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The Modification and Use of an Electron Paramagnetic Resonance Spectrometer for Data Collection at Liquid Nitrogen Temperature

Vernon Lee Baumberger

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THE MODIFICATION AND USE OF AN
ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER
FOR DATA COLLECTION AT LIQUID NITROGEN TEMPERATURE

BY

VERNON LEE BAUMBERGER

A thesis submitted
in partial fulfillment of the requirements for the
degree Master of Science, Major in
Engineering, South Dakota
State University

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THE MODIFICATION AND USE OF AN
ELECTRON PARAMAGNETIC RESONANCE SPECTROMETER
FOR DATA COLLECTION AT LIQUID NITROGEN TEMPERATURE

This thesis is approved as a creditable and independent investigation by a candidate for the degree, Master of Engineering, and is acceptable for meeting the thesis requirements for this degree. Acceptance of this thesis does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

Thesis Adviser

Date

Head, Physics Dept.

Date
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CHAPTER I

INTRODUCTION

Electron Paramagnetic Resonance Use In Science

Electron paramagnetic resonance (EPR) has increased dramatically in importance as a research technique in recent years. EPR conceptually had its beginning when resonance absorption was attempted by Gorter in 1936. Gorter's attempt failed because of improper technique and a successful detection of resonant absorption awaited the development of microwave technology. The first EPR spectrum was observed in Russia by E. Zavoyskiy in 1945. Since that time, the technique has progressed rapidly to its present prominent position as a research tool in science and industry.

Although EPR spectroscopy is restricted to systems that have a net electron spin magnetic moment, there are many systems which satisfy this criteria including:

1. Free radicals in the solid, liquid, or gaseous state. These are systems with one unpaired electron which may include both organic and inorganic substances.

2. Point defects. That is, trapped negative ions or the deficiency of electrons (a hole). These may include irradiated samples where defects are produced by the radiation.

3. Biradicals. Systems with two unpaired electrons sufficiently remote from one another that their interactions are very weak. Systems of this sort are similar to two slightly interacting free radicals.
4. Systems in a triplet state. That is, systems of two unpaired electrons which have a triplet ground state, or are excited to a triplet state by either thermal or optical excitation.

5. Systems with three or more unpaired electrons.

6. Most transition metal ions and rare earth ions, including semiconductors and metals.

These systems are found in many general areas of study including: Nuclear Physics, Chemical Physics and Chemistry, Solid State Physics, Low Temperature Physics, Geophysics, Archaeology, and Biophysics including biological and medical studies.  

Some typical applications have included effects of irradiation on the lattice structure of various crystalline materials, where the damage centers are readily detected. Natural defect centers are also studied with EPR since they are responsible for many of the electronic properties in solids together with other properties such as color, luminescence, photoconductivity, and photographic latent imagery. Another area utilizing EPR is polymer science where an extensive number of inorganic radicals are studied. One example is the detection of vanadium in crude oil. Vanadium in crude oil acts as a poison to the catalyst used to crack the oil; if sufficient quantities are detected, the vanadium must first be removed before the cracking process.

In biological and medical applications the scope seems endless. The primary reason for this broad usage is that EPR allows for nondestructive examination with great sensitivity. EPR has been used to study enzyme reactions in germinated and ungerminated seeds, pigmentation studies in biological tissues, the detection of malignant tissues in mice, the
examination of cancerous tissues of organs, and studies of proteins, hormones, vitamins, and nucleic acids DNA and RNA. EPR has also been used for other medical purposes such as radiation dosimetry and the diagnosis of a certain strain of jaundice.

In solid state physics areas EPR has become extremely important. It is used for the detection of donor levels in semiconductors and for the design of laser and maser amplifiers. Studies of crystalline samples yield information on local lattice structure and the fields existing within the lattice structure. EPR has also been used for mineralogical studies of the earth's mantle.

Although some substances have very simple spectra, others are very complex. EPR analysis is therefore often used in conjunction with other techniques such as NMR, X-ray diffraction, and optical studies. EPR is also frequently used as a verifying technique.

These applications are only a few of the potential uses of EPR as a scientific tool, both in research and in industrial applications. They have facilitated the formation of a volume of EPR spectra and theoretical atlases. Thus, EPR spectroscopy has become a useful and important tool.

Scope of Study

The scope of this study includes the modification of an EPR spectrometer for acquisition of low temperature data. The modification involved adaptation of the system for use with a cylindrical cavity specifically designed for low temperature operation. This modification increased the capability of the present system for data collection at liquid nitrogen temperature and gave much greater stability than the
rectangular cavity previously used.

A comparison was made of signal to noise for the two cavities. This study showed a somewhat greater signal to noise ratio for the low temperature cylindrical cavity. Operation at low temperatures also allowed the observation of structure not observable at room temperature.

The particular ion investigated was the Mn$^{++}$ ion in zinc hyperphosphate which has not previously been reported in the literature. Its spectrum is reported and a preliminary analysis presented. This spectrum is then compared to that of Mn$^{++}$ doped into a MnO crystal since it results in a much simpler spectrum which is well understood.
Use of an EPR system necessitates the understanding of the theory of the resonance condition. There are many excellent books written on EPR which include discussion of the general theory. These authors introduce the theory from a classical point of view, then proceed to include quantum effects on this theory. Only a general overview will be presented here and the reader requiring more specific detail is referred to these sources.

As previously mentioned EPR may occur only in systems with a net spin angular momentum. As an example, consider a system consisting of one unpaired electron surrounding the nucleus. The magnetic moment of this system is due to the motion of the electron about the nucleus together with its spin angular momentum (s) about its own axis. Since the electron carries a negative charge, the spinning motion gives rise to a magnetic moment (µ), opposite to that of the spin angular momentum as shown in Figure 1.

![Figure 1](image-url)
The free electron state has no preferred direction for the electron's magnetic moment. However, if the system is placed in a magnetic field ($H$), this field exerts a torque on the electron moment in such a manner as to cause it to align with the magnetic field. The associated spin angular momentum must be conserved and thus will resist any change in its direction. The net result is an applied torque to the system causing the spin moment to precess around the applied magnetic field direction as shown in Figure 2.

![Figure 2](image)

The relationship between the spin angular momentum and the magnetic moment of the electron system is given by

$$\mu_z = g\beta M_z$$  \hspace{1cm} (1)

where $\mu_z$ and $M_z$ are the components of magnetic moment and spin angular momentum along the applied field direction respectively. $\beta$ is a constant called the Bohr Magneton and has a value $\beta = 9.273 \times 10^{-24}$ Joules/Tesla. The quantity $g$ is the spectroscopic splitting factor, which is simply a constant relating magnetic moment to spin, or more specifically, a measure of the contribution of spin and orbital motion to the total angular momentum.
Since the electron is a subatomic particle, ordinary classical laws no longer apply. Electron behavior must be described by quantum theory. One result of this theory is that the electron possesses total spin angular momentum in integral multiples of quantum units given by

\[ M_s = [s(s + 1)]^{\frac{1}{2}} \hbar \]  

(2)

where \( s \) is the spin quantum number associated with an electron and is given the value \( s = \frac{1}{2} \). The quantity \( \hbar \) is Planck's constant divided by \( 2\pi \). The component of the total spin angular momentum along the direction fixed by the external magnetic field is given by

\[ M_s = s\hbar \]  

(3)

as shown in Figure 3.

