



The forbidden hyperfine paramagnetic resonance spectrum of vanadium in magnesium oxide
by David Hugh Dickey

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
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Abstract:

An X-Band electron paramagnetic resonance spectrometer has been built. The instrument's sensitivity, for a signal-to-noise ratio of unity, has been found to be $2 \times 10^{13} \Delta H$ spins, under the conditions of 10-3 watts of incident microwave power and a time constant of one second. The spectrometer has been used to observe the previously unreported forbidden hyperfine spectrum of vanadium in magnesium oxide.

A quantum-mechanical justification for the existence of the forbidden spectrum is given.

THE FORBIDDEN HYPERFINE PARAMAGNETIC RESONANCE
SPECTRUM OF VANADIUM IN MAGNESIUM OXIDE

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ABSTRACT

An X-band electron paramagnetic resonance spectrometer has been built. The instrument's sensitivity, for a signal-to-noise ratio of unity, has been found to be 2×10^{13} ΔH spins, under the conditions of 10^{-3} watts of incident microwave power and a time constant of one second. The spectrometer has been used to observe the previously unreported forbidden hyperfine spectrum of vanadium in magnesium oxide. A quantum-mechanical justification for the existence of the forbidden spectrum is given.

CHAPTER I

INTRODUCTION

An electron paramagnetic resonance spectrometer may be used to determine the spin state of the unpaired electrons in a sample of paramagnetic material. The spin degeneracy of the paramagnetic ion's ground state configuration is lifted by applying a magnetic field, and then transitions among these Zeeman levels are induced by exposing the sample to microwave radiation of the appropriate frequency. One can obtain the energies of all the transitions involving populated states, and from this can deduce a vast amount of information about the various mechanisms which determine the energy levels. A few of the mechanisms which can be studied are the hyperfine interaction, crystal Stark fields, dipolar interactions and lattice defects.

The phenomenon of magnetic resonance can be explained on a classical basis, as well as quantum-mechanically.^(1,2) Classically, the magnetic moment μ resulting from the electron's intrinsic spin will experience a torque when the electron is placed in an external magnetic field. If the external field is uniform, this torque will induce a precession of the magnetic moment around the direction of the external field; the well known Larmor precession. If now a small magnetic field is applied at right angles to the external field H_0 , and is made to rotate around H_0 at the Larmor frequency, it will appear to be stationary in the reference frame of the electron's magnetic moment. The magnetic moment will then experience a torque which will try to cause a precession around the direction of H_1 ,

the small applied field. This precession is in the rotating reference frame, where μ and H_1 are stationary relative to each other. The tendency to precess about H_1 will result in a change in the orientation of μ in the external field, to the opposite direction. The energy required for the change in orientation (spin-flip) is supplied by H_1 . The occurrence of a spin-flip can therefore be detected by observing the absorption of power in the microwave beam which induces H_1 .

The small field H_1 , must be applied in a manner such that it appears to rotate in a plane perpendicular to H_0 . This can be achieved by applying a linearly oscillating field, since such a field can be resolved into two rotating fields moving at the same frequency in opposite directions. The component which rotates in the direction opposite to the Larmor precession has no large effect on the system, since it has no stationary orientation with respect to the precessing dipole.

The condition necessary for resonant absorption, namely that the oscillation frequency of H_1 be equal to the Larmor frequency, is stated in the following equation:

$$h\nu = -2\vec{\mu}_e \cdot \vec{H}_0 = g_0 \beta H_0 \quad (1)$$

where g_0 is the free electron g -value (2.0023), β is the Bohr magneton and μ_e is the magnetic moment of the electron. For fields commonly available in the laboratory, (1,000 to 10,000 gauss) the frequency ν lies in the microwave region.

A quantum-mechanical description of magnetic resonance is straightforward if one takes as a valid representation the set of sets $|M\rangle$,

where M is the electron spin magnetic quantum number. The Hamiltonian function for an electron in the magnetic fields H_0 and H_1 is:

$$\begin{aligned} \hat{H} &= g\beta [(\vec{H}_0 + \vec{H}_1) \cdot \vec{S}] = g\beta [H_0 S_z + H_1 (\cos \omega t) S_x] \\ &= g\beta [H_0 S_z + \frac{1}{2} H_1 (\cos \omega t) (S_+ + S_-)] \end{aligned} \quad (2)$$

where H_0 is assumed to be directed along the z axis, and H_1 is assumed to lie in the x direction. The substitution $2S_x = S_+ + S_-$ has been used. Operating on the state $|M\rangle$ with this Hamiltonian, one sees that a transition to a higher or lower spin state is possible:

$$\begin{aligned} \hat{H}|M\rangle &= g\beta [H_0 M |M\rangle + \frac{1}{2} H_1 (\cos \omega t) \times \\ &\quad (\sqrt{S(S+1) - M(M+1)} |M+1\rangle + \sqrt{S(S+1) - M(M-1)} |M-1\rangle)] \end{aligned} \quad (3)$$

The line intensity, or transition probability per unit time, for the state $|M+1\rangle$ is proportional to the matrix element squared:

$$I \sim | \langle M+1 | \hat{H} | M \rangle |^2 = \frac{g^2 \beta^2}{4} H_1^2 |\cos \omega t|^2 [S(S+1) - M(M+1)]. \quad (4)$$

The transition is allowed only if the condition for conservation of energy, Eq. (1), is satisfied.

There are several varieties of paramagnetic resonance spectrometer. (4-8) A common feature of all designs is a resonant cavity which contains the sample and for which there is some means of determining the amount of microwave power absorbed. It is difficult to change the resonant frequency of a cavity during an experiment, so the frequency is usually kept constant and the magnetic field is varied in order to explore the various Zeeman levels.

The purpose of this thesis is to describe the design and construction of a paramagnetic resonance spectrometer, and to indicate one application of its use.

CHAPTER II

THE SPECTROMETER

General Description of the Spectrometer

The spectrometer may be briefly described as a superheterodyne system with balanced mixer detection and magnetic field modulation. The klystrons operate at about 10 GHz, the IF amplifier operates at a nominal 30 MHz, the stabilization frequency is 22 KHz, and the field modulation is at 400 Hz. Figure I shows a block diagram of the entire system. The basic parts of the spectrometer are:

1. Signal and local oscillators, operating at X-band.
2. Microwave bridge, with magic tee.
3. Resonant cavity, containing the sample.
4. Magnet, adjustable from 0 to 10 kilogauss.
5. System to modulate magnetic field up to 50 gauss peak-to-peak at 400 Hz.
6. Microwave mixer, preamplifier, and IF amplifier.
7. Automatic frequency control system.
8. 400 Hz phase sensitive detector.
9. Strip-chart recorder.

