STUDIES IN PARAMAGNETIC RESONANCE.

Thesis by

Floyd Bernard Humphrey

In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
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Beati gyro-vertatores, quia ipsorum est paritas Pauli.

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ABSTRACT

A paramagnetic resonance spectrometer has been designed and constructed which is particularly adaptable to problems in the field of chemistry. It is a wide range, high resolution instrument suitable for investigating the spectrum of paramagnetic substances from $g = 0.7$ to $g = 7.5$ with resonance lines from a fraction of a gauss to 1000 gauss wide. Spectra can be observed at temperatures from room temperature to liquid helium temperature using single crystals, powders, or solutions as samples. The sensitivity is such that 10^{15} paramagnetic atoms are needed per sample.

The spectrum of gadolinium ion in a micro-crystalline sample of ceric oxide has been investigated. The observed resonance line contained structure that could not be resolved with extreme magnetic dilution (100,000:1), low temperature (4.5°K) or both. An explanation for this structure is suggested. The value of g for the line was measured at two different magnetic field strengths, as was the zero-field splitting. An anomalous shift in the direction of the free ion value of g was found when the field was changed from 3400 gauss to 8600 gauss.

The spectrum of manganous ion in a micro-crystalline sample of aragonite was observed at both 3400 gauss and 8600 gauss. An isotropic hyperfine structure of 6 lines was observed. A precise comparison between theory and experiment was made showing excellent agreement.

Work on other compounds is also reported.

TABLE OF CONTENTS

Section	Title	Page
	ACKNOWLEDGEMENTS	
	ABSTRACT	
I.	INTRODUCTION	1
II.	GADOLINIUM IN CERIC OXIDE	10
III.	MANGANESE IN CALCIUM CARBONATE	22
IV.	OTHER COMPOUNDS WHICH HAVE BEEN INVESTIGATED	27
V.	SPECTROMETER	31
	APPENDIX I	79
	APPENDIX II	81
	REFERENCES	84
	PROPOSITIONS	87

I. INTRODUCTION

It is well-known that an atomic system possesses characteristic energy levels and that absorption or emission of electromagnetic radiation occurs when a transition is made between these energy levels. Energy is absorbed if the atomic system goes from a state of lower energy to a state of higher energy, and emitted for the converse case. In general, the energy of a particular state depends not only upon the structure of the atom or ion but also to some extent upon its surroundings, especially if this atom or ion is in a solid. Therefore, from a study of the absorption of electromagnetic radiation by an atom or ion in a crystalline lattice, it should be possible to obtain information about the ion itself and also about the lattice structure. The energy of an atomic system is mostly of an electrical nature and familiar optical and infrared spectroscopy is used to investigate this nature. Some atomic systems are also magnetic in character and a special type of spectroscopy (called paramagnetic resonance spectroscopy) is used to investigate them. It gives precise information about the magnetic energy levels and allows a critical comparison between theory and experiment to be made.

Information obtained by the paramagnetic resonance method can be of interest to chemists in many ways. Direct measurement of the effective magnetic moment(μ_{eff}) can be made without the necessity of corrections for diamagnetism or diamagnetic impurities. Knowledge of μ_{eff} can indicate the oxidation state of an ion. From fine and hyperfine structure, information about the nature of the crystalline electric field can be obtained as well as about the nature of the chemical bond. A method is provided to determine the existence of free radicals, eliminating the usual indirect methods so common in chemistry.

As the name implies, paramagnetic resonance has to do with paramagnetic substances, i.e., atoms which have permanent magnetic dipole moments essentially independent of one another. Such a condition generally occurs whenever an atom or ion contains a partly filled electron shell,as in the iron transition group,where the 3d shell is incomplete, and in the rare earth (4f), palladium (4d), platinum (5d), and uranium (6f-6d) transition groups.

Discovered in 1945 by Zavoisky(1) in Russia and shortly after by Cummerow and Halliday(2) in America and Baggerley and Griffiths(3) in England, paramagnetic resonance (an example of something the Russians did, indeed, discover) represents a new method for obtaining information about paramagnetic substances. Since the initial experiments, many investigators have been active in the field; a bibliography of the work before 1953 can be found in Gordy, Smith and Trambarulo(4). Several good survey articles have been written; in particular, Darrow(5) has written an excellent review for the layman and Bleany and Stevens(6) for those active in the field. Since these surveys are available, great detail will not be included here.