![Figure 3](image)

Figure 3

The magnetic moment of this system is also quantized as given by equation 1. The possible values of magnetic moment will then be

\[ \mu_z = -\frac{1}{2}g\beta \quad \text{spin up} \]  

(4)

\[ \mu_z = +\frac{1}{2}g\beta \quad \text{spin down} \]  

(5)

The energy that is associated with a magnetic moment in a magnetic field is given by

\[ \mathbf{E} = -\mathbf{\mu} \cdot \mathbf{H}. \]  

(6)
Applying equations (4) and (5) to equation (6) gives an energy expression for the separation between the two states as

$$\Delta E = g\beta H.$$  

(7)

If an alternating electromagnetic field is applied perpendicular to the magnetic field ($H$) at a frequency $\nu$, a magnetic dipole transition may occur between the two levels when

$$\Delta E = h\nu = g\beta H.$$  

(8)

That is, the transition between levels may occur only at a discrete energy level separation equal to the energy supplied ($h\nu$), as shown in Figure 4.

![Figure 4](image)

The upward transition corresponds to the electron absorbing energy from the oscillating electromagnetic field and changing its spin direction. The downward transition results in a loss of the same amount of energy and again changes the spin direction. Both of these transitions have the same probability of occurrence. Thus a net absorption will only occur if the lower state has the larger population.

The population distribution of a system in thermal equilibrium is
given by the Boltzmann expression

\[ \frac{N_+}{N_-} = \exp \left( \frac{-\Delta E}{kT} \right) \]  

where \( N_+ \) and \( N_- \) are the number of electrons in the upper and lower states respectively, \( k \) is the Boltzmann constant and \( T \) is the temperature in Kelvin. This ratio has a typical value of approximately 0.99 for room temperature. An increase in the lower state population can be arrived at by either working at high frequencies, or working at low temperature. This allows for a greater difference in population between the states and consequently a larger net absorption may occur.

Spontaneous transitions downward are also needed to cause a net absorption. If they were not present the resulting absorption would equalize the populations in both levels, at which time net energy would be zero. The process of spontaneous emissions is termed relaxation and the time required for this relaxation is a very important factor.

In a paramagnetic system there are two relaxation processes. The first is an interaction between paramagnetic centers called spin-spin relaxation. This type of relaxation is dependent upon the concentration of the paramagnetic centers and is simply a de-phasing time of the centers. The second type of relaxation is of more interest because this allows for the transfer of energy out of the spin system. It is due to an interaction between the paramagnetic centers and their diamagnetic neighbors. This type of interaction is called the spin-lattice relaxation and is characterized by a time given by \( \tau_1 \). In general, the vibrations of atoms surrounding the dipole creates an oscillating field which acts to absorb energy. At a high temperature there is greater vibration resulting in a shorter spin-lattice relaxation time. It is
usually found that $\tau_1 \propto \frac{1}{T}$, a typical value at liquid nitrogen temperature, is $\tau_1 \approx 10^{-6}$ sec.\(^{17}\) This process is also dependent upon the crystal field of the host and thus measurement of the relaxation time may yield information about the crystal field.

The one electron system is oversimplified and more detail must be included as systems become more complex. Not only does the host lattice which generates the crystal field become more important, but other effects also become apparent. A more detailed analysis is then necessary to explain the energy levels of the systems and the resulting spectra.

Energy Considerations

In order to fully understand the energy transitions that occur in a paramagnetic substance, the energy of the system must be clarified. The energy of a quantum mechanical system is found by solving the Schrodinger equation, which has the form

$$H\psi_n = E_n\psi_n$$

(10)

where $\psi_n$ are the energy eigenfunctions and $E_n$ are the eigenvalues for the possible states of the system. The quantity $H$ is called the Hamiltonian operator and represents the total energy at the system. Solutions given by this equation give the acceptable energy levels in which the system can exist. The solution of the equation is then of fundamental importance to the understanding of the energy transitions observed in EPR spectra. The use of this equation is described by several authors,\(^{10,14,17}\) and only briefly mentioned here.

For the case of a transition metal ion at some position in a solid, the Schrodinger equation would have to be solved for the complete system.
to obtain the energy levels. This represents a very difficult problem
and one which has not yet been done. The system may instead be explained
by approximating the paramagnetic ion as residing in a crystalline
electric potential whose sources are point charges or point dipoles
lying wholly outside the ion. Interaction of this type is added to the
Hamiltonian of the free ion, and the energy levels are obtained. This
approximation is called the crystal field theory and the Hamiltonian
obtained is the spin Hamiltonian of the system. Several good explana-
tions of this method are available. $^6,8,10,11$

The Hamiltonian of a paramagnetic ion under these assumptions is
divided into several parts

$$H = H_1 + H_2 + H_3 + H_4 + H_5$$  \hspace{1cm} (11)

where

- $H_1$ = the Hamiltonian of the free ion which is spin independent
- $H_2$ = the potential of the crystal field
- $H_3$ = the spin-orbit coupling term
- $H_4$ = the Zeeman term responsible for paramagnetism
- $H_5$ = the hyperfine interaction term

The orders of magnitude for these energies are found to be: $^6,8$

$$H_1 \sim 10^5 \text{ cm}^{-1}$$
$$H_2 \sim 10^4 \text{ cm}^{-1}$$
$$H_3 \sim 10^2 \text{ cm}^{-1}$$
$$H_4 \sim 1 \text{ cm}^{-1}$$
$$H_5 \sim 10^{-2} \text{ cm}^{-1}$$

In this model the quadrupole moments and the direct nuclear inter-
action are neglected. However, both of these are very small and are
considered insignificant for this study.

The spin Hamiltonian is easily written from that of the ion. Taking the spin dependent terms the general spin Hamiltonian is

\[ H_s = H_2 + H_3 + H_4 + H_5. \]  

(12)

This equation gives the energy associated with the paramagnetic ion that gives rise to the spin dependent splitting of energy levels. It is this splitting of the energy levels that allows transitions to occur. The form of this equation is then important in analyzing observed spectra and will be considered in more detail.

The Spectroscopic Splitting Factor

As previously discussed, the g-factor is a measure of the contributions of orbital and spin motions to that of the total angular momentum which in turn causes an effective magnetic moment. The g-value obtained is very often not the value predicted by the free ion model. In fact the g-value may depend on the orientation of the external magnetic field with respect to the crystal field and instead of being a scaler, it must be described by a tensor of the second rank.\(^7\,11\)

\[ g = \begin{pmatrix} g_{xx} & g_{xy} & g_{xz} \\ g_{yx} & g_{yy} & g_{yz} \\ g_{zx} & g_{zy} & g_{zz} \end{pmatrix} \]  

(13)

This can be diagonalized by transformation which allows it to be written in dyadic notation as

\[ g = \hat{1}g_{xx} + \hat{j}g_{yy} + \hat{k}g_{zz} \]  

(14)

where the axis taken are magnetic axis and in general may not coincide with the crystal axis.
In this notation the relationship between the magnetic moment and the spin angular moment as given by equation 1 takes the form

$$\mu = -\beta g \cdot \hat{S}$$

(15)

where $\hat{S}$ is the effective spin angular momentum of the system.

Spin Orbit Coupling

In a free atom the spin and angular momentum couple to give a resultant which has constant magnitude. For the case of light elements Russel-Saunders coupling applies in which the total angular momentum ($J$) is formed by coupling the total spin angular momentum ($S$) and the total orbital angular momentum ($L$) of all the electrons.

$$J = L + \hat{S}$$

(16)

The magnetic moment associated with this total angular momentum is then found to have the form

$$\mu = -g_J \beta J$$

(17)

where

$$g_J = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}$$

(18)

The quantity $g_J$ is called the Landé g-factor or more generally the spectroscopic splitting factor.

The energy of an electron spin moment in a magnetic field is $-\mu \cdot \hat{H}$, and the Hamiltonian for the spin orbit coupling is given as

$$\lambda L \cdot \hat{S}$$

(19)

where $\lambda$ is the spin orbit coupling constant.