This spectrometer is designed, with the exception of a few modifications, after the instrument described by Locher.⁽⁸⁾

The spectrometer's operation can be generally described as follows: microwave power, frequency modulated at 22 KHz, is fed to a reflection-type cavity which is in one arm of a balanced bridge. The cavity, containing the sample, is in a dc magnetic field of appropriate magnitude such

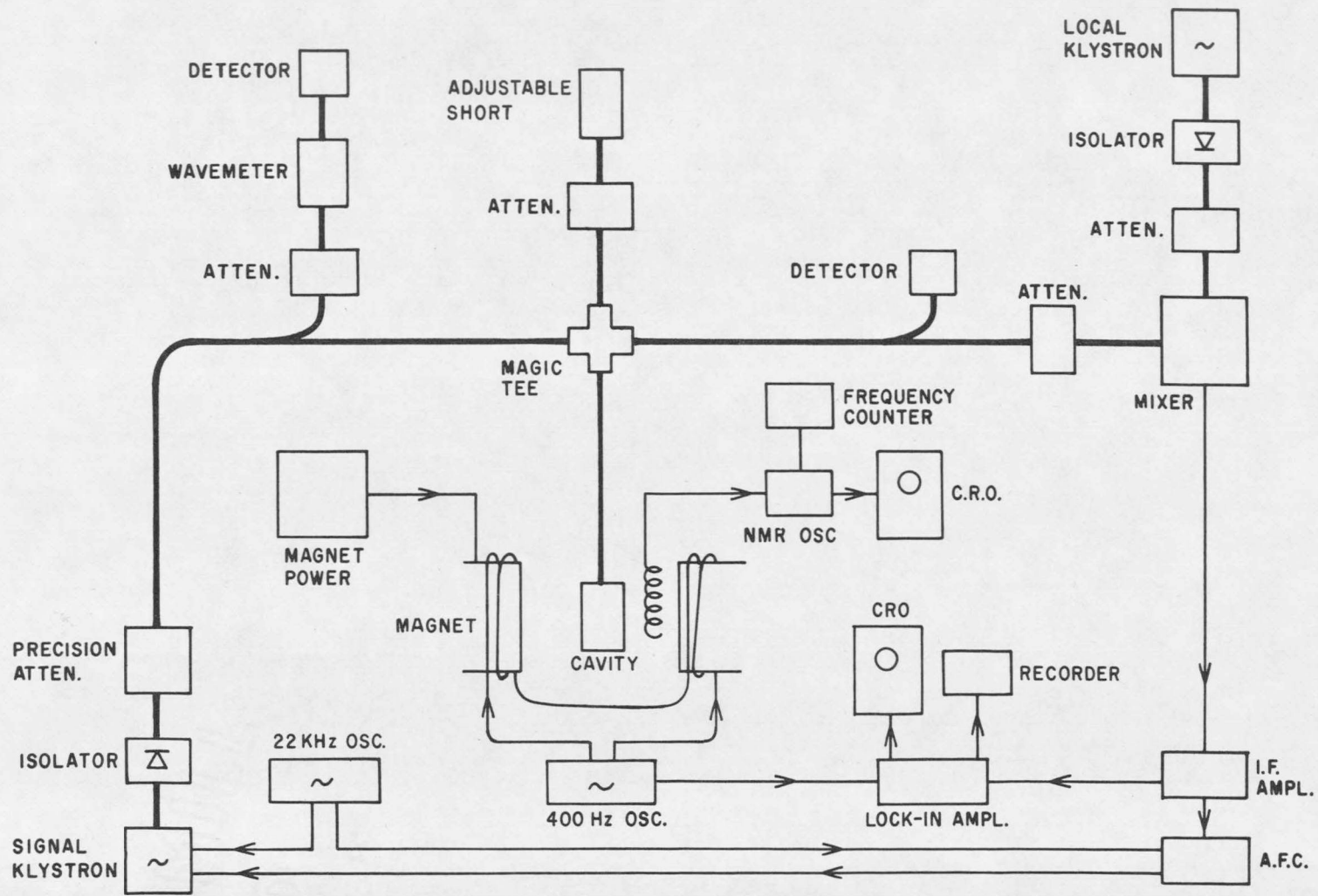


FIG. I

SPECTROMETER SCHEMATIC

as to cause paramagnetic absorption of the microwave power according to Eq. (1). The magnetic field is modulated (about one gauss peak-to-peak) at 400 Hz, so that the resonant condition of Eq. (1) is varied at that frequency. The microwave power returned from the cavity is therefore amplitude modulated at 400 Hz, the amplitude depending on the strength of the paramagnetic absorption.

The phase of the 22 KHz frequency modulation is also shifted in the returned signal. The direction of the phase shift depends upon whether the klystron frequency is above or below the cavity's resonant frequency.

The reflected power, with its modulations, is mixed with a microwave signal from the local oscillator. The local klystron oscillates at a frequency nominally 30 MHz higher than the signal klystron. The 30 MHz beat signal is preamplified and fed to the IF amplifier. At the last stage of IF amplification, the 30 MHz is detected, producing the "control" signal at 22 KHz, and the resonance signal at 400 Hz. Each of these signals is filtered and further amplified. The control signal is phase compared with a 22 KHz reference to generate a correction voltage which is applied to the signal klystron. This keeps the klystron locked to the cavity frequency. The 400 Hz signal is phase-sensitive detected, using the field-modulation source as a reference, and the resulting dc output is displayed on a strip-chart recorder. In an experiment, the magnetic field is slowly increased so that the time axis on the strip-chart can be read as a magnetic field axis.

Construction of the Spectrometer

The microwave system. The microwave power is generated by two Varian X-13 klystrons. Each klystron is enclosed in a seven inch diameter brass can filled with transformer oil, to stabilize the temperature. The microwave circuit is shown on the spectrometer's schematic diagram, Figure I. Power from the signal klystron passes first through an isolator, and then a precision attenuator which is adjustable from 0 to 50 db. A 10 db directional coupler takes off some power to the cavity wavemeter. The remaining power reaches the magic tee where it is divided into two equal beams, in the cavity arm and the balancing arm of the microwave bridge. The amplitude-modulated power reflected from the cavity is again divided at the tee, as is that returning from the balancing arm. The net signal entering the fourth arm of the bridge goes into the microwave mixer where it is beat against a microwave signal from the local klystron. The beat signal, nominally at 30 MHz, is preamplified in the mixer and is then fed to the IF amplifier. A directional coupler between the magic tee and the mixer takes a small fraction of the signal for monitoring and tuning purposes.

The cavity, which contains the sample, has a tunable iris which allows some control over the amount of microwave power which can enter or leave the cavity. The resonant frequency of the cavity is tunable. The design and construction of the cavity is described in a separate section.

The balancing arm of the bridge consists of a level-set attenuator and an adjustable short. This allows the phase and intensity of the micro-

wave signal to be adjusted so that they closely match those of the signal reflected from the cavity.

