

# The Investigation of an Electron Resonance Spectrometer Utilizing a Generalized Feedback Microwave Oscillator\*

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**Summary**—In this investigation, an entirely different approach is taken toward the development of a “self-stabilized” paramagnetic resonance (EPR) spectrometer system which eliminates the usual low-power klystron oscillator, electronic frequency stabilizing equipment, and the complex superheterodyne detector without sacrificing loss of detection sensitivity. This system which is known as an oscillator spectrometer consists of a microwave amplifier containing a sample-carrying network element in the positive feedback loop. The microwave device oscillates at the network’s central resonant frequency with essentially instantaneous frequency stability. Expressions relating the change in power level and frequency of oscillation as a function of the change in the network attenuation and phase at magnetic resonance are derived. The system’s ultimate sensitivity is determined by analyzing the noise within the oscillator loop. In general, the noise that limits the detection of the resonance signal is principally that generated by the amplifier, and thus a simple video detector can be used. The sensitivity of this spectrometer was found to be comparable with that of the conventional bridge type spectrometer.

## INTRODUCTION

ELECTRON SPIN resonance absorption studies have made important contributions to science. These studies range from solid state physics through chemistry to the biological and medical sciences.<sup>1</sup> Typical applications of electron spin resonance [also known as paramagnetic resonance (EPR)] are found in the study of conduction electrons in metals and semiconductors, radiation damage in insulating materials, resonances from *F* centers and free radicals, chemical analysis, etc.

The physical methods that are employed to detect and measure the electron spin characteristics of materials (such as *g* value, anisotropy, line width, multiplicity of lines, etc.) are nearly all based on the fact that the unpaired electron has a magnetic dipole moment.

When a solid or a liquid specimen is placed between the poles of a magnet and subjected to radio frequency radiation, spin resonance occurs at a particular frequency of the radiation or set of frequencies which depend on the strength of the magnetic field.

An extensive literature survey has revealed that most modern microwave paramagnetic spectrometers take the general form as shown in Fig. 1. Here a low power

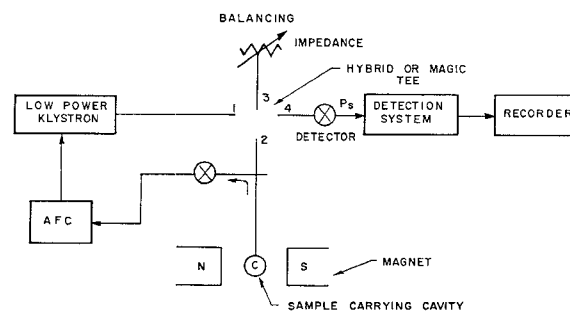


Fig. 1—Conventional bridge spectrometer.

klystron oscillator operating between 8 and 50 kMc supplies RF energy to a balanced magic or hybrid tee (arm 1). The sample carrying cavity is placed on one of the symmetrical arms (arm 2), and a balancing impedance is placed on the other arm (arm 3) of the tee. When magnetic resonances occur, the resultant change in the cavity impedance unbalances the tee producing a signal at the output port (arm 4).

The maximum detection sensitivity is usually limited by the detector’s noise figure which is reduced by using superheterodyne methods. With the high degree of bridge balance required with a superheterodyne detector, some frequency stabilization method must be employed to hold the klystron at the cavity frequency. Frequency stabilizers usually utilize one of three methods: 1) the klystron is frequency modulated and the resultant signal is phase detected to produce a correction voltage as used by Jung,<sup>2</sup> 2) an elaborate detection method as first used by Hirshon and Fraenkel<sup>3</sup> which involves additional high frequency oscillators and components, 3) Pound<sup>4</sup> stabilization employing a microwave discriminator, as used by Beringer and Castle.<sup>5</sup>

The construction of a superheterodyne detector and stabilization system requires a great deal of care and caution.

The purpose of this paper is to determine the *technical feasibility* and the *attainable sensitivity* of a “self-stabilized” oscillator-spectrometer system in terms of a gen-

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<sup>1</sup> D. J. Ingram, “Free Radicals as Studied by Electron Spin Resonance,” Butterworth Scientific Publications, London, pp. 1–31; 1955.

<sup>2</sup> P. Jung, “Transistorized frequency stabilization for reflex klystrons used in magnetic resonance,” *J. Sci. Instr.*, vol. 37, p. 372; October, 1960.