The effect of the magnetic moment is generally described in terms of an effective spin ($S$). The moment is then related to the effective spin by the $g$-tensor such that

$$\mu = -\beta g \cdot \hat{S}$$

(20)

The energy associated with this magnetic moment in a magnetic field
then leads to the general Zeeman Hamiltonian given as
\[ H = \beta \overset{\rightarrow}{H} \cdot g \cdot \overset{\rightarrow}{S} \]  
(21)

The g-tensor and the effective spin are then combined to reduce the spin-orbit and Zeeman terms of the spin Hamiltonian into this term.

Crystal Field Effects

The effect of the surrounding atoms on the paramagnetic ion is termed the crystal field. This effect is treated as a perturbation of the spin orbit coupling and is distinguished by its relative strength compared to the spin orbit coupling and the shape or structure of the host lattice. The strength of the crystal field is considered for cases of weak, intermediate, and strong interactions.

In the weak field case the crystal field is smaller than the spin orbit coupling, thus the free ion calculation is valid to a first approximation. The effect of the crystal is to reduce the degeneracy of the states. That is, the crystal field separates the energy states without application of the magnetic field. For ions of an odd number of paired electrons, the total angular momentum will be half integral and an even number of states occurs. For this situation the levels are split into doublets \( M_J = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}, \ldots J \). Ions with an even number of electrons give rise to energy level singlets which may be separated by energies too large for resonance to be observed.

In the intermediate field case the crystal field is stronger than the spin orbit coupling and must be considered first. The orbital momentum is "quenched" by the crystal field, and is unable to respond to the applied magnetic field. The crystal field acts to lift the
degeneracy of the orbital momentum so that only the lowest level is populated. The spin moment then couples to these levels and accounts for magnetic properties of this type of system to good approximation.

In the strong field case the crystal field effects are such that the free ion model is no longer accurate. The same method may only be used if the crystal field is considered to be large enough to break down coupling between electrons. Typically the crystal field causes large separation of orbital states. Often the separation between orbital states may be sufficient so that electrons pair up in lower orbitals before upper levels begin to fill. Spins may couple to give a maximum total spin with this restriction.

The effect of symmetry further complicates the splitting of energy levels. Not only does the symmetry affect the strength of the crystal field, but it also affects the g-value for different orientations. Cubic, axial, or rhombic symmetries must be considered separately for each type of spin state.

The overall effect of the symmetry and the crystal field strength gives rise to the fine structure coefficients $D$ and $E$. These coefficients account for the zero field splitting that is observed in the absence of an external magnetic field. This zero field splitting is simply the lifting of the degeneracy previously mentioned. The coefficients are added to the spin Hamiltonian so that the resulting spin Hamiltonian now takes the form

$$H = \beta H \cdot g \cdot \mathbf{S} + D[S_z^2 - \frac{1}{3} \mathbf{S} \cdot (\mathbf{S} + 1)] + E [S_x^2 - S_y^2].$$  \hspace{1cm} (22)
Hyperfine Interaction

The effect of the nearby nuclei has been neglected thus far in the analysis. This effect is described by the hyperfine coupling which acts to provide additional energy level separations observed in the magnetic field. There are two causes for these separations. The first is isotropic splitting and arises from the possibility that the unpaired electron may find itself in the vicinity of the nucleus. This interaction is given by

$$\frac{8\pi}{3} g g_N \beta N \delta(r) \mathbf{I} \cdot \mathbf{S}$$

(23)

where $g_N$ and $\beta_N$ are the nuclear g-value and the nuclear magneton respectively. $I$ is the spin quantum number of the nucleus and $\delta(r)$ is the Dirac delta function, making the quantity zero outside of the nucleus.

To illustrate this effect more clearly consider the effect of the proton ($I=\frac{1}{2}$) added to the Zeeman level splitting. Since this interaction depends on the electron being in the nucleus, only the S orbital which has a non-zero value inside the nucleus will be considered. This orbital has a spin $S=\frac{1}{2}$ and splits into two Zeeman levels interacting with the proton as shown in Figure 5.

![Figure 5](image-url)
The second type of hyperfine splitting term is the anisotropic splitting and arises from the classical dipole-dipole interaction between nuclear and electron magnetic moments. This interaction is given by

$$\approx_N^{3}I_{3} - \frac{3(I \cdot r)}{r^5}$$

where $r$ is the radius vector between the electron and the nucleus.

This effect has essentially the same result as the isotropic effect except that it arises from the electron being outside of the nucleus. Thus orbitals other than $S$ orbitals, may also give rise to a hyperfine interaction.

The two types of interaction are taken into account by letting the Hamiltonian for the hyperfine interaction take the form

$$\hat{S} \cdot A \cdot \hat{I}$$

where $A$, like $g$, is a tensor of the second rank whose values are consistent with the interaction that applies.

The total spin Hamiltonian may then be written in the form

$$H = \beta(g_z H_z S_z + g_y H_y S_y + g_x H_x S_x) + D[S_z^2 - \frac{1}{3}S(S+1)]$$

$$+ E[S_x^2 - S_y^2] + A_z S_z I_z + A_y S_y I_y + A_x S_x I_x.$$ (26)

This equation describes the various energy levels of a paramagnetic ion. The constants of the equation, $g$, $D$, $E$, and $A$, may be determined either from theoretical considerations or from the EPR data.

**Energy level Diagram**

A clear way of illustrating the splitting of energy levels associated with the various effects on the paramagnetic ion is with an energy level diagram. This type of diagram shows in a step-by-step approach, each parameter giving rise to the energy level separations.
As an example consider the case of the Mn$^{++}$ ion in cubic symmetry. This ion has a 3d$^5$ electron configuration, which is a half filled shell. The electron configuration is designated $^6S_{5/2}$, allowing for six fold degeneracy. The ion also possesses a nuclear spin of $I=5/2$. For this case the hyperfine splitting constant is larger than the zero field splitting, and the energy levels take the form shown in the energy level diagram of Figure 6.

Figure 6: Energy Level Diagram
CHAPTER III

EXPERIMENTAL APPARATUS

General Considerations

EPR Spectrometer systems vary widely to fit many experimental needs. They range from experimental units to commercial units operating at various microwave frequencies and temperature ranges. Their design may have many different configurations of varying complexity to gain sensitivity. However complex, each system consists of a general core which may be modified for a particular application.

A system sufficient for detection of the resonance condition is shown in Figure 7.8,17

![Diagram of EPR Spectrometer System]

Figure 7

This system consists of four basic elements that are common to all detectors: 1) The energy source providing electromagnetic radiation. 2) The electromagnet to separate energy levels related to spin orientation. 3) The sample cell containing the sample to be analyzed. 4) The detector or receiver.

Discussion of the selection of these elements is found by several authors.6,8,15 Typically this selection is found to depend upon the particular application. However, there are typical elements and
parameters that have found general use. The primary consideration in this choice is the sensitivity required.

Sensitivity increases approximately as the square of frequency \( v \), but design factors of cavity size and magnetic field strengths limits the frequency. The cavity size must decrease as frequency increases to maintain a resonant condition, and consequently sample size becomes prohibitively small. The magnetic field is essentially set by the choice of the frequency, through the resonance equation \( h\nu=g\beta H \). High frequencies then may require prohibitively high magnetic fields. Based upon these and other considerations the source frequency is typically found in three different ranges, X band (8.2--12.4 GHz), K band (18.0--26.5 GHz), and Q band (33.0--50.0 GHz).

Other components of the spectrometer shown in Figure 7 have some general features in common. The magnetic field is generated by an electromagnet slowly sweeping the magnetic field over the desired range. Sample cells may be either transmission or reflection cavities. These are further classified according to the geometry of their resonating electromagnetic field. The detecting element and the system used are found to determine much of the electronics associated with the microwave section. Either bolometer or crystal diode detectors are used but the system may take on many configurations. Excellent discussions of various systems are provided by Alger and Poole.