Klystron power control. The power requirements for the klystrons are supplied by three sources, all of which are highly regulated. The heater current is supplied at 6.3 v dc from a regulated supply which has a maximum current output just slightly greater than that required by the klystrons at their operating temperature. The filaments are heated more slowly in this way, since their cold resistance is much lower than their operating resistance. The beam current is supplied at +350 v by a standard 300 v power supply modified for the higher voltage. The reflector voltage is obtained from two modified standard supplies wired in series to produce -700 v. The control circuit is shown in Figure II.

An unusual feature in this spectrometer is the single set of power supplies used to power both klystrons. The duplicated circuitry is indicated in Figure II, except that the local klystron has no interconnection with the AFC. Other features of the control circuit are a delay relay which allows the reflector voltage to build up before the beam supply is switched on, and a safety mechanism to prevent the reflector voltage from going positive with respect to the cathode. The safety mechanism consists of a diode which can support only a negative reflector voltage, in series with a 4.5 v battery which in fact prevents the reflector from reaching a potential more positive than -4.5 v.

The high voltage power supplies are hand-made from a circuit given by Elmore and Sands. (9)

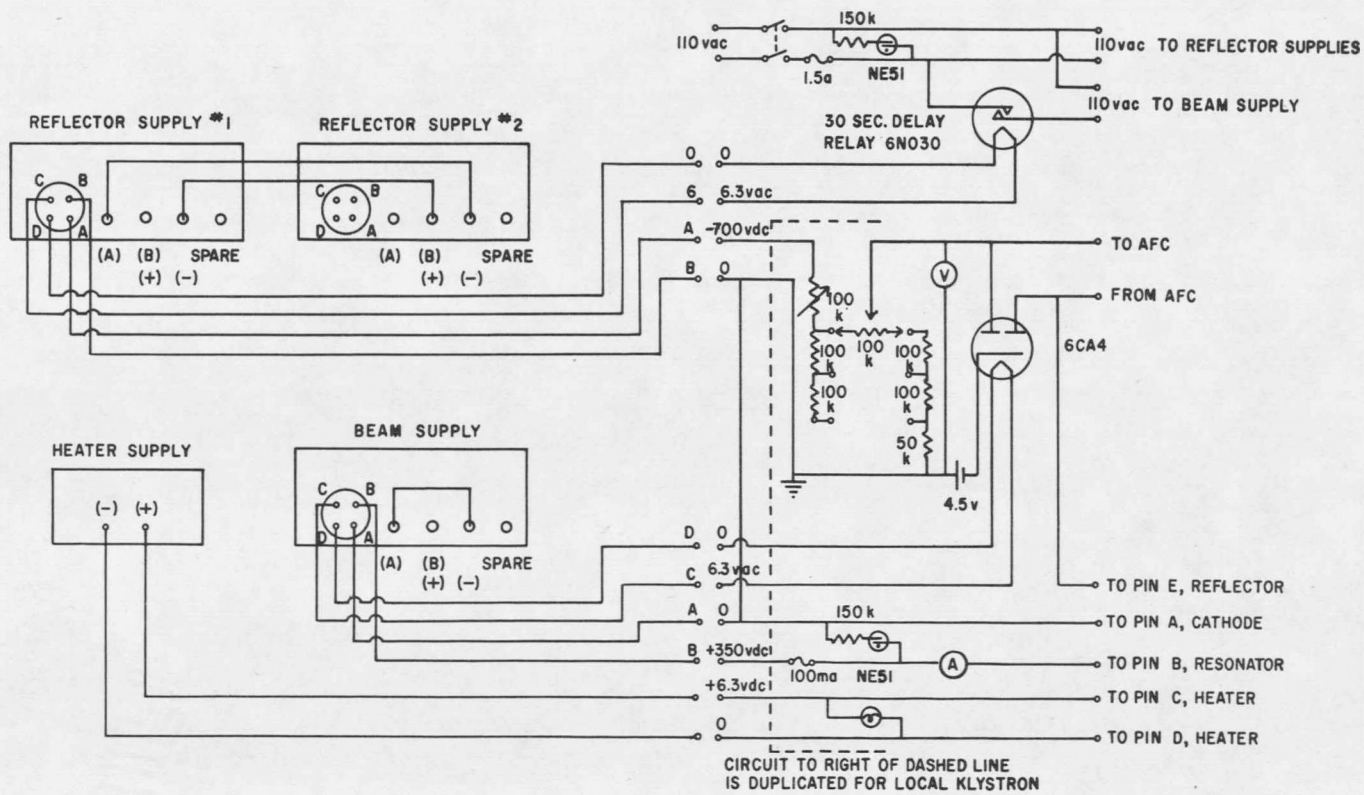


FIG. II

KLYSTRON POWER CONTROL CIRCUIT

Automatic frequency control. The signal klystron must oscillate at the resonant frequency of the cavity at all times. The circuit used to accomplish this stabilization is shown in Figure III. The AFC (for automatic frequency control) operation is described as follows: a 22 KHz oscillator provides a very low-level "tickle" signal which is applied to the signal klystron reflector. This signal frequency-modulates the klystron at 22 KHz. The phase-shifting characteristics of the resonant cavity are such that the 22 KHz signal returning in the microwave carrier is shifted ahead or behind depending on whether the klystron frequency is above or below the cavity frequency. The returning signal is amplified and phase-compared with a reference signal from the 22 KHz oscillator. The phase detecting circuit has a dc output whose polarity depends on the sign of the phase shift. The dc output is applied directly to the klystron reflector, which automatically corrects the klystron frequency.

The AFC circuit includes two extra amplification stages in the "tickle" section which may be switched in, to provide a gross 22 KHz modulation of the klystron frequency. This is useful in tuning the spectrometer, since the entire klystron mode, with the cavity absorption band superimposed, may be observed.