Resonance Condition.

The total angular momentum of an atom is characterized by a vector $\vec{J}$. Very often Russell-Saunders coupling is a good approximation for the coupling of the component momenta, so that $\vec{J} = \vec{L} + \vec{S}$, where $\vec{L}$ characterizes the orbital angular momentum and $\vec{S}$ characterizes the spin angular momentum. A magnetic moment is associated with the spin and orbital angular momentum such that $\vec{\mu}_S = g_S \vec{S}$ and $\vec{\mu}_L = g_L \vec{L}$ where the magnetic moment is measured in Bohr magnetons, the angular momenta are measured units of $\hbar$ (Planck's constant over 2π) and g is a proportionality constant. The total magnetic moment is a vector

$$\vec{\mu} = \vec{\mu}_L + \vec{\mu}_S = g_L \vec{L} + g_S \vec{S} .$$

To account for the anomalous Zeeman effect it is necessary to say that $g_L = 1$ and $g_S = 2$; hence $\vec{\mu} = \vec{L} + 2\vec{S}$. It is clear that $\vec{\mu}$ is not parallel to $\vec{J}$. Actually, the quantity of interest is μ_{eff} which is a sort of projection of $\vec{\mu}$ along the direction of $\vec{J}$, so $\vec{\mu}_{eff} = g \vec{J}$.

If we suppose that a magnetic field is present which is too weak to disturb the Russell-Saunders coupling, then the projection of $\vec{J}$ along the axis of quantization (the direction of the field) is the magnetic quantum number M. M can have as values

$$M = -J, -J+1, \ldots , J-1, J$$

where J is the quantum number associated with $\vec{J}$. The energy of interaction between the effective magnetic moment and the magnetic field is

$$W = \vec{\mu}_{eff} \beta \cdot \vec{H} = \beta g \vec{J} \cdot \vec{H} = \beta g MH$$

where g, for a free ion, is the Lande splitting factor

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

and

$$\beta = \frac{eh}{4\pi mc} ,$$

the Bohr magneton. Since M can assume various values, there is a set of energy levels corresponding to different values of M. The selection rule for transitions between these levels is $\Delta M = \pm 1$ and the energy for such a transition is

$$W_M - W_{M-1} = g\beta H = h\nu \, .$$

The condition for paramagnetic resonance is then

$$\nu = g\frac{\beta H}{h} \, . \tag{2}$$

The value of g can be calculated from (1) and is in fairly good agreement with experiment when the atom or ion is a gas. In solids, g can vary considerably from the free ion value and generally it must be determined experimentally. If proton resonance is used to measure the magnetic field expression (2) becomes

$$g = 3.04194 \frac{\nu_e}{\nu_p} \times 10^{-3} \tag{3}$$

and is the expression used to indicate the position of the resonance lines, where ν_e is the frequency of the radiation and ν_p is the frequency of a proton resonance in the same field. The constant is corrected for the shielding effect of water since water is used here as a reference. The details are given in Appendix I.

Magnetic Interaction.

The resonance condition was calculated using a free ion for a model. Actually, most of the ions or atoms of interest are in a solid and intimately associated with their surroundings, so that interactions are expected. Indeed, it is these interactions which, in many cases, are of primary interest in the investigation because an insight into the nature of the crystalline field surrounding the paramagnetic ion can be obtained. These interactions are generally small and can be considered as perturbations of a free ion. The most important results of these perturbations are line broadening, fine structure, and hyperfine structure.

The two main causes of line broadening are spin-lattice and spin-spin interaction. Through the former interaction, the spin can make transitions by exchanging a quantum of energy with a lattice vibration of the appropriate frequency. Spin-spin interaction arises from the interaction between the magnetic dipoles, which can be regarded as being situated in a rigid lattice. Two types of spin-spin interactions have been recognized, a dipole-dipole process which gives a broadening like that arising from the use of an inhomogeneous magnetic field and an exchange interaction which gives a broadening because it tends to reduce the lifetime of an ion in a given state.