Type of System

The particular system used in this study was a reflection homodyne type, with the Klystron microwave generator locked to the cavity resonance. A diagram describing this type of system is shown in Figure 8.
Figure 8: Reflection Homodyne Spectrometer

The klyston provides the source of electromagnetic radiation of a specific frequency for this system. It is isolated from the rest of the microwave circuit by a ferrite isolator which prevents the microwave from being reflected back into the Klystron and interfering with its stability. Following the isolator, the attenuator controls the power level of the microwave field. After the attenuator the microwave reaches a tee, typically called a hybrid or magic "T", which splits the microwave equally into two arms. One of these arms includes the cavity, the other a matched load. The microwaves are reflected from both arms back to the tee where they combine and pass down the remaining arm containing the detector. In the "off-resonant condition" the matching arm is adjusted to give a reflection equal in amplitude and 180° out of phase to the reflection from the cavity. This adjustment balances out cavity reflection and sends zero power to the crystal detector. When resonance occurs these waves no longer cancel and power is received at the crystal detector from the microwave circuit. Thus the resonance
condition is detected and recorded.

Increased sensitivity and decreased noise are achieved with this system as a result of two additional techniques being employed. The first technique reduces klystron noise that may be introduced into the system due to the thermal or mechanical environment of the klystron or instabilities that may occur within the klystron. The second technique allows for a phase sensitive detection which limits the overall noise of the entire system.

Reduction of klystron noise is achieved by two methods. The klystron's thermal and mechanical environment is stabilized, and secondly the frequency of the klystron is locked to a reference. In this system the thermal and mechanical environment of the klystron is controlled by cooling in a water cooled oil bath. This not only allows for a relatively constant temperature, but also eliminates vibrations that may arise with an air cooling unit. The frequency stability of the klystron is assured through the use of an automatic frequency control (AFC). Discussion of this technique is provided by several authors. The technique locks the klystron frequency to an external reference which in this case is the resonant cavity. The stabilizer unit used places a small FM component on the microwave generated by the klystron. This component is detected by the crystal detector by allowing a small amount of continuous power to be incident on the detector. The detected FM component is then compared with respect to phase, with the FM signal sent. When the stabilizer has been adjusted and locked any changes in phase cause an error signal to be sent to the klystron adjusting it to compensate for the change.
This method requires continuous power to be incident on the crystal detector at all times. However this is an advantageous condition since a better signal-to-noise ratio is obtained by operating a higher voltages as demonstrated by typical diode characteristic curves. This excess signal allows the crystal detector to be working in the optimum slope of the characteristic when a EPR signal is obtained. 6

A phase sensitive detection is achieved by superimposing a modulating magnetic field on the static magnetic field. This is accomplished by driving a coil placed on or around the cavity with a sinusoidal signal. If the amplitude of the modulating field is kept small the detected signal will be of the same frequency as the modulation and the amplitude will be approximately proportional to the slope of the absorption curve. If the detected signal is then compared with the modulating signal the resulting output will be the first derivative of the absorption curve as shown by Figure 9.

![Diagram of phase sensitive detection](image)
A principle advantage gained by this technique is the limitation of noise to frequencies close to the modulation frequency. This is achieved by narrow band amplification around the modulation frequency. The use of AC amplifiers employed with this technique also increases sensitivity somewhat because of their greater stability compared to their DC counterpart.

The complete system used is shown in Figure 10. The system uses a cathode ray oscilloscope (CRO) for tuning and the chart recorder for data collection. Isolation from mechanical vibration was achieved by mounting the complete system on a heavy wooden frame. The klystron and the microwave bridge were placed on top of the wooden platform with the magnet and instrumentation directly beneath. This arrangement helped prevent vibrations from the instrumentation and reduced vibrations of the room and building.

Instrumentation

The system shown in Figure 10 is driven by a Varian 153C reflex klystron. This particular klystron operates over a range of 8.5 to 10 GHz, providing approximately 390 milliwatts of power. The actual power incident on the cavity is controlled by the waveguide attenuator. The power unit used for the klystron is the Hewlett Packard model 716U klystron power supply.

Stabilization for the klystron is provided by a Micro-Now model 210 stabilizer. This unit has a modulation frequency of 70 khz and a locking range of ± 50 microamps.

The magnetic field is generated by a Varian model V-3703-1 6-inch electromagnet and controlled by a Fieldial model V-FR2900 magnetic
Figure 10: System Block Diagram
field regulator. The electromagnet has a pole gap of 2.75 inches, with a field homogeneity of 1.0 gauss across the diameter of the pole. The field regulation is consistent to 10 PPM with a stability of 1 PPM as controlled by a hall probe. This system allows for field strengths up to 5.0 kilogauss. It also allows a wide variety of sweep times over several magnetic field ranges.

Signal amplification for the system may be provided by two units. If weak signals are expected a preamplifier may be used. This amplifier is the Micro-Now model 521 preamp. It provides a minimum gain of 36db and a dynamic gain of 55db over a bandwidth of 400Hz to 250 KHz. The maximum output of the device is 2.5 volts peak-to-peak at 25 KHz.

The phase locking amplifier for the system is the PAR model 128 lock-in amplifier. This amplifier provides the narrow band amplification which is centered at the modulating frequency. It has selectable low pass and high pass filters ahead of the phase sensitive detector which allow band widths of 0.5 Hz to 100 KHz. The unit also has 12 selectable sensitivity ranges from 1 microvolt to 250 millivolts. This particular unit is equipped with an internal oscillator which may be used to drive the modulating field. If desired, this field may also be driven by an external oscillator.

Cavity Discussion

In this study two different cavity systems were used with the spectrometer. The original system consisted of a rectangular cavity with the iris located such that the cavity operates in the TE\textsubscript{102} mode as shown in Figure 11. For this cavity the sample is mounted on a quartz rod and
Figure 11

Cavities used for this study
suspended at the cavity center where the microwave field is maximum. Modulation is applied by coils attached to the side of the cavity walls. These walls are made of thin silver foil which allows the modulating field to penetrate into the cavity at frequencies up to 100 KHz.

The rectangular cavity operates most conveniently at room temperature, but with accessories it can be used in low-temperature studies. The cavity has a large opening so that aqueous solutions may be studied, and allows samples to be irradiated if desired. Orientation studies may also be performed with this cavity, but requires the sample to be rotated within the cavity. This process changes the sample position slightly and consequently is not a desirable device for orientation studies.

The second cavity was a cylindrical cavity designed by L. Halliburton at Oklahoma State University. This cavity operates in the $TE_{011}$ mode as shown in Figure 11b. The sample is mounted on a quartz rod and placed in the center of the cavity where the microwave field is maximum. The design of this cavity makes no allowances for attaching modulation coils to the cavity, therefore external modulation coils were constructed.

The construction of this cavity was somewhat unique. It was designed to operate at low temperature and consists of a copper top and bottom plate with walls made of wound copper wire embedded in epoxy. The cavity is filled with teflon allowing it to have smaller dimensions. The presence of teflon in the cavity causes very high microwave losses at room temperature resulting in poor $Q$. The $Q$ value is a measure of the quality or sharpness of response of any resonant system and is defined as

$$Q = \frac{2\pi \text{ energy stored}}{\text{energy dissipated}}.$$  \hspace{1cm} (27)
The Q value for this cavity was observed to increase significantly as the temperature of the cavity was lowered. At the operating temperature of 77°K the cavity resonance was very sharp and the Q value was considerably higher than that observed for the rectangular cavity.

Another advantage of the cylindrical cavity compared to the rectangular cavity is its application to orientation studies. Orientation data is obtained by rotating the magnetic field around the cylindrical cavity. This method allows the sample to remain fixed within the cavity.