Audio frequency system. The EPR signal is induced at 400 Hz by the magnetic field modulation at that frequency. After amplification at the IF strip, the carrier is detected, leaving only a 400 Hz signal, whose amplitude, for field modulation less than the linewidth, is proportional to the first derivative of the absorption vs field curve. The 22 KHz

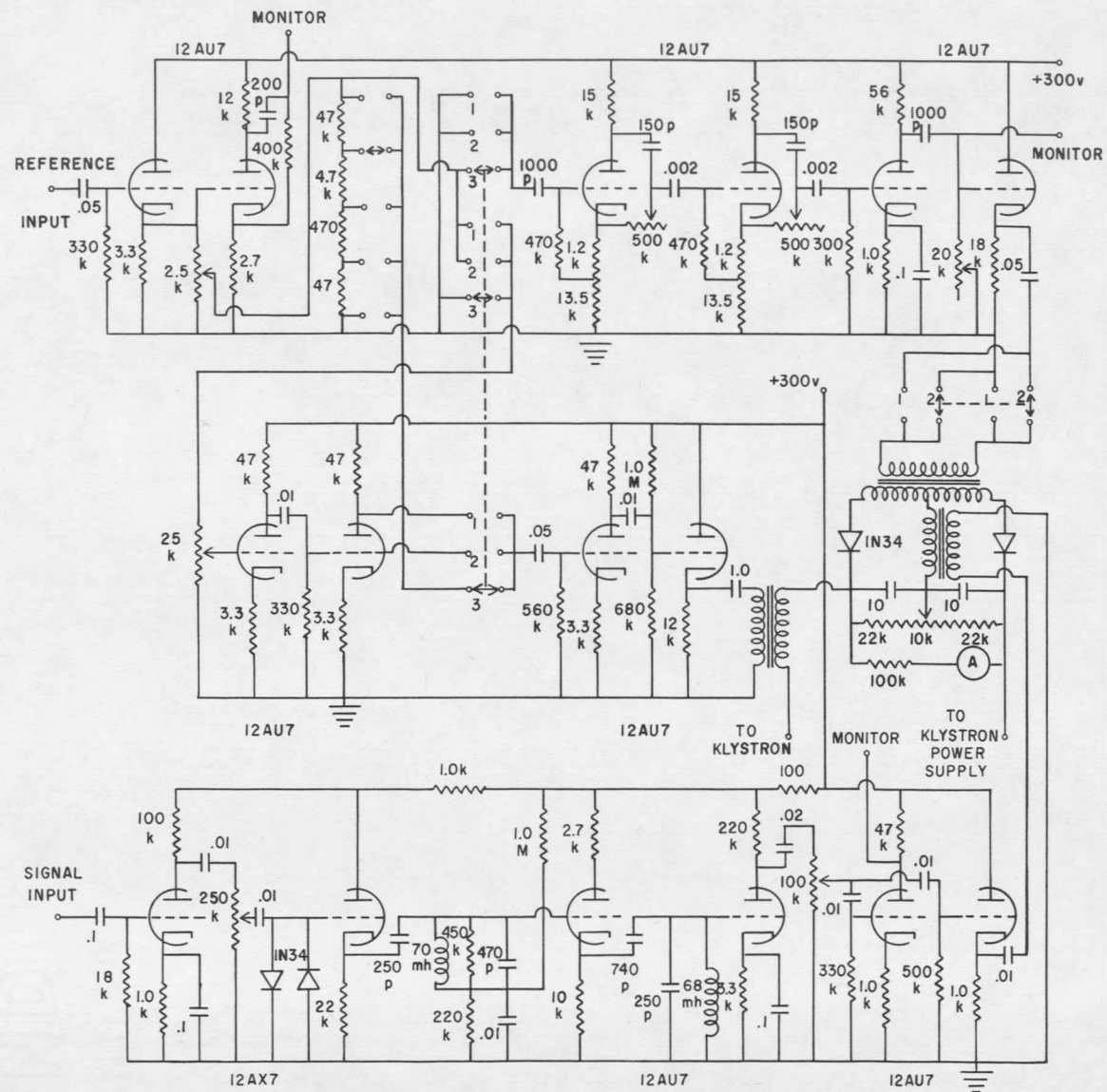


FIG. III

AUTOMATIC FREQUENCY CONTROL CIRCUIT

stabilization signal is superimposed, but this is filtered out in the early stages of audio amplification. The audio frequency lock-in amplifier has an overall gain of unity, with range switches to attenuate the signal by as much as five orders of magnitude. Figure IV is a schematic of the amplifier. After filtering and amplification, the signal enters the phase sensitive detector ⁽¹⁰⁾ where it is compared with the reference and detected. The dc output is filtered by one or several capacitors, which limits the time constant of the entire system, and then the signal goes to the strip-chart recorder.

The reference input from the field-modulation oscillator goes through a phase-shifting network before entering the phase sensitive detector. The reference phase is adjusted to match the signal returning from the microwave system, and usually does not require readjustment.

The phase-sensitive detection, in conjunction with the filtering capacitors, ensures that the only signals reaching the recorder are those which have a phase and frequency that exactly match those of the reference signal.

Design and construction of the resonant cavity. A tunable, cylindrical cavity, with resonant frequency near 9.6 GHz, is desired. The TE_{011} mode is chosen as the operating mode in order that:

1. The cavity be tunable.
2. The region of maximum rf magnetic field shall lie at the center of the cavity (at the sample position).
3. The region of minimum rf electric field shall lie at the sample position, to minimize dielectric loss.