<sup>3</sup> J. M. Hirshon and G. K. Fraenkel, “Recording high-sensitivity paramagnetic resonance spectrometer,” *Rev. Sci. Instr.*, vol. 26, p. 34–41; January, 1955.

<sup>4</sup> R. V. Pound, “Frequency stabilization of microwave oscillators,” *Proc. IRE*, vol. 35, pp. 1405–1415; December, 1947.

<sup>5</sup> R. Beringer and J. G. Castle, “Magnetic resonance absorption in nitric oxide,” *Phys. Rev.*, vol. 78, pp. 581–592; June, 1950.

eralized sample-carrying feedback element to replace the above conventional spectrometer systems. The "self-stabilized" oscillator spectrometer consists of a microwave amplifier containing the generalized network element in a positive feedback loop as shown in Fig. 2. The principle advantage of the oscillator spectrometer over the conventional spectrometer lies in its simplicity of construction and operation. The microwave device oscillates at the network's central resonant frequency with essentially instantaneous frequency stability which eliminates the need for the electronic frequency stabilizing equipment.

In addition only a simple video detector is required for good sensitivity as compared to the superheterodyne detector used in conventional high performance spectrometers. The oscillator spectrometer's sensitivity is limited primarily by the microwave amplifiers noise figure. Thus the most desirable spectrometer system from the standpoint of sensitivity would depend on the state of the art of low noise detectors vs microwave amplifiers.

The oscillator spectrometer is similar in principle to the autodyne detector. Little work has been done toward analyzing the autodyne's theoretical sensitivity. Furthermore, no attempt has been made to extend the autodyne's use into the microwave region where it can be used for EPR work. Much work and analysis on stability and noise in feedback type oscillators has been carried out by such investigators as Meacham<sup>6</sup> and Van der Pol<sup>7</sup> on feedback oscillator theory in general, Sooy *et al.*,<sup>8</sup> and Price and Anderson<sup>9</sup> on the extension of feedback oscillators into the microwave region. A considerable number of investigators,<sup>10-13</sup> have concerned themselves with the more special problem of noise in oscillators. However, little, if any work has been done toward applying the microwave feedback oscillator to the study of EPR detection. The above workers have been primarily interested in the oscillators stability whereas here interest is not so much in high stability as in how the frequency and amplitude vary as a result of a perturbation due to EPR within the frequency determining cavity. The noise in such an oscillator is of extreme importance since it will limit the detection sensitivity of the system. With such a system for EPR

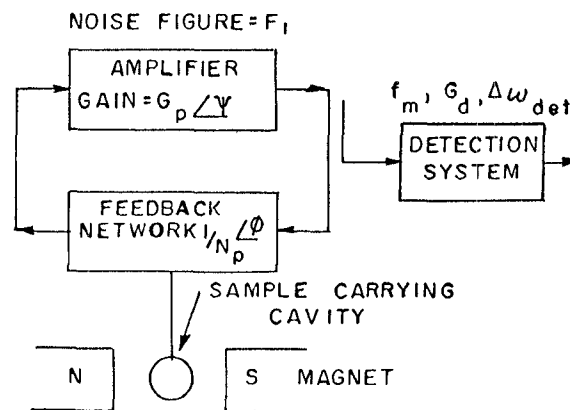


Fig. 2—Block diagram of oscillator spectrometer system.

detection, we are able to discard the conventional electronically stabilized lower power klystron and superheterodyne detection systems and replace them with this "all-microwave" device.

Since the analysis presented here is for a generalized feedback network, the system sensitivity for any specific feedback network such as Chodorow *et al.*,<sup>14</sup> the microwave bridge as used by Sooy,<sup>8</sup> the magic tee bridge, or a conventional transmission cavity can readily be calculated.

#### DESCRIPTION OF BLOCK DIAGRAM

A block diagram of the "self-stabilized" microwave oscillator spectrometer is shown in Fig. 2. The microwave amplifier (parametric or klystron amplifier, maser or the TWT) is assumed to have a power gain  $G_p$  and noise figure  $F_1$ .

With the paramagnetic test sample located in the  $H$  field of the generalized feedback element, the network's attenuation and phase characteristics are altered when magnetic resonance occurs. The problem is to determine the effect that a change in the network attenuation and phase characteristics will have on the oscillator's amplitude and frequency of oscillation. From this, the system's ultimate sensitivity must be determined from a consideration of the noise within the oscillator loop. With this general analysis, the system sensitivity for any specific feedback network can readily be calculated.