The advantages provided by the use of the cylindrical cavity over the rectangular cavity then include an increased cavity Q, ease of orientation studies, and the advantages provided by working at low temperatures. As a result of these advantages, the cylindrical cavity was used extensively in the study of the zinc hyperphosphite crystalline sample.

**Cylindrical Cavity Adaptations**

In order for the cylindrical cavity to be used three adaptations to the system were required including, the location of the cavity resonant frequency, the provision for a cavity dewar system, and the modulation of the magnetic field within the cavity.

The frequency of resonance of the cavity was determined by attaching the cavity in a direct reflection microwave circuit and scanning the range of the klystron (8.2→10 GHz). This procedure carried out at room temperature gave a resonant frequency observed at approximately 9.15 GHz. When the cavity was cooled to its operating temperature of 77°K, the
The resonant frequency of the cavity was observed to decrease to a value of approximately 8.85 GHz. The instability at this temperature in the resonant frequency was observed to be as much as $\pm 0.03$ GHz although the cavity was isolated from air convection with a thin plastic seal.

The cylindrical cavity was designed to be immersed in liquid coolant, in this case liquid nitrogen. This required a dewar flask large enough to contain the cavity but small enough to fit between the magnet poles. The separation between the magnet poles was approximately 7 cm and the cavity diameter 4.3 cm. A commercial dewar flask of these dimensions could not be found and thus one was constructed by R. E. Ashmore of the South Dakota State University Chemistry Department.

Considerable difficulty was encountered in mounting external modulation coils for use with the cylindrical cavity. Several unsuccessful attempts were made at constructing coils fitted on the pole faces of the magnet. However, best results were obtained by placing the coils directly on the dewar flask, wrapping them around the curvature of the flask, and securing them with silicon glue. This design required the magnetic field produced by the coils to penetrate both the cavity and the dewar. Therefore the frequency used must be limited to an upper limit of 10 KHz.

Calculations and construction parameters for the coils are given in Appendix A. The final operating frequency of the coils was obtained by capacitively coupling the coils through an amplifier to produce sufficient amplitude at a value of 7.4 KHz.
CHAPTER IV

SYSTEM COMPARISON

General Analysis

The operation of an EPR spectrometer at liquid nitrogen temperature (77 K) allows for increased capability in data collection. One reason for this increased capability is system stability. The stability of the system increases due to the very constant temperature of the cavity immersed in the liquid nitrogen.

Further increases of system capabilities arise from sensitivity increases at low temperatures allowing for observation of structure which can not be distinguished at room temperature. Sensitivity is a function of temperature since differences in electron population between energy levels increases with decreasing temperature as given by equation 9.

\[
\frac{N_+}{N_-} = \exp\left(-\frac{\Delta E}{kT}\right)
\]

(9)

This increase in population difference then increases the net absorption of energy as discussed in Chapter II.

A simpler relationship between sensitivity and temperature called Curie's Law may be derived from equation 9. This relationship is given as

\[
I = \frac{AH}{T}
\]

(28)

It shows the magnetization intensity (I) to be inversely proportional to absolute temperature (T) through Curie's Constant (A) and the magnetic field strength (H). Since the magnetization intensity is directly related to the amplitude of absorption, maximum sensitivity is obtained with the
sample cooled to as low a temperature as possible.7

To study the capability of the low temperature system a comparison was made with data obtained using the room temperature system. This was carried out to further clarify the potential gains associated with the low temperature system and to compare the respective qualities of one system with respect to the other. Specifically, the comparison involved the sensitivity and stability associated with each system.

Experimental Technique

The quality of the data obtained with the spectrometer was found to vary with several different instrumentation parameters. To obtain data with the systems which could be compared directly to one another, effects of these parameters were investigated. This investigation involved tuning procedure, amplification settings, magnetic field sweep rates, and modulation field adjustments. Results of this work suggest the best operating procedure is that suggested in Appendix B.

Before examining the systems for comparison the actual amplification of the detector signal was determined. As previously discussed, data may be obtained with or without the use of the preamplifier. Without the use of the preamplifier the gain may be determined from settings of the lock-in amplifier and the chart recorder. With the use of the preamplifier, the gain cannot be determined because the gain of the preamplifier is unknown. However, an approximation of preamplifier gain was made by comparing data obtained using the preamplifier with that obtained after removing it from the system.

Many variables affect the amplitude of the response. Its value may vary from one run to the next using identical settings. As a result,
the value calculated for the gain of the preamplifier was considered only an approximation. However, when the data is obtained consecutively this calculated value will more closely reflect the actual value of gain. Since the preamplifier gain may not be constant over its operating range, the value of gain was determined for both operating frequencies.

For cavity sensitivity comparisons the spectrometer was adjusted as described in Appendix B. In addition the modulation field present within the cavities was matched to insure the effect observed was not due to differences in the modulation field amplitude. This was accomplished by measuring the field strength within each cavity using a matching test coil. The output of the coil was monitored with an oscilloscope and the observed amplitude adjusted at the oscillator. The amplitude of the modulating field was adjusted to give the same peak to peak value for both cavities at their respective modulation frequencies. Referring to the phase detection diagram, Figure 9, one can see this procedure assures that the output will be the same for the same microwave absorption in the sample.

Samples

One of the samples used was a standard commonly used for calibration. This sample was a dilution of DPPH (α-diphenyl-β-picryl hydrazyl) which has a known g-value of 2.0036, very close to the free spin value of 2.0023. The dilution was prepared by dissolving pure DPPH in alcohol and placing a small amount of this solution in a sample quartz cell where it was allowed to dry. The amount of DPPH in the sample used was measured to be approximately $1 \times 10^{-5}$ gm. Using the molecular weight of
DPPH, which contains one spin per molecule, the total number of spins in the sample was calculated to be about $1 \times 10^{16}$.

The second sample used was a magnesium oxide crystal with manganese ($\text{Mn}^{2+}$) impurities. This sample exhibits cubic symmetry and shows the spectrum associated with the $\text{Mn}^{2+}$ ion in a simple form. Although the actual concentration of ions within the sample is not known it can be approximated from the intensity of the observed spectrum.

The final sample used was a zinc hyperphosphite crystal with one percent $\text{Mn}^{2+}$ impurities. This particular crystal was supplied by Dr. William Jensen of the South Dakota State University Chemistry Department and is used here for stability comparisons. Greater detail of this particular sample and its spectrum is presented in Chapter V.

**System Response**

The EPR signal detected by the crystal may be amplified in three stages before being recorded. These stages include amplification by the chart recorder, the lock-in amplifier, and the preamplifier if used. The recorded data may be represented by the formula

$$\text{Recorder Signal} = \text{crystal signal} \times \text{recorder gain} \times \frac{1}{\text{lock-in gain} \times \text{preamplifier gain}}$$

(29)

Both the chart recorder and the lock-in amplifier may be adjusted for various amplifications, with only the preamplifier supplying a constant amplification. The crystal signal of the system can then be expressed in terms of the amplifiers setting and equation 29 as

$$\text{Crystal Signal} = \frac{\text{recorded signal (units)}}{\text{recorder gain (volts)}} \times \frac{1}{\text{lock-in gain (input volts)}} \times \frac{1}{\text{preamplification (output volts)}}$$

(30)
Using equation 30 for the calculation of response, the value of amplification of the preamplifier was determined. Table 1 shows data for consecutive runs of preamplified and nonpreamplified responses. This data was calculated from response curves of Figures 12 and 13.