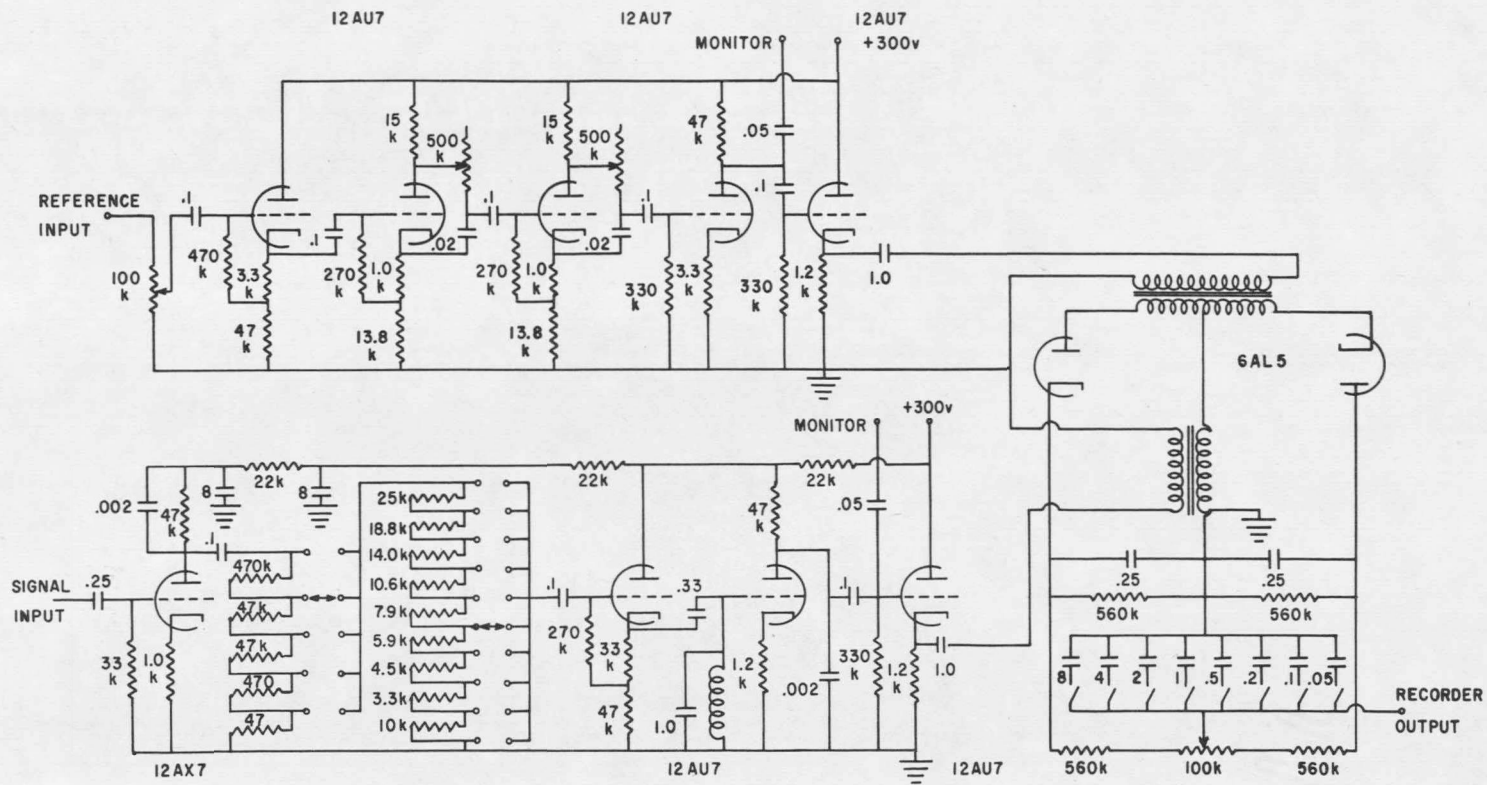


FIG. IV

LOCK-IN AMPLIFIER CIRCUIT

4. The cavity size be as small as practicable.

The resonant frequency, as a function of length and radius, for TE modes, is given by: ⁽¹¹⁾

$$\omega_{mnp} = \frac{c}{\sqrt{\mu\epsilon} R} \left[x_{mn}'^2 + p^2 \pi^2 \frac{R^2}{L^2} \right]^{1/2} \quad (5)$$

where x_{mn}' is the n^{th} zero of the derivative of the Bessel function of order m . For the TE_{011} mode, the frequency is:

$$\omega_{011} = \frac{c}{\sqrt{\mu\epsilon} R} \left[3.832^2 + \pi^2 \frac{R^2}{L^2} \right]^{1/2} \quad (6)$$

Inspection of a mode chart ⁽¹²⁾ indicates that a mean value for R^2/L^2 of 0.237 will put the region of operation at frequencies such that no extra-neous modes, except the TM_{111} mode, can propagate. The TM_{111} mode can be eliminated by the use of choke rings at the cavity ends.

The cavity is machined from brass. The inside diameter is turned approximately to size, (2.05 cm radius), the iris hole is bored in the side, and then the inside surface is finished. The threads for the end plates are cut next (40 threads per inch), and finally, the outside diameter is turned to its finished size. This sequence minimizes the danger of distorting the cavity during machining. The end plates are made from brass, with care taken to leave a good finish on the inside surfaces. Choke rings, having a depth-plus-width equal to a quarter wavelength, are cut in the end plates.

A silver coating may be applied to the inside surfaces by vacuum evaporation. The waveguide can be attached at the iris position with

solder, or preferably, with conducting epoxy cement.

A tunable iris can be made by partially plugging the wave-guide adjacent to the iris with brass, and filling the remaining cross-section with Teflon. The dielectric constant of Teflon is high enough that the waveguide can still propagate microwaves even though its dimensions are small enough to cut off the beam. By sliding the Teflon slug up, and introducing an air gap smaller in cross section than the cut-off dimensions, the degree of coupling into the cavity can be varied.

Several cavities have been built, with Q's ranging from 8,000 for plain brass to more than 15,000 for one with a good coating of silver on the inner surfaces. The theoretical maximum Q for a cavity of this design is 30,000.

Magnetic field measurement. For most EPR experiments, it is of interest to know the magnetic field intensity for a given line to an absolute accuracy of at least one part of 10^5 . The magnetic moment of the proton is known to this accuracy, so the phenomenon of nuclear magnetic resonance (on protons) can be used to obtain the value of the magnetic field intensity. A separate system is used for this measurement. The sample used is a test tube filled with machine oil, which is placed in the magnet gap as close as possible to the cavity. The circuit used is a marginal oscillator, and is shown in Figure V. The circuit consists of a tank circuit coupled to an oscillator tube, which drives an amplifier stage and detector, as well as a separate amplification stage with output to the frequency counter. The oil sample is

placed in the center of the coil of the tank circuit. The detected output, containing the NMR signal, is put on the vertical plates of an oscilloscope whose horizontal plates are driven by the same oscillator as used to modulate the magnetic field. When the displayed signal appears symmetric, one assumes that the dc magnetic field is exactly at the resonance condition and the modulation drives the total field equally above and below the resonance condition. The oscillation frequency of the tank circuit is read at this time, and is used to compute the magnetic field from the equation:

$$h\nu = 2\mu_p H \quad (7)$$

where μ_p is the magnetic moment of the proton, and has the value 1.41044×10^{-23} erg/G.

With a sample coil of about 15 turns of #21 copper wire on a 1/2 inch diameter, the frequency is tunable over a range from about 8 MHz to 20 MHz. The magnetic field which can therefore be measured is in the range 2,000 G to 4,500 G. Use of more or fewer turns in the sample coil moves the useful range down or up in magnetic field. Coils have been wound which allow measurement as low as 1,400 G, and as high as 7,000 G.

The level of oscillation is varied with the potentiometer in the cathode circuit of the oscillator tube. This resistance should be adjusted so that the oscillation is nearly turned off. Under this condition of marginal oscillation, any change in the Q of the tank circuit will change the level of oscillation significantly. When the external magnetic field and the oscillator frequency meet the resonance condition

of Eq. 7, rf power is absorbed by the protons in the oil sample, thus lowering the tank circuit Q.

Operation of the Spectrometer

The turn-on procedure for the spectrometer consists of providing power for the klystrons and allowing them to warm up, tuning the signal klystron to the cavity frequency, tuning the local klystron to a frequency 30 MHz above or below the cavity, and then balancing the microwave bridge. As the bridge is brought nearly to balance, the AFC circuit should begin to operate.

The klystrons should be tuned both mechanically and electrically, so that the final frequency will lie at the center of the klystron mode. If a tunable cavity is used, the start-up procedure is simplified in that the signal klystron can be tuned to the center of the mode without regard for the cavity frequency. The cavity can then be tuned to the klystron frequency. The local klystron must still be tuned, but the 8 MHz bandwidth of the IF stages simplifies this process, since it allows the local klystron frequency to lie anywhere in the ranges 26 to 34 MHz above or below the cavity frequency.