Fine structure is a general term used to describe those interactions attributed to the crystalline electric field which remove the spin degeneracy in zero magnetic field. When transitions are allowed between the separated levels, in principle, the splitting could be found by the method of paramagnetic resonance in zero field since the absorption of energy will only occur when the frequency of the applied radiation is equal to that of the splitting. Experimentally it is more convenient to apply a magnetic field to vary the splittings and then examine the spectrum as a function of field at a constant frequency. From this it is possible to pass from high field measurements to zero field splittings. Figure 2, page 16, is an example of how such zero field splitting affects the resonance line. Here it can be seen that a transition which would have occurred only at H_0 and hence give only one resonance line, is split into three lines by the action of the crystalline field. Two additional resonance lines would be observed equally spaced about H_0 at H_1 and H_2.

When the nucleus of the paramagnetic ion possesses a magnetic moment, hyperfine structure may be observed in the resonance spectrum. The interaction between the electrons and nucleus split each electron spin level into $2I + 1$ equally spaced levels where I is the nuclear spin quantum number. The radiation exerts a negligible effect on the nucleus since the frequency is quite far from that needed to excite transitions between ajoining nuclear levels* so that the allowed transitions are those in which m, the magnetic quantum number for the nucleus, does not change. The effect on the paramagnetic resonance spectrum is to split the resonance line into $2I + 1$ equally spaced lines.

Application to Chemistry.

Paramagnetic resonance absorption has been used to help understand a wide variety of problems associated with chemistry and still the full potentialities of the method have not been exploited. This method does not suffer from the difficulties encountered in the application of conventional magnetic techniques such as magnetic susceptibility measurements. These difficulties are three fold: (1) relatively

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* The type of spectroscopy that does excite transitions between these levels is called nuclear magnetic resonance. The magnetic field controller utilizes this effect and makes possible precise control and measurement of the magnetic field.

large amounts of diamagnetic material may obscure the paramagnetism from susceptibility measurements, (2) even when the paramagnetism is not obscured, the measured susceptibility must be corrected for diamagnetism and there is usually no reliable method of estimating or measuring the amount of this correction, and (3) susceptibility measurements lack the accuracy necessary to make a precise comparison between the experimental data and theory.

By far the greatest activity in the field of paramagnetic resonance has been in the investigation of the effect of the crystalline electric field on a paramagnetic ion. The iron transition group elements and copper have received the most attention in this regard. Many salts have been investigated in considerable detail, resulting in the formulation of precise expressions for the crystalline electric field and a detailed knowledge of the ground state of the paramagnetic ion.

In recent years the importance of free radicals has been recognized in many phases of chemistry. The paramagnetic resonance method represents a quick and positive method for the detection of free radicals and, in favorable cases, considerable information as to the nature of the free radical can be obtained. Hutchinson, Kowalsky, Pastor and Wheland(7) have discussed the application of this method to the detection of organic free radicals and Hutchison, Pastor and Kowalsky(8) have shown the nature of the odd electron in diphenylpicrylhydrazyl which is an example of added information which may be obtained. An application of free radical detection to the field of inorganic chemistry is illustrated in the work of Livingston, Zeldes, and Taylor(9) where they found free radicals after irradiating various frozen acids with gamma rays. They were also able to show that the free radicals were hydrogen atoms. The work of Commoner, Towsend, and Pake(10) indicates that paramagnetic resonance might be of considerable use in the field of biology. They have been able to measure the free radical content of living cells and have found a correspondence between the amount of free radical and the rate of metabolism.

By capitalizing on the magnetic interactions of the paramagnetic ion with its surroundings and with the nucleus, information can be obtained as to the nuclear spin and nuclear quadrupole moment. The magnetic ground state of an ion can also be determined(11) as can the type of bonding.(12) Although the discussion here has been limited to atoms or ions, the method is not limited in this way. Considerable work has been done on F and V centers,(13) on the conduction electrons in semi-conductors(14) and in conductors,(15,16) and on the alkali metals dissolved in liquid ammonia.(19)

Purpose.

It was the purpose of the first phase of this research to design and construct a paramagnetic resonance spectrometer that would be particularly adaptable to the problems of chemistry. Since the potentialities of this method are numerous, the spectrometer must be versatile. Since it is desirable to measure very small perturbations of the free ion by the surroundings, the spectrometer must be one of high resolution and considerable accuracy. In many cases, this method must compete with more established methods of investigation so that the spectrometer must be simple and fast in its operation as compared to indirect chemical methods. The spectrometer described herein has these features.