**TABLE 1**

**PREAMPLIFICATION DETERMINATION**

<table>
<thead>
<tr>
<th>Cavity</th>
<th>Sample</th>
<th>Non preamped Response (volts)</th>
<th>Preamped Response (volts)</th>
<th>Preamp gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>rectangular</td>
<td>MgO peak 1</td>
<td>$1.92 \times 10^{-5}$</td>
<td>$9.25 \times 10^{-4}$</td>
<td>48.18</td>
</tr>
<tr>
<td>rectangular</td>
<td>MgO peak 2</td>
<td>$1.93 \times 10^{-5}$</td>
<td>$9.22 \times 10^{-4}$</td>
<td>47.78</td>
</tr>
<tr>
<td>rectangular</td>
<td>MgO peak 2</td>
<td>$1.97 \times 10^{-5}$</td>
<td>$9.25 \times 10^{-4}$</td>
<td>46.95</td>
</tr>
<tr>
<td>rectangular</td>
<td>MgO peak 6</td>
<td>$1.88 \times 10^{-5}$</td>
<td>$8.90 \times 10^{-4}$</td>
<td>47.34</td>
</tr>
<tr>
<td>rectangular</td>
<td>MgO peak 7</td>
<td>$1.86 \times 10^{-5}$</td>
<td>$8.52 \times 10^{-4}$</td>
<td>45.90</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>DPPH</td>
<td>$8.48 \times 10^{-6}$</td>
<td>$3.99 \times 10^{-4}$</td>
<td>47.05</td>
</tr>
</tbody>
</table>

Average: 47.23

Overall Average: 47.14

Although each cavity operates at a different frequency, the gain supplied by the preamplifier seems to be consistent for each. Since the gain is only an approximation, the value used for the gain of the preamplifier will be taken as 47.0.

**Sensitivity Comparison**

The sensitivity of a system is typically measured by the signal to noise ratio of the system. This ratio is ultimately the limiting factor in determining the smallest concentration the spectrometer can detect. Table 2 shows the signal to noise ratio observed for the two cavity
Figure 12 (a)
MgO:Me+² spectrum without preamplification taken with the rectangular cavity

Figure 12 (b)
MgO:Me+² spectrum with preamplification taken with the rectangular cavity
Spectra obtained for the DPTC sample using the cylindrical cavity, (a) was taken with the preamplifier and (b) was taken without using the preamplifier.
Figure 14

Spectra obtained for the standard DPPH sample. (a) was taken using the cylindrical cavity, (b) was taken using the rectangular cavity.
systems. This data was calculated from the response curves of Figure 14. The signal to noise ratio (S/N) is calculated by taking the ratio of the peak to peak signal response and the peak to peak noise response as given by equation 31

\[
S/N = \frac{\text{p to p signal response}}{\text{p to p noise response}} \quad (31)
\]

This ratio is then typically extrapolated to unity to determine the ultimate detectable spin concentration.

**TABLE 2**

**SIGNAL TO NOISE RATIO DETERMINATION**

<table>
<thead>
<tr>
<th>Cavity</th>
<th>Sample</th>
<th>Noise Response</th>
<th>Signal Response</th>
<th>S/N</th>
<th>Detectable Spin Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical</td>
<td>DPPH</td>
<td>3.5</td>
<td>199.5</td>
<td>57</td>
<td>(1.75 \times 10^{14}) spins</td>
</tr>
<tr>
<td>Rectangular</td>
<td>DPPH</td>
<td>7</td>
<td>81</td>
<td>11.57</td>
<td>(8.64 \times 10^{14}) spins</td>
</tr>
</tbody>
</table>

Note a near order of magnitude improvement with the low temperature cylindrical cavity system.

**Stability Comparison**

Stability of a spectrometer system is difficult to measure quantitatively although it is a very important parameter. The effects of instability typically appear as a voltage increase or decrease with time. It is observed as a movement of the recorder pen with time which is typically called "recorder drift". Although the rate of drift can be measured, the significance of the value is questionable. This is primarily due to the fact that instabilities may arise from several different causes such as changes within the recorder, the amplifier,
or the stabilizer. Stability is also decreased by changes in cavity temperature, mechanical vibrations of the system, sample changes, changes in conductivity of the sample or impurities not associated with the sample but present in the cavity system (i.e. grit, metals, etc.). Drift which probably originates from these causes is considerable despite the fact that the system is frequency stabilized when the system is operated for high sensitivity. Isolation of the exact cause of a particular drift however, is very difficult.

Experimentally several techniques were discovered to help decrease the observed drift. Allowing for a long system warm up time, temperature stabilizing the cavity system, retuning the system, and cleaning the cavity system all had positive effects at eliminating drift. However, these techniques will not completely eliminate the observed drift.

Data obtained using the standard DPPH sample for each cavity is shown in Figure 14. Note that both cavity systems show some drift. The same observation can be made by comparing the MgO data obtained with each cavity as shown in Figure 15. Both these examples would indicate no appreciable differences in the stability of the systems. However, these examples neglect effects that may arise from the sample. This is clearly shown by the data obtained with the Zn(H₂PO₂)₂ sample as shown in Figure 17. The drift present at room temperature seems to vanish at 77 K, clearly demonstrating a significant decrease of drift with reduced temperature. Data analysis of this crystalline sample would have been very difficult without the use of a low temperature system for this reason.
Figure 15
Spectra obtained for the \textit{MgO::Mn}^{++} sample with the rectangular cavity (a), and the cylindrical cavity (b)
Figure 17

Spectra obtained for the Zn(H₂PO₄)₂⁺:In⁺⁺ sample with the rectangular cavity (a), and the cylindrical cavity (b).
CHAPTER V

CRYSTAL ANALYSIS

Introduction

An excellent example of an analysis of an EPR spectrum is presented by Collins, Morrison, and Donoho\textsuperscript{19} in which they examine the Cr\textsuperscript{3+} ion in ruby. In their study knowledge of the crystalline structure allowed for a theoretical calculation of the spin Hamiltonian for the system. The presented detailed analysis of this calculation includes the calculation of transition probabilities for the ion. The EPR data is then used to confirm the calculated values.

Although this method of analysis is excellent, it requires prior knowledge of the crystalline structure which is not available for some crystals. However, EPR data may also be used to gain information about the crystalline structure by considering the local symmetry which would give rise to the observed spectrum. This study is an analysis of that type.

To accomplish this goal, two crystals were studied. The first crystal used was a MgO with Mn\textsuperscript{2+} as an impurity ion (MgO:Mn\textsuperscript{2+}). EPR data for this sample is well understood and has been reported by several authors.\textsuperscript{20-23} The second crystal studied was a zinc hyperphosphite crystal whose structure is unknown. To determine possible local symmetries present a crystalline sample was prepared with one percent Mn\textsuperscript{2+} ions. EPR data was then collected on this sample Zn(H\textsubscript{2}PO\textsubscript{2})\textsubscript{2} + 1\% Mn\textsuperscript{2+}.

Magnesium Oxide

A detailed analysis of the Mn\textsuperscript{2+} ion impurity in a MgO crystal is
presented by Low and a good qualitative discussion of this structure is given by Wertz, Orton, and Auzins. Both describe the Mn++ ion which has five 3d electrons making a half filled electron shell. The resultant orbital angular momentum is zero and thus paramagnetism arises from the electron spin. Therefore, the spectroscopic g value should have a value very close to that of the free electron in which \( g = 2.0037 \).

The Mn++ ion is found to take a substitutional position in the MgO crystal. The MgO crystal has a cubic structure causing an cubic electric field around the Mn++ ion.

The ground state of the Mn++ ion arising from its electron state is the \( ^6S_{5/2} \) state, allowing for six fold degeneracy. This is further complicated by a hyperfine structure arising from a nuclear spin of \( I = 5/2 \). If the hyperfine splitting were small, as one would normally expect, the spectrum arising from electron and nuclear states could consist of five groups of six lines. However, for this ion the hyperfine splitting is larger than the zero field splitting causing the spectrum to appear as six groups of five lines as was shown in the diagram of Figure 6. Of these 30 possible lines, the \( +1/2 \leftrightarrow -1/2 \) transition is found to be the most intense and appears in the center of the quintet. There is a sufficient angular dependence for the four remaining satellite transitions (\( 5/2 \leftrightarrow 3/2, 3/2 \leftrightarrow 1/2, -1/2 \leftrightarrow -3/2, -3/2 \leftrightarrow -5/2 \)) that overlapping may occur at some orientations. Also, the presence of another ion in the sample may cause these transitions to become very weak or absent.