Tuning for minimum noise. There are several adjustments which may be made in the electronic circuits of the spectrometer to optimize the signal-to-noise ratio. These may be classified according to whether or not they affect the absolute sensitivity of the system. Those parameters which directly affect the signal amplitude will be discussed first.

Audio amplifier gain ordinarily varies any noise to the same extent that the signal is varied. The phase and frequency of the field modulation signal however, have a marked effect on signal amplitude without changing the noise level. Both of these parameters can ordinarily be set once and then forgotten, but occasionally some drift occurs which requires correction. The audio amplifier has a high-Q filter which passes only a narrow band near 400 Hz, so the field modulation oscillator must be set to this frequency to achieve maximum sensitivity. Phase adjustment between signal and reference in the lock-in amplifier is, of course, necessary.

Signal amplitude is directly proportional to modulation field amplitude for peak-to-peak fields up to twice the line width, so ordinarily this can be adjusted to maximize the signal. Some noise is induced by eddy currents in the cavity walls by the modulation field, so the onset of this noise will determine the upper limit on modulation field if the above criterion does not.

IF amplifier gain does not affect the signal-to-noise ratio, even though crystal noise is much reduced at the operating frequency of 30 MHz. The reason for this is that the klystron noise entering the IF amplifier is at least an order of magnitude higher than the crystal noise, and is the major source of noise in the entire system. If the klystron noise were negligible, the signal could be amplified at the IF strip without changing the noise level because most of the remaining noise is introduced at stages later than IF. The klystron noise is introduced mainly by ripple and other fluctuations in the reflector power supply.

Local klystron power level has some effect on both signal and noise, although this has not been carefully investigated. The essential purpose for varying this level is to adjust the microwave detector crystal bias in order to optimize the crystal noise, but the crystal noise is not a factor to consider, in view of the existing klystron noise level.

Bridge balance influences signal amplitude markedly and is usually set quite close to null. Microphonic noise becomes more noticeable and the line shapes become distorted if the balance is too near null, so there is an optimum region which must be found. For one milliwatt of microwave power entering the cavity, and 40 db of IF gain, this region is usually found near an IF leakage current of 100 μ a.

Signal klystron power level is known to change the signal amplitude more rapidly than the noise level, although this effect is not very noticeable due to the high level of klystron noise.

The AFC reference oscillator phase and frequency influence the noise level just as the same parameters in the audio amplifier affect signal amplitude. In addition to these adjustments, there are adjustments for signal and reference gain in the AFC, tickle voltage amplitude, and signal limiter level. These parameters are all somewhat inter-related and must be adjusted and readjusted as the spectrometer is brought to optimum tuning.

Calibration and sensitivity. The absolute sensitivity of the spectrometer has been found by observing the resonance spectrum of a sample of DPPH dissolved in benzene. The spectrum consists of five lines with intensity in the ratio 1:2:3:2:1.⁽⁵⁾ Each line is about 5 G wide, so the observed intensity of the central line must be multiplied by 15 to normalize to

a single line of one gauss linewidth. The number of unpaired electrons in the sample was determined from the sample weight by assuming one electron per molecule and using a molecular weight of 394.3. The microwave power entering the cavity was adjusted to one milliwatt, and the time constant set to one second. The normalized sensitivity was found to be 2×10^{13} spins, based on a signal-to-noise ratio of 24 for the central DPPH line in a sample containing 7.3×10^{15} spins.

The signal intensity was checked for linearity by observing the spectrum of vanadium in MgO in samples assumed uniform in doping and varying in mass from about one-half milligram to several hundred milligrams. The signal intensity was found to be directly proportional to mass, after taking into account the difference in cavity loading for the largest sample.

CHAPTER III

THE FORBIDDEN HYPERFINE SPECTRUM OF V^{++} IN MgO

Theory of Forbidden Hyperfine Transitions

The electron paramagnetic resonance spectra of divalent manganese in several single crystals have shown weak lines occurring between the usual intense main hyperfine lines,⁽¹³⁻¹⁹⁾ These are transitions for which $|\Delta M|=1$, $|\Delta m| = 1$, where M is the electron magnetic quantum number and m is the nuclear magnetic quantum number. They are called forbidden because they violate the magnetic dipole selection rules, which are $|\Delta M| = 1$, $|\Delta m| = 0$. The transitions come about because of the mixing of neighboring hyperfine levels by the interaction of the crystal field with the hyperfine interaction. These transitions can occur for paramagnetic ions other than manganese, and have now been observed for divalent vanadium.

The energy levels of doubly ionized vanadium in the cubic field of magnesium oxide are described by the spin-Hamiltonian:⁽²¹⁾

$$H = g\beta\vec{H}\cdot\vec{S} + A\vec{S}\cdot\vec{I} + D\left[S_y^2 - \frac{1}{3}S(S+1)\right] \quad (8)$$

where $S (= \frac{3}{2})$ is the effective spin due to the three unpaired electrons in the doubly ionized configuration, A is the hyperfine splitting parameter, and D is the axial crystal field splitting parameter. The spectrum can be described by a spin only, because the cubic field of MgO splits the seven-fold orbital degeneracy into a ground state singlet and two higher-lying triplets. A weak crystal field of symmetry lower than cubic is present at the site of the vanadium ions, and this is described by the last

term above. The y axis is the principal axis of the lattice distortion which causes this field.

The eigenfunctions of the Hamiltonian are not the pure basis states $|M, m\rangle$; but rather are mixtures of these basis states:

$$\psi_{M', m'} = \sum a_{M, m} |M, m\rangle \quad (9)$$

The reason for the mixture is that \mathcal{H} is not diagonal as it is written in Eq. (8). The coefficients $a_{M, m}$ are most easily found by resort to perturbation theory, since \mathcal{H} is a 32-square matrix, and cannot be readily diagonalized. The forbidden transition from the state $\psi_{M, m}$ to the state $\psi_{M-1, m+1}$ can now be seen to be an allowed transition between the appropriate parts of each state. The intensity of such a transition is given by:

$$I \sim |a_{M, m+1} + b_{M-1, m}|^2 \quad (10)$$

where $b_{M, m}$ is the counterpart of $a_{M, m}$, for the state $\psi_{M-1, m+1}$.