Although the feedback network may take on any configuration desired, it must contain a resonant cavity in one form or another. This cavity must 1) be the frequency determining element of the network, and 2) contain the paramagnetic sample. When the proper feedback loop phase and amplitude conditions are met, oscillation will occur at the resonant cavity frequency.

A directional coupler at the amplifier output is used to sample the microwave power. The amplitude change is monitored by a crystal detector. To detect the frequency shift, the coupled energy could be passed through a frequency discriminator and then detected.

<sup>14</sup> M. Chodorow, E. L. Ginzton and F. Kane, "A microwave impedance bridge," *Proc. IRE*, vol. 37, pp. 634-639; June, 1949.

<sup>6</sup> L. A. Meacham, "The bridge stabilized oscillator," *Bell Sys. Tech. J.*, vol. XVII, pp. 574-591; October, 1938.

<sup>7</sup> B. Van der Pol, "The nonlinear theory of electric oscillations," *Proc. IRE*, vol. 22, pp. 1051-1084; September, 1934.

<sup>8</sup> W. R. Sooy, F. L. Vernon and J. Munushian, "A microwave Meacham bridge oscillator," *Proc. IRE*, vol. 48, pp. 1297-1306; July, 1960.

<sup>9</sup> V. G. Price and C. T. Anderson, "X-Band travelling wave tube feedback oscillator," *IRE NATIONAL CONVENTIONAL RECORD*, pt. 3, vol. 5, pp. 57-65; March, 1957.

<sup>10</sup> W. A. Edson, "Noise in oscillators," *Proc. IRE*, vol. 48, pp. 1454-1466; August 1960.

<sup>11</sup> M. A. Garsten, "Noise in nonlinear oscillators," *J. of Appl. Phys.*, vol. 28, pp. 352-356; March, 1957.

<sup>12</sup> J. L. Stewart, "Frequency modulation noise in oscillators," *Proc. IRE*, vol. 44, pp. 372-376; March, 1956.

<sup>13</sup> G. Hetland, "The Effect of Noise on Oscillator Stability," *Appl. Electronics Lab., Stanford University, Stanford, Calif., Tech. Rept. No. 40*; Aug. 1, 1955.

### FREQUENCY VARIATION PRODUCED BY PARAMAGNETIC RESONANCE

When electron paramagnetic resonance occurs, the properties of the sample carrying cavity are altered by the test sample. Both the cavity  $Q$  and resonant frequency are affected by the sample susceptibility  $\chi_m$  which is in general a complex tensor due to the anisotropic properties of such materials. Any change in the sample cavity at resonance causes a change in the feedback network.

For the more common feedback elements (Meacham bridge, magic tee, transmission cavity, etc.), the electron absorption (produced by the imaginary component  $\chi_m''$ , of  $\chi_m$ ) amplitude modulates the oscillation, the electron spin dispersion (produced by the real component  $\chi_m'$ , of  $\chi_m$ ) detunes the oscillator feedback network; the result is frequency modulation.

A change in the cavity phase shift or resonant frequency due to  $\chi_m$  will produce a change in the feedback network phase shift  $\theta$  or resonant frequency  $\omega_0$ .

In the absence of paramagnetic resonance, the resonant sample-carrying cavity within the feedback network is purely resistive. The total loop phase shift for oscillation to occur must be  $2\pi n$ , where  $n$  is an integer.

When magnetic resonance occurs, the cavity resonant frequency will change by  $\delta\omega_r$ , introducing a reactive component into the feedback network. The total loop phase shift must remain constant at  $2\pi n$  if oscillation is to continue. The only variable that can change, in order to preserve this relationship, is the frequency of oscillation  $\omega$ .

The amplitude of the frequency variation can then be written as

$$\delta\omega_r = \omega_0 - \omega = \frac{\partial\omega_r}{\partial\chi_m} \Delta\chi_m. \quad (1)$$

This indicates that the frequency of oscillation is a direct function of the sample susceptibility  $\chi_m$ . The complex susceptibility  $\chi_m$  is used throughout to keep the analysis in general terms since for example,  $\Delta\omega_r$  is not always a function of the dispersive components. For such calculations as applied to specific networks, see Payne.<sup>15</sup>

### AMPLITUDE VARIATION PRODUCED BY PARAMAGNETIC RESONANCE

At magnetic resonance, the susceptibility  $\chi_m$  will affect the sample carrying cavity  $Q$  and be reflected as a change in the feedback attenuation  $N_v$ .