**Experimental Results**

A spectrum was obtained for the MgO crystal at both operating
temperatures (290°K and 77°K) and is presented in Figure 15. For both cases the six equally spaced Mn^{++} transitions are indicated. In both cases an additional transition between peaks 3 and 4 of Mn^{++} is present. This transition would indicate the presence of an additional paramagnetic impurity or defect in the sample.

Examination of data taken at 290°K showed only the +1/2 ↔ -1/2 transitions present. Absence of the satellite transitions was attributed to a combination of the presence of the additional ion in the structure, and low transition probabilities at this temperature.

Examination of the data taken at 77°K produced different results. This spectrum not only shows the +1/2 ↔ -1/2 transitions, but also what appears to be additional structure. This structure was attributed to a combination of the satellite transitions, and its low intensity attributed to the presence of the additional ion in the structure. The appearance of the structure at this lower temperature must be attributed to an increase in population of the satellite levels as described by Low.20

\[ g\text{-factor} \]

The \( g \) factor of the Mn^{++} ion was calculated at both temperatures. For this calculation the +1/2 ↔ -1/2 transition was used, with the magnetic field calibrated with the DPPH standard (\( g = 2.0037 \)). Allowing for an uncertainty of 4 gauss, \( g \) values of 2.0012±.001 at 77°K and 2.0014±.001 at 290°K were obtained and are displayed in Table 3. These results are consistent with the generally accepted value of 2.0014±.20
TABLE 3

g values of Mn\textsuperscript{++} in MgO

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Temperature</th>
<th>( g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>290°K</td>
<td>2.0012( \pm )0.001</td>
</tr>
<tr>
<td>MgO</td>
<td>77°K</td>
<td>2.0014( \pm )0.001</td>
</tr>
</tbody>
</table>

accepted 2.0014\( \pm \)5

Unidentified Transition

The transition located between peaks 3 and 4 of Mn\textsuperscript{++} was not identified, however some characteristics of this transition were noted. The position of the transition with respect to the Mn\textsuperscript{++} spectrum varies by as much as 30 gauss, but always remaining between the 3rd and 4th peaks of Mn\textsuperscript{++}. The resulting g value varies from 1.9865\( \pm \)0.001 to 2.0003\( \pm \)0.001. These variations suggest that the ion or defect is non-isotropic which may result from it assuming an interstitial position in the cubic crystalline structure. This transition is observed as a single line of linewidth greater than the Mn\textsuperscript{++} transition. Thus no hyperfine structure exists except for a possibility of the very small structure which could be a possible cause for this line broadening.

Zinc Hyperphosphite

The structural formation of zinc hyperphosphite is unknown. Attempts at resolving the structure using X-ray diffraction techniques have yielded no significant results. This study is an attempt to obtain information about the crystal structure using EPR techniques. Samples were prepared by introducing Mn impurities into the crystalline structure.
forming Zn(H₂PO₂)₂:Mn⁺⁺. It was hoped that effects of the local environment on the EPR spectra of Mn⁺⁺ would yield structural information about the crystal.

EPR spectra of the Mn⁺⁺ ion arise from its interaction with its local environment, including hyperfine interactions from hydrogen and phosphorous. Both hydrogen and phosphorous have a net nuclear spin of \( I = 1/2 \) with a large hyperfine constant. Interactions associated with the hydrogen ions are given by Assigheim⁶ and Alger.⁸ A study by Horsfield, Morton and Whiffen²⁴ shows the hyperfine interaction of phosphorous in the PO₃⁻⁻ ion.

Before examining the complex spectra obtained for the crystalline sample, some possible energy level splitting interactions were examined. The Mn⁺⁺ ion is believed to take a substitutional position for the Zn ion in the crystal because it has the same valence state and the same relative size. This position would place the Mn⁺⁺ ions between two hyperphosphite ions since the hyperphosphite ion is found to have a tetrahedral or slightly distorted tetrahedral configuration.¹⁸ The Mn⁺⁺ ion would then be in the environment of at least two phosphorous and four hydrogen atoms. Possible energy level splitting for the Mn⁺⁺ ion under these interactions is shown in Figure 16.

For Figure 16 only the six equally spaced hyperfine lines of the Mn⁺⁺ ion are assumed to interact with the hydrogen and the phosphorous. Splitting of the Mn⁺⁺ structure by 4 hydrogens will result in 5 groups of six spectral lines with an intensity ratio of 1:4:6:4:1. Although the hyperfine interaction of the 4 hydrogens is large, overlapping of the structure may be possible as depicted. The interaction of the
phosphorous may split the \( \text{Mn}^{++} \) spectra into triplets with an intensity ratio of 1:2:1.

\[
\begin{array}{c}
\text{Splitting associated with 4 equally coupled hydrogens.}
\end{array}
\]

\[
\begin{array}{c}
\text{Splitting associated with 2 equally coupled phosphorous nuclie.}
\end{array}
\]

**Figure 16: 4 Hydrogen and 2 Phosphorous Hyperfine Interactions**

Figure 16 assumes the \( \text{Mn}^{++} \) ion to interact only with two hyperphosphite ions, however, interactions with more ions may be possible. The spectra that would arise from interaction of \( \text{Mn}^{++} \) with increased numbers of hyperphosphite ions becomes increasingly complex. As a result, the spectra obtained for the crystalline sample is examined before additional interactions are considered.

\[
\text{Zn(H}_2\text{PO}_4)_2: \text{Mn}^{++} \text{ Spectra}
\]

For this study the crystal was aligned to a symmetry plane using X-ray diffraction techniques. Data was collected for magnetic field orientations every 5° over a total angle span of 180°. Typical spectra obtained for this plane are shown in Figure 18. Previous orientation
Typical spectra obtained with the cylindrical cavity for consecutive 5° magnetic field orientations of the Zn(H₂PO₂)₂ sample

Figure 13
Figure 19

Typical spectra obtained for the Zn(H₂PO₂)₂ sample taken in a perpendicular plane.
data taken in a plane perpendicular to this plane at room temperature shows a similar spectra as seen in Figure 19.

An analysis of the orientation data showed that no distinct separation of spectral lines occurred. This data showed some shifting of lines with the overall width of the spectrum varying by as much as 700 gauss. However, the basic structure of the spectrum obtained remains approximately the same for all orientations. This behavior is typically attributed to ions in a near cubic local symmetry suggesting a local symmetry for Mn$^{++}$ ions in Zn(H$_2$PO$_2$)$_2$.

Uniquely resolving the interactions giving rise to the observed spectra is difficult since sufficient overlapping of structure is present causing line broadening and masking the line structure. An example of the resolution of structure obtained is shown in Figure 20.

It was observed that generally each spectrum began and ended with three peaks indicated in Figure 18. The number of total peaks was also observed to be approximately 18. A comparison of the possible structure of Mn$^{++}$ interacting with 4 hydrogens shown in Figure 16, with the spectra obtained shows a significant similarity. Although the observed intensities are somewhat different, the relative number of lines and shifting of intensities observed are very similar.

This assumption would require hyperfine interaction of the hydrogen causing a separation of approximately 250 gauss. Hyperfine interactions of this magnitude are not unreasonable since a single proton interaction has been measured to be 504 gauss.