The coefficient $a_{M, m+1}$ is obtained in first order perturbation from the expression:

$$a_{M, m+1} = \frac{\langle M, m+1 | \mathcal{H} | M, m \rangle}{E_{M, m} - E_{M+1, m}} \quad (11)$$

There are no terms in the Hamiltonian, however, which raise m without changing M , so to first order $a_{M, m+1}$ vanishes. In second order though, $a_{M, m+1}$ is given in part by:

$$\frac{\langle M, m+1 | \mathcal{H} | M+1, m \rangle \langle M+1, m | \mathcal{H} | M, m \rangle}{(E_{M, m} - E_{M, m+1})(E_{M, m} - E_{M+1, m})} \quad (12)$$

The part of \mathcal{H} which connects $|M+1, m\rangle$ to $|M, m\rangle$ is the crystal field potential, and the part which connects $|M, m+1\rangle$ to $|M+1, m\rangle$ is the hyperfine interaction. This can be seen by rewriting Eq. (8) for the special case for which the y axis lies in the x - z plane, the z direction being that of the magnetic field:

$$\begin{aligned} \mathcal{H} &= g\beta H S_z + A S_z I_z + A(S_x I_x + S_y I_y) + D \left[(-S_x \sin\theta + S_z \cos\theta)^2 - \frac{1}{3} S(S+1) \right] \\ &= g\beta H S_z + A S_z I_z + \frac{A}{2} (S_+ I_- + S_- I_+) + \\ &D \left[\frac{(S_+ + S_-)^2}{4} \sin^2\theta + S_z^2 \cos^2\theta - \frac{1}{2} (S_+ S_z + S_z S_+ + S_- S_z + S_z S_-) \sin\theta \cos\theta - \frac{1}{3} S(S+1) \right] \end{aligned} \quad (13)$$

where θ is the angle the y axis makes with the z axis, and the substitutions $S_x = \frac{1}{2}(S_+ + S_-)$, $S_y = \frac{1}{2i}(S_+ - S_-)$ have been used.

There will be contributions to $a_{M, m+1}$ from all higher orders of perturbation theory, but in the case considered here, they are negligible. The forbidden line intensity, relative to the main allowed lines, is given by Bleaney and Rubins⁽¹⁶⁾ and is:

$$I = I_0 \left(\frac{3D \sin 2\theta}{4H} \right)^2 \left[1 + \frac{S(S+1)}{3M(M-1)} \right]^2 \left[I(I+1) - m(m-1) \right] \quad (14)$$

where $S = \frac{3}{2}$ and $I = \frac{7}{2}$ for vanadium.

The forbidden transitions will occur in pairs between each hyperfine group, and will be separated by a characteristic distance δH , given by:

$$\delta H = \frac{2A^2}{2H_0} + 2 \frac{\sqrt{BN}}{g\beta} H - \frac{5A^3}{H_0^2} (2m+1) + \frac{3}{2} \frac{A^2 D}{H_0^2} (3 \cos^2\theta - 1) (2m+1) \quad (15)$$

The entire spectrum is shown schematically in Figure VI. There are twenty-four allowed lines in eight groups of three each, and fourteen forbidden lines in pairs between each hyperfine group. The forbidden lines indicated in Figure VI are those for which $M = +\frac{1}{2} \leftrightarrow M = -\frac{1}{2}$, and are the only ones observed, so far.

Experimental Results

A crystal of MgO weighing 170 mg and containing nominally 0.5 molar percent vanadium was used for the experiments. A small chip from the crystal which weighed 0.3 mg was compared in the spectrometer with a standard DPPH sample, and was found to contain 1.2×10^{16} vanadium ions. The molar concentration calculated from these data is 0.3%.

The forbidden lines were observed at a number of orientations in the magnetic field in an attempt to verify the angular dependence specified by Eq. 12. The forbidden doublet corresponding to the transitions

$|+\frac{1}{2}, +\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}, +\frac{3}{2}\rangle$ and $|+\frac{1}{2}, +\frac{3}{2}\rangle \leftrightarrow |-\frac{1}{2}, +\frac{1}{2}\rangle$ is shown in Figure VII. Some of the lines were completely hidden by superimposed lines in the spectrum of divalent manganese, which was also present in the crystal. The manganese spectrum consists of six pentads whose average positions are indicated by the dashed lines in Figure VI. Four of the five manganese lines of each group move around, ⁽²⁰⁾ as much as 100 G, as the crystal is rotated, and it was these lines which masked part of the forbidden vanadium spectrum. The vanadium lines which could be observed did not show an angular dependence as expected, and the reason for this is not completely understood. The seven sets of forbidden doublets were observed to have