For sustained oscillation the relation between the

amplifier gain and the feedback networks attenuation is given by

$$G_v = N_v. \quad (2)$$

A change in  $\chi_m$  will change the network attenuation. Since oscillation must be sustained, we can write

$$\frac{\partial N_v}{\partial\chi_m} = \frac{\partial G_v}{\partial\chi_m}. \quad (3)$$

Here the partial derivative had been used in place of the total derivatives since  $G_v$  and  $N_v$  are functions of several variables. This relation indicates that a change in the feedback network attenuation due to a change in  $\chi_m$  must be accompanied by an equal change in the amplifiers gain if oscillation is to continue. Under the conditions of operation, the gain of the amplifier is a function of the input signal  $V$ . An exaggerated plot of gain vs input signal is shown in Fig. 3. Therefore the problem is to detect the change in amplifier gain in order to detect  $\chi_m$ . The desired gain change can be measured indirectly by measuring the change in input signal for a given  $\chi_m$ . This can be shown as indicated below.

The measured quantity is

$$V_s = \frac{\partial V}{\partial\chi_m} \Delta\chi_m, \quad (4)$$

where  $\Delta\chi_m$  is the finite change in the susceptibility  $\chi_m$ . For sustained oscillation, we can write from (2) and (3)

$$\left(\frac{\partial N_v}{\partial G_v}\right)\left(\frac{G_v}{N_v}\right) = 1. \quad (5)$$

Multiplying (4) by (5) and rearranging gives, without loss of generality,

$$V_s = K_v \frac{\partial N_v}{\partial\chi_m} \Delta\chi_m \frac{V}{N_v}, \quad (6)$$

where

$$K_v = \frac{\partial V}{\partial G_v} \frac{G_v}{V}. \quad (7)$$

Here, the term  $\partial V/\partial G_v$  is the inverse slope of the gain vs input signal curve of Fig. 3. The term  $K_v$  shall be referred to as the "regenerative amplification" and can be as high as  $10^6$ . Rearranging (6), the final result can be written as

$$V_s = -K_v V_0 \frac{\partial(1/N_v)}{\partial\chi_m} \Delta\chi_m, \quad (8)$$

where

$V_0 = N_v V =$  network input = amplifiers output

$$\partial(1/N_v)/\partial\chi_m = -\frac{1}{N_v^2} \frac{\partial N_v}{\partial\chi_m}.$$

<sup>15</sup> J. B. Payne, "The Investigation of an Electron Resonance Spectrometer Utilizing a Cavity-Feedback Microwave Oscillator," Ph.D., dissertation, Dept. of Elec. Engrg., Pennsylvania State University, University Park; 1962.

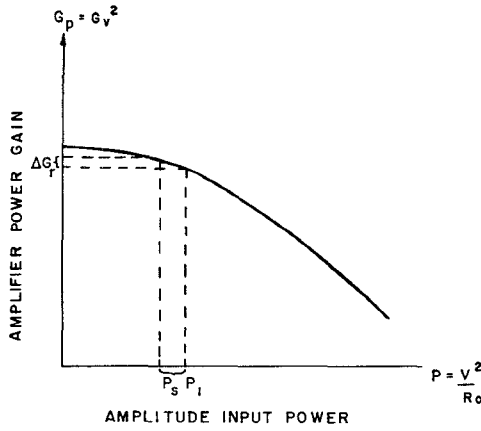


Fig. 3—Amplifier power gain vs input signal.

$V_s$  is the paramagnetic resonance signal at the amplifier input.

The resonance signal given by (8) can be written in terms of power. That is

$$P_s = \frac{V_s^2}{R_0} = K_p P_0 \left[ \frac{\partial(1/N_v)}{\partial \chi_m} \Delta \chi_m \right]^2, \quad (9)$$

where

$$K_p = \frac{\partial P}{\partial G_p} \frac{G_p}{P}. \quad (10)$$

$K_p$  is obtained by substituting  $P = V^2/R_0$  and  $G_p = G_v^2$  into (7).

The paramagnetic resonance signal at the output of the detector system can be written as

$$P_{s-d} = K_p G_p G_d' P_0 \left[ \frac{\partial(1/N_v)}{\partial \chi_m} \Delta \chi_m \right]^2, \quad (11)$$

where  $G_d'$  is the effective power gain of the detection system. This includes the attenuation introduced by the directional coupler and microwave detector.