The line width of the Mn$^{++}$ ion in Zn(H$_2$PO$_2$)$_2$ is approximately 40 gauss. This is considerably larger than the 4 gauss width observed for
Mn$^{++}$ in MgO. One possible explanation for this broadening is a combined hyperfine interaction with phosphorous. If this interaction is small, structure would not be resolved and the effect would be line broadening.

Although this analysis does not confirm a local environment and a structure for the Zn(H$_2$PO$_2$)$_2$·Mn$^{++}$ sample, it does suggest one possibility. Further analysis of this sample would be required to clearly identify the interactions present and the crystalline structure.
Figure 20: Attempted Resolution of Spectra
CHAPTER VI

SUMMARY

The scope of this study has included the modification of an EPR spectrometer previously operated with a rectangular room temperature cavity for operation with a cylindrical liquid nitrogen cavity. The modification was carried out so the spectrometer cavities can be easily changed. Thus EPR data can be easily obtained at two operating temperatures.

Comparison between the cavities showed an improved sensitivity and stability associated with the cylindrical cavity. This improvement was attributed to the low temperatures and the better Q value of the cylindrical cavity. Data obtained resulted in a resolution capability of approximately $10^{14}$ spins for the cylindrical cavity compared to approximately $10^{15}$ spins for the rectangular cavity.

The crystal analysis of MgO:Mn$^{++}$ was found to be consistent with that previously reported. The spectrum obtained showed the six hyperfine lines associated with the $+1/2 \leftrightarrow -1/2$ transition. Low temperature also showed the presence of some satellite transitions. The weak intensity of the satellite transitions was attributed to the presence of an additional ion or defect in the sample. Weak intensities of the satellite transitions caused by additional ion concentrations is consistent with what has been previously reported.

The spectrum associated with the Zn(H$_2$PO$_2$)$_2$:Mn$^{++}$ crystal is presented. Since the spectrum is very close to being isotropic with orientation, a cubic local symmetry is postulated for the Mn$^{++}$ ion. The hyperfine structure of the spectrum indicates considerable interaction with the
Mn\textsuperscript{++} nucleus. Additional structure indicates a hyperfine interaction also exists with hydrogen or phosphorous ions in the proximity of the Mn\textsuperscript{++} ion. An interaction with four nearby hydrogen ions is proposed to account for this structure. A much smaller hyperfine interaction with phosphorous ions is proposed as a cause of line broadening.
CHAPTER VII

SUGGESTIONS FOR FURTHER STUDY

A difficulty observed with the cylindrical cavity system which warrants further study is the fluctuation of its resonant frequency. One possible cause of this fluctuation is liquid nitrogen bubbling into the inside of the cavity. This situation might be corrected by either sealing the cavity or allowing the liquid nitrogen to flow easily to the inside of the cavity. If this fluctuation were eliminated, sensitivity may be increased.

Another area for further study involves the unknown transition observed in the MgO crystal. Identification of the ion or defect giving rise to this transition may require data in two perpendicular planes of the crystal. Data of this type may also show the shifting of the satellite transitions discussed by Low.20 Determining the ion and its concentration level may result in further explanation of the weakness of the Mn^{++} satellite transitions.

The EPR spectrum of the Zn(H₂PO₂)₂: Mn^{++} crystal also warrants further study. Data should be collected using a single crystal of Zn(H₂PO₂)₂ with no impurities to see if any part of the observed spectrum arises from the phosphorous ion. Also an analysis of an irradiated sample similar to the study by Horsfield24 may yield the magnitude of the phosphorous hyperfine information. Line width analysis together with a more detailed orientation study might lead to further information about the Mn^{++} local symmetry. Data obtained from this study suggest orientation increments as small as one degree may be necessary to resolve the internal shifting of the structure. These additional studies will
probably be necessary to identify the splitting, the structure, and parameters for the spin Hamiltonian of Mn$^{++}$ in this crystal.


Appendix A

Calculation and Construction Parameters for the Modulation Coils

The magnetic field (H) supplied by a current carrying loop can be determined using the Biot-Savart law in the form,

$$ H = \frac{\mu IR^2}{2(R^2 + z^2)^{3/2}} $$

where,

- \( R \) = The radius of the loop,
- \( z \) = The perpendicular distance from the center of the loop,
- \( I \) = The current of the loop,
- \( \mu \) = The permeability.

For \( N \) such loops the magnetic field will be,

$$ H = \frac{\mu NI R^2}{2(R^2 + z^2)^{3/2}} $$

For two such coils in a Helmholtz configuration like that of typical modulation coils, the field will be,

$$ \Pi = \frac{R^2}{(R^2 + z^2)^{3/2}} \mu NI $$

When a coil is made each overlapping loop has a larger radius. To obtain an exact value for the magnetic field, the radius of each loop would have to be taken into account. However, an approximation can be made using an average radius.

Applying the average radius approximation and noting that for this case the distance to the center of the coils is half the radius, the equation for the magnetic field becomes,
The current drive capability of the amplifier driving the modulating coils is on the order of a few amps. For a modulating field of a few gauss, the equation yields approximately 400 turns per coil.

Coils of approximately 400 turns were constructed and tested. The wire used for the coils was 26 gauge copper. The coils were wrapped and bonded with epoxy. When the coils were operated at maximum drive, the field strength measured inside the cavity at the frequency of 7.2 KHz was 2 to 3 gauss.

The operation at 7.2 KHz was achieved by capacitively coupling the coils to the amplifier. This coupling allowed for maximum drive by operating at the resonant frequency of the circuit.
Appendix B

Operation and Tuning of the Spectrometer

The instrument settings used for each cavity were found to differ somewhat. For the rectangular cavity the following settings pertain:

- Frequency set at approximately 9.49 GHz.
- Klystron power supply reflector at 3.2, beam voltage at 350, and the intensity modulation amplitude at 1/2 to 1/3 full.
- Stabilizer set as described in the instruction manual.
- Lock-in amplifier adjusted as desired.
- Modulation frequency set at approximately 70 KHz.

For the cylindrical cavity the settings should be,

- Frequency set at approximately 8.95 GHz at liquid nitrogen temperature or approximately 9.0 GHz at room temperature.
- Klystron power supply reflector at 1.3, beam voltage at 350, and the intensity modulation amplitude at 1/2 to 1/3 full.
- Stabilizer set as described in the instruction manual.
- Lock-in amplifier adjusted as desired.
- Modulation frequency set at approximately 7 KHz.

With these adjustments the system may be tuned using the following procedure;

1. Connect cavity and modulation coils.
2. Turn on cooling system and the modulation amplifier.
3. Flip stabilizer bypass switch to 'out'.
4. Connect the oscilloscope to the two detector outputs. The A input should be connected to the 'magic T', and the B input to the wave meter.
5. Turn on the klystron power supply, the stabilizer, and the lock-in amplifier to allow for system warm up. Note: When turning on the klystron power supply, leave the switch on 'filament' for 30 sec. before turning it to 'high voltage'. The power supply function should be on 'N', with the oscilloscope on input A, AC-sweep of 1 msec/cm.

6. Find the initial resonance pip by adjusting the SWR of the detector and the slide screw turner. Adjust these devices so that the image on the oscilloscope takes the following form.

7. Turn the function switch of the power supply to 'CH' and set the oscilloscope to DC. There should now be a flat line on the scope which moves up and down corresponding to the peaks of step 6 by adjusting the klystron reflector. Adjust the flat line for the resonant frequency by setting the line in the center of the pip. At this time it is a good idea to recheck the frequency and the adjustments of step 6.

8. Flip the stabilizer switch on, making sure the stabilizer is set in the tune mode.

9. Adjust the attenuation and the stabilizer as described in the stabilizer instruction manual. Note: It was found that a better signal could be obtained by allowing approximately 200 to 250 microamps of signal current, rather than the 100 microamps suggested. When this step has been completed the system will be locked to the cavity resonant frequency for phase errors up to ± 50 microamps.