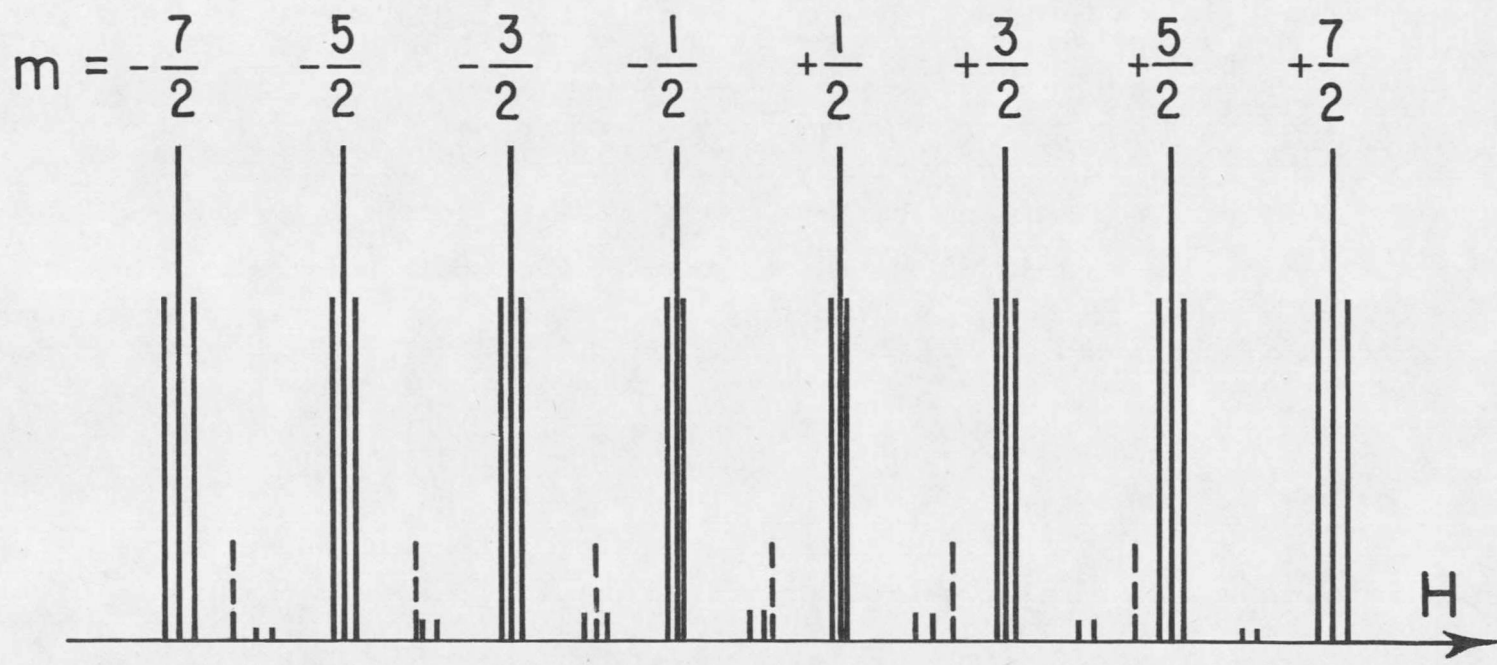


FIG. VI

SCHEMATIC OF MgO=V⁺⁺ SPECTRUM

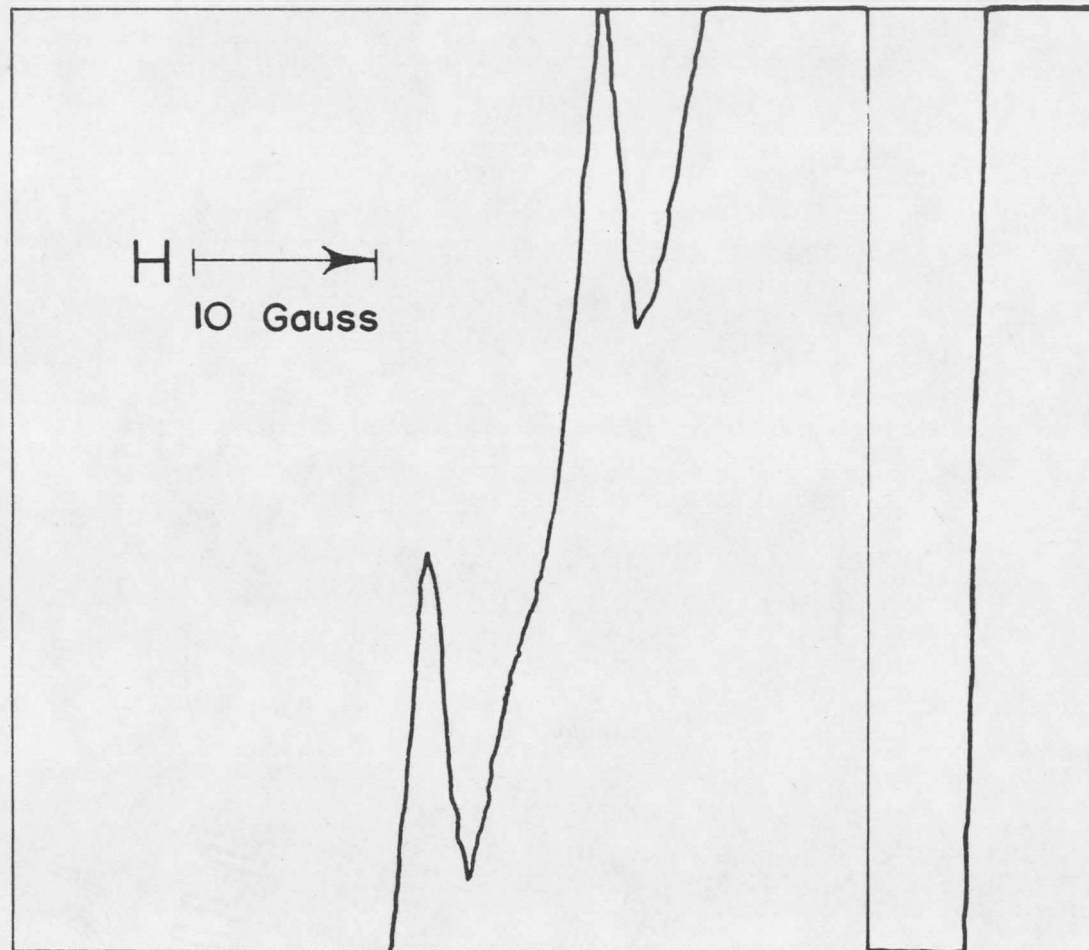


FIG. VII

FORBIDDEN LINES

relative intensities of 7:12:15:16:15:12:7, however, as specified by Eq. (14).

The splitting of the doublets was also measured for each case where both lines could be observed, and compared with the splitting predicted by Eq. (15). Each of the splittings was about 10 gauss, and agreed with the theoretical prediction within experimental error.

Discussion

The allowed spectrum of vanadium in MgO can be described almost completely by a spin-Hamiltonian which contains only a Zeeman term and a hyperfine term. The crystal field term is necessary, however, to explain an angular-dependent line broadening⁽²¹⁾ in some of the allowed lines. As outlined above, the crystal field term is also necessary to explain the very existence of the forbidden spectrum. The fact that the forbidden line intensities do not have a definite angular dependence indicates that the axis of the axial crystal field does not have a single set of definite directions.⁽²²⁾ This supposition is supported by data on the angular dependence of the allowed spectrum mentioned above. The situation is somewhat unsatisfactory, since an exact specification of the possible directions of the crystal field axis is not possible, and the exact mechanism that induces the lattice distortion is unknown.

The main purpose of the investigation on vanadium in MgO was to demonstrate that the spectrometer has sufficient sensitivity and

versatility to be useful as a research tool. This purpose was fulfilled. The machine will be used for other similar investigations into crystal fields as well as for general-purpose studies in paramagnetism.

APPENDIX

APPENDIX

Spectrometer Parts List

Component	Manufacturer	Model
2 - Klystrons	Varian	X-13
1 - Isolator	Kearfott	W-177
1 - Isolator	Lewis and Kaufman	R-88-96
1 - Attenuator	Hewlett-Packard	X-382A
4 - Attenuators	Hewlett-Packard	X-375A
1 - Attenuator	Sperry	47X-2
1 - Adjustable short	Hewlett-Packard	X-920A
1 - Frequency Meter	Hewlett-Packard	X-532B
2 - Detector mounts	Microwave Components	X-331
1 - Magic tee	Microwave Components	X-353
2 - Topwall coupler	Microwave Components	X-360B
1 - Mixer-preamplifier	LEL, Inc.	X-BH-2
1 - IF Amplifier	LEL, Inc.	IFGOB-50
1 - Audio Oscillator	Hewlett-Packard	200 CD
1 - Audio Oscillator	Hewlett-Packard	200 AB
1 - Oscilloscope	Hewlett-Packard	130 BR
2 - Monitor scopes	Surplus	---
3 - 350 v dc power supplies	hand-made	---
4 - 300 v dc power supplies	hand-made	---
1 - 7.5 v dc power supply	Kepeco	ABC 7.5-2
1 - 6 v dc power supply	Kepeco	PRM 6-25
1 - Magnet system	Varian	V-3400
1 - AFC circuit	hand-made	---
1 - lock-in amplifier	hand-made	---
1 - Klystron power control circuit	hand-made	---
1 - Marginal oscillator (NMR)	hand-made	---
1 - Strip-chart recorder	Varian	G-14A
1 - Frequency counter	Hewlett-Packard	5245L

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