At this point, a brief qualitative explanation should be given concerning the phenomenon that produces  $K_p$ . From (2), for sustained oscillation the amplifier gain must equal the feedback network attenuation. At magnetic resonance, the feedback attenuation changes. For oscillation to continue, the amplifier gain must change by the same amount as shown by (3). From Fig. 3, it is apparent that the only way the gain can be altered is for the input level to change in the proper direction. If the amplifier is operated in a highly linear region of the curve, the input level must change by a considerable value in order to alter the gain by only a slight amount. The amplification obtained by this change in level is  $K_p$ .

It only remains to determine  $K_p$  as a function of the amplifier parameters, and  $N_v$  as a function of  $\chi_m$ .

## SYSTEM NOISE

In the preceding sections, only the signal generated by paramagnetic resonance has been considered. There is, however, a fundamental limitation on the sensitivity of the system. This limitation is due to sources of noise in the system elements or from external sources. It is equally important to study the noise as well as the signal strength arriving at the detector.

In the conventional bridge spectrometer, using either a square law or superheterodyne detection system, the noise that limits the system sensitivity is introduced largely by the crystal detector or mixer. Klystron noise and frequency fluctuations are usually considered to introduce a negligible amount of noise.

In order to determine the amplitude noise appearing at the output of the crystal detector of the microwave oscillator spectrometer, an entirely different approach must be taken. Unlike the bridge spectrometer, the oscillator spectrometer has an amplifier preceding the detector, and this must be considered. The amplifier not only amplifies the signal, but also introduces noise. The derivation used to obtain the noise expression given here (see Payne<sup>15</sup> for detailed derivation) utilized the Van der Pol equation<sup>7</sup> and followed an approach similar to that taken by Caughey.<sup>16</sup>

The problem reduces to the fact that if an amplifier with noise figure  $F_1$  is connected as an oscillator, then, what will be the resultant noise fluctuations of the oscillator's frequency and output amplitude?

If  $V_0$  is the amplifiers output voltage and  $V$  is the input voltage, then we can represent the amplifiers characteristic curve, as suggested by Van der Pol,<sup>6</sup> by

$$V_0 = \alpha V_{in} - \gamma V_{in}^3, \quad (12)$$

where  $\alpha$  is the linear small signal gain of the amplifier and  $\gamma$  is a measure of the amplifiers nonlinearity. If we let the amplifier noise

$$\overline{e_n^2} = F_1 k T_0 R_0 B_n \quad (13)$$

be a driving source as shown in Fig. 4, then by using expressions worked out by Rice<sup>17</sup> and Caughey,<sup>16</sup> the noise fluctuations of the oscillator's input amplitude becomes<sup>15</sup>

$$\begin{aligned} P_N &= F_1 k T_0 \frac{(\alpha - 3/2 \gamma P R_0)}{3 P \gamma R_0} B_{osc} \\ &= \frac{\overline{e_n^2} (\alpha - 3/2 \gamma P R_0)}{3 P \gamma R_0^2}, \end{aligned} \quad (14)$$

<sup>15</sup> T. K. Caughey, "Response of Van der Pol's oscillator to random excitation," *J. Appl. Mech.*, vol. 81, pp. 345-348; September, 1959.

<sup>17</sup> S. O. Rice, "Mathematical analysis of random noise," *Bell Sys. Tech. J.*, vol. 24, pp. 46-158; January, 1945.

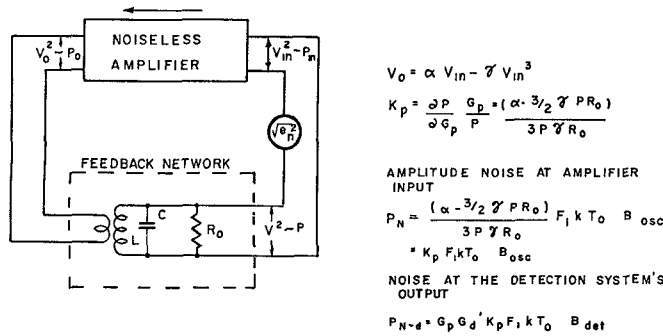


Fig. 4—Generalized diagram for noise calculations.

and the oscillator's frequency variation due to noise becomes

$$\delta\omega_n = \sqrt{\frac{F_1 k T_0 B_{osc}}{P}} B_{osc}. \quad (15)$$

Here  $k$  is Boltzmann's constant,  $T_0$  room temperature in degrees Kelvin,  $B_{osc}$  is the oscillator's noise bandwidth. Neglecting the crystal and detection system noise, the noise at the detection system output from (14) becomes

$$P_{N-d} = G_p G_d' F_1 k T_0 \frac{(\alpha - 3/2 \gamma P R_0)}{3 P \gamma R_0} B_{det}. \quad (16)$$

Here, the oscillator's noise bandwidth is reduced to the detection system's noise bandwidth  $B_{det}$ .

