take a series of scans with decreasing modulation amplitude of about 4, 2, and 1 Gauss. These spectra should necessarily cross at one common point, which is the center of the resonance. Please use this point to calculate the measured $g$-factor. Please compare your measured $g$-factor with the standard value of 2.0036 and determine the calibration factor of our instrument.

If the spectrometer has a good uniform magnetic field, for a small sample the linewidth should approach an intrinsic value of DPPH at the smallest modulation amplitude. Please
measure the linewidth of the DPPH spectrum and then estimate the spin-lattice relaxation time $T$ for DPPH.

![Fig. 10 EPR spectrum of DPPH](image)

**4.4 LabVIEW control of the chart recorder**

In Fall 2017 I spent some time to automate the scanning of the EPR spectrum by using a LabVIEW program to control the chart recorder. The largest benefit of doing this is that the EPR spectrum is now digitized. A screenshot of the LabVIEW program is shown in Fig. 11. As can be seen, various control buttons and the graph of the EPR spectrum originally on the chart recorder now appear on the computer screen. When using the LabVIEW program instead of the chart recorder itself, please keep in mind the following.

1) Use a new file name for each scan.

2) Set the appropriate sample rate according to the total scan time and the detail of the spectrum you need.

3) Reset X when the pen hits on the left limit to remove accumulated step errors.

4) Start saving data immediately after the scan begins. It automatically stops when the pen hits on the right limit.
5) X steps 0-10000 corresponds to the whole SCAN RANGE you have set on the magnetic field controller. The X-step should be transferred into the actual magnetic field when you present your EPR spectrum.

6) For each spectrum please fill in the “EPR Spectrum Fileheader” which records the necessary settings of the spectrometer.

![EPR Spectrometer Interface](image_url)

Fig. 11 Recording the EPR spectrum using a LabVIEW program

4.5 Measurement of the hyperfine structure of V$^{2+}$ in MgO

Please change the sample into the MgO:V$^{2+}$ crystalline, which contains V$^{2+}$ as a substitutional impurity. Remember this is a paramagnetic 3$d^3$ ion with a $^4F$ ground state split by the cubic crystal field, so that the lowest occupied state has $S = 3/2$. The spin of the V nucleus is $I = 7/2$. We expect 8 hyperfine lines in the spectrum. As an initial try you may set the center of the magnetic field roughly at 3000 Gauss, and the scan range at 1000 Gauss. After one or two trial scans you can then determine the optimized parameters. If you are well adjusted, a certain
amount of fine structure appears inside each hyperfine line. This is caused by a second order
hyperfine term, which is different for different \( M_S \) transitions. Please refer to Abragam and
Bleaney’s *Electron Paramagnetic Resonance of Transition Ions*.

Please measure and calibrate the \( g \)-factor of the \( V^{2+} \) ions in this sample. Please measure the
separation between adjacent hyperfine spectral lines. Please list the line separation values in a
table. From the average line separation please calculate the hyperfine splitting constant of this
sample. Please express your result in cm\(^{-1}\). Please compare your \( g \)-factor and hyperfine splitting
constant of the \( V^{2+} \) ions with commonly accepted values.

Please see if your spectrum of the MgO sample shows other less abundant impurities. For
example, the \( S = 3/2, I = 3/2 \) line of \( Cr^{3+} \) should appear mainly as a central line in the spectrum
with a very small hyperfine splitting. The \( g \)-factor should be about 1.9800. Please measure the \( g \-
factor of \( Cr^{3+} \) if it appears in your spectrum.

5. Additional questions, required (10%)

1) Starting from Eq. 10, please derive Eqs. 11, 12 and 13.
2) Starting from Eq. 11, please derive Eq. 14.
3) Please explain why in Fig. 10 the three spectra with different modulation amplitudes should
cross at one common point.

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