#### REGENERATIVE AMPLIFICATION

From (12) the regenerative amplification as defined by (7) or (10) can be expressed in terms of amplifier parameters. That is,  $K_p$  becomes

$$K_p = \frac{\partial P}{\partial G_p} \frac{G_p}{P} = \frac{-(\alpha - 3/2 \gamma P R_0)}{3 P \gamma R_0}. \quad (17)$$

Here, the noise voltage has been neglected so that  $P = P_{in}$  and  $V_{in}^2/R_0 = P$ . It is important to note that the amplitude noise at the detection system output is simply the thermal noise  $F_1 k T_0 B_{det}$  amplified by the regenerative amplification.

#### EQUIVALENT SYSTEM DIAGRAM

Eqs. (11), (14), and (17) fit into place like a puzzle to form the magnetic resonance spectrometer. Fig. 5 can be drawn from these equations to represent the system for detection of the amplitude variations. Here, the feedback network is driven from an ideal noiseless generator whose output is set equal to the amplifier power output  $P_0$ . A similar system diagram can be drawn from (1) and (15) to represent the system for frequency detection.

The detector noise is the limiting factor in determining a bridge spectrometer's sensitivity. In the oscillator-spectrometer of Fig. 5 two noiseless amplifiers are seen to precede the detector. The noise  $P_{N'}$  produced within the oscillator is amplified by the amplifiers to a point where the detector noise is negligible. Changing  $K_p$  does

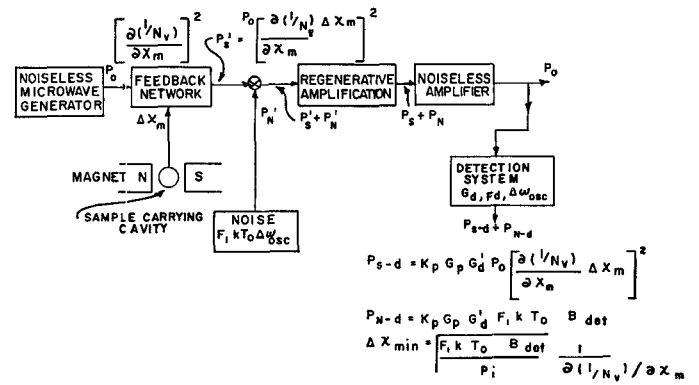


Fig. 5—Equivalent diagram of the oscillator spectrometer for amplitude detection.

not affect the signal to noise ratio but only needs to be large enough to amplify the amplifier noise above the detector noise.

From Fig. 5, the expression for the total noise power  $P_{N'-d}$  at the detection system output including crystal detectors noise figure  $F_x$  and the detection system noise figure  $F_d$  can be written as

$$P_{N'-d} = -[F_1 K_p G_p G + F_x + F_d] G_d k T_0 \Delta\omega_{det}, \quad (18)$$

where  $G =$  loss introduced by directional coupler and  $G_d' = GG_d$ . The amplifier power gain  $G_p$  is largely determined by the type amplifier and the feedback network used.

From the above expression, the importance of the regenerative amplification can be seen. By making  $K_p$  large, the internal noise of the oscillator is amplified along with the resonance signal to a point where it is large compared to that of the crystal and amplifying system. In order to obtain a large  $K_p$ , the amplifier must be operated at a fairly low power level so as to make  $\gamma P_0$  in (17) small. Lowering the level of oscillation will also effect the resonance signal since it is proportional to the network's input power,  $P_0$ . Also, lowering the power level of oscillation or the power incident on the crystal detector lowers  $F_x$ , the crystal noise figure. However, on the other hand, increasing the level of oscillation will decrease  $K_p$ , increase the resonance signal, and increase the oscillator and crystal noise. Thus, from the above considerations it can be seen that a compromise must be made.

There is a particular power level of oscillation that will give optimum performance. Since every amplifier has a different  $\gamma$ , and crystal detectors differ, the point of optimum operation is found by experimentally plotting the signal-to-noise ratio as a function of the power level of oscillation.

#### MINIMUM DETECTABLE SUSCEPTIBILITY

If we divide the signal by the noise from equations (11), (16), and (17) and set the resulting signal-to-noise ratio equal to unity, the minimum detectable change in susceptibility  $\Delta\chi_m$  becomes

$$\Delta\chi_m|_{\min} = \sqrt{\frac{F_1 k T_0 B_{\text{det}}}{P_0}} \frac{1}{\partial(1/N_v)/\partial\chi_m}. \quad (19)$$

This result is identical to Feher's<sup>18</sup> expression for the sensitivity of the conventional type spectrometers. The noise figure  $F_1$  would correspond to the detectors noise figure, and  $\partial(1/N_v)/\partial\chi_m$  yields the sample cavity  $Q$  and filling factor.

### EXPERIMENTAL RESULTS

In order to demonstrate the technical feasibility and to experimentally verify the attainable sensitivity, an electron-paramagnetic resonance oscillator spectrometer was designed and constructed. The spectrometer utilized a 100 mw travelling wave tube with a noise figure of 20 db operated at a power level of 6 mw and frequency of 9.7 kMc. Fig. 6 is a block diagram of the complete spectrometer system constructed. Three networks were analyzed. This included a magic tee bridge, an ordinary transmission cavity, and a modified transmission cavity known as a bimodal cavity. In selecting the feedback element, the network that yields the largest  $\partial(1/N_v)/\partial\chi_m$  is desirable. The calculations given in Payne<sup>15</sup> show the magic bridge tee to be twice as sensitive as the transmission cavity. However, with the addition of the filter cavity shown in Fig. 6 for stabilizing the loop, more than the two-to-one advantage is lost. The ordinary transmission cavity was thus used providing a simpler arrangement.

The Meacham bridge was not considered as a feedback element. An improvement over the magic tee would not be expected since it can be shown that a magic tee gives a two to one improvement in stability over the Meacham bridge. The only penalty paid for this improvement is less freedom in choosing the matching impedance. A filter cavity is required with the Meacham bridge also, which introduces additional signal loss.

The transmission cavity used here is operated in the  $TE_{111}$  mode with the sample placed in the center of the end plate. The cavity is oriented so its  $H$  field is normal to that of the static magnetic field. Magnetic field modulation at 100 kc was employed by use of a small loop within the cavity and oriented so as not to effect the microwave fields.

When paramagnetic resonance occurs, both the amplitude and frequency will be modulated at 100 kc as a result of the magnetic field modulation. If the modulating field is small, the detected amplitude of the 100 kc modulation will represent the derivative of the susceptibility.

Fig. 7 is a plot of the signal to noise ratio vs level of oscillation for a small test sample of DPPH. The X's

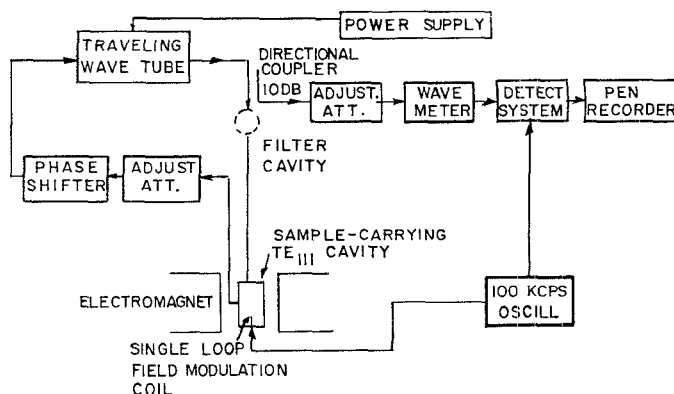


Fig. 6—Detailed block diagram of the experimental spectrometer system.

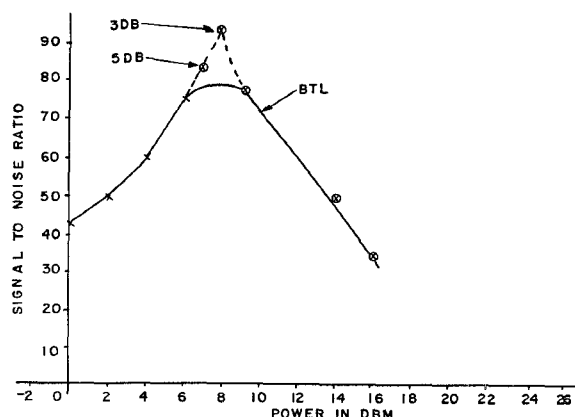


Fig. 7—Signal-to-noise ratio vs level of oscillation.

on the plot of Fig. 7 indicate the resultant signal-to-noise ratio with no attenuation inserted between the directional coupler and the crystal detector. The Chi's indicate the resulting signal to noise ratio when 3 to 6 db of attenuation was introduced between the coupler and detector so as to maintain a constant crystal bias.

Theoretical calculations indicated a minimum detectable susceptibility of  $1.19 \times 10^{-11}$  for this system. A test sample of Bruceton Coal diluted in silica containing a  $1.5 \times 10^{14}$  spins was used to verify the system sensitivity. This corresponded to a sample susceptibility of  $4.7 \times 10^{-11}$ . Fig. 8 shows the absorption for the recorded derivative. The signal-to-noise ratio is approximately 3.5. Thus, the minimum detectable susceptibility becomes

$$\chi_m'' = 1.35 \times 10^{-11}.$$

Thus, the microwave oscillator spectrometer resultant sensitivity is seen to be in agreement with the theoretically calculated sensitivity. If an amplifier with a noise figure of 10 db was used with a level of oscillation of one watt, the minimum detectable susceptibility would be  $7.8 \times 10^{-14}$ .

This is the same sensitivity the conventional bridge spectrometer would have if its detection system had a 10-db noise figure and its klystron delivered 1 watt to

<sup>18</sup> G. Feher, "Sensitivity in microwave paramagnetic resonance absorption techniques," *Bell Sys. Tech. J.*, vol. 36, pp. 449-484; March, 1957.

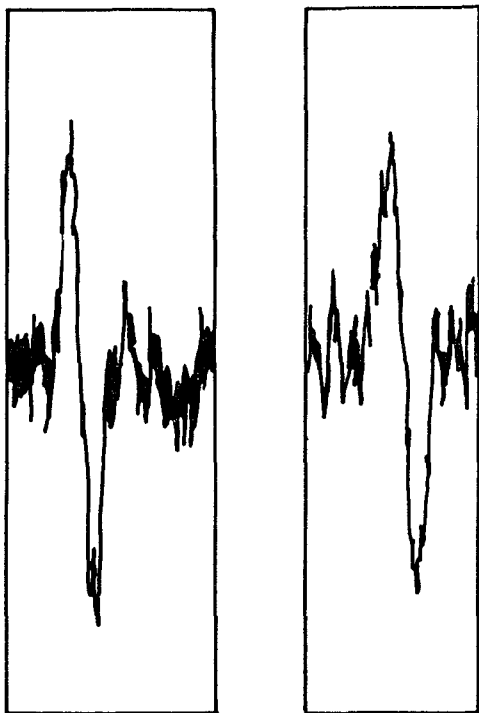


Fig. 8—EPR absorption spectrum of  $1.5 \times 10^{14}$  spins of Bruceton coal in silica powder, level of oscillation = 8DBM, modulation amplitude 2 gauss, time constant = 1 sec.,  $\frac{1}{2}$  line-width = 12 Gauss.

the bridge. In order to obtain this sensitivity, a bridge spectrometer would have to utilize frequency stabilizing equipment for the klystron in addition to superheterodyne detection. The oscillator spectrometer does not require stabilizing equipment nor superheterodyne detection, thus yielding a far simpler and less complex system without sacrificing loss in sensitivity.

## CONCLUSIONS

The purpose of this paper was to determine the technical feasibility and the attainable sensitivity of a "self-stabilized" microwave oscillator-spectrometer system for the detection of paramagnetic resonance.

The principle advantages of such a device are the elimination of the usual low-power klystron oscillator, electronic frequency stabilizing equipment, and the complex superheterodyne detector without loss of detection sensitivity. This system is, in effect, a self-stabilized oscillator that oscillates at the sample-carrying cavities resonant frequency with essentially instantaneous frequency stability. Thus, the conventional spectrometer system can be discarded and replaced with this "all microwave" device.

It was shown that the minimum detection sensitivity is determined by the amplifier's noise figure, power output, and linearity. That is, in the oscillator spectrometer, the noise that limits the detection of the magnetic resonance signal is principally that generated by the amplifier.

Expressions relating the change in power level and frequency of oscillation as a function of the change in network attenuation and phase have been developed. These expressions are given in terms of a generalized feedback network.

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