The purpose of the second phase of this research was to use this method where it should prove fruitful. This phase was guided mostly by interest. The reasons for this interest are contained at the first of each section of results.

II. GADOLINIUM IN CERIC OXIDE.

Introduction.

Considerable interest has been shown by Duwez(18) in the ability of the calcium fluoride like lattice of CeO_2 and TiO_2 to dissolve trivalent metal ions. McCullough and Britton(19) give a summary of the work done involving the use of x-ray powder photographs, density determinations, and measurement of electric conductivities. All of the systems studied show a homogeneous solid solution of the trivalent atom when in concentrations of less than 60 atom per cent. With so much work having been done on these systems, it seems appropriate to record the paramagnetic resonance spectrum of at least one system and examine the spectrum for any anomalies. Best results were obtained with gadolinium ion in ceric oxide (see also page 28).

Ceric oxide has the fluorite structure. Each ceric ion is in the center of a cube with eight oxygens around, one at each corner of the cube. The ceric ions form a larger face centered cubic structure. The lattice constant as determined by McCullough and Britton is 5.411 ± 0.001 Å.

Sample Preparation.

A stock solution of Ce(III) was prepared from ceric oxide, 99.8 per cent, obtained from Research Chemicals Inc. Lot No. 528. The ceric oxide was dissolved in a hot solution, 8F in nitric acid and 0.02F in HF.(20) After heating for about one hour the solution turned yellow. Slow addition of 30 per cent hydrogen peroxide then dissolved 25 grams of CeO_2 in about 15 minutes. The solution was diluted to a known volume.

Enough stock solution to form one gram of ceric oxide was added to 100 ml. at H_2O in a beaker. The acid concentration was adjusted to about 0.1N with nitric acid. A known amount of gadolinium nitrate was added by previously dissolving a weighed portion of gadolinium oxide, > 98 per cent, obtained from Research Chemical, Inc., in nitric acid and taking an aliquot portion. While the solution was vigorously boiling and was being stirred, a saturated solution of oxalic acid was added until precipitation was complete. After continued boiling and stirring for one minute, the solution was filtered with a suction filter. The resulting solid cerous and gadolinium oxalates were transferred to a platinum boat. The boat was heated in air to about 900°C for 30 minutes, forming ceric and gadolinium oxides. Portions of this resulting pale yellow powder were used in the spectrometer.

Experimental Results.

The ceric oxide powder was pressed into a lucite pillbox holding about 30 mg for the K band spectrometer or into a lucite trough holding about 100 mg for the X band spectrometer. This sample was then placed in the spectrometer.

Three times during the course of the experiment, a sample of ceric oxide was made in the way described above except that the addition of the gadolinium was omitted. These blanks were run in the spectrometer and no absorption was observed. This was done with the spectrometer dial settings the same as for a previous run where a spectrum was observed. The sample was again placed in the cavity after the blank was run and the spectrum was again observed.

Two typical absorption lines (derivatives) are shown in Figure 1. They are direct copies of typical absorption lines, one at X band and one at K band, as recorded on the Brown recorder. Accurate measurements were made on lines taken with considerably higher resolution than is shown here.

A summary of the data obtained is found in Tables I and II. At the top of each table is noted a typical frequency and magnetic field; the actual frequency changed slightly from one run to the next. Table I has one run at 0.29 atom per cent and one at 0.05 atom per cent. These are included to show how broadening sets in as the concentration of gadolinium is increased. It was impossible to resolve the upper line (2) at this high concentration. The value of g_1 for the low field and strongest line was calculated using the field value at point A Figure 1.

In many runs, diphenylpicrylhydrazyl* was used as a magnetic field marker. In these cases, the values of g were calculated using a simple proportion with $g = 2.0036 \pm 0.0002$ for diphenylpicrylhydrazyl. When it was not present the wavemeter was used as discussed under the operation section and the value of g was calculated by formula (3), page 4.

The line width given in Tables I and II is the separation measured in gauss between the two points of inflection (Figure 1, B and C)

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* Diphenylpicrylhydrazyl, $(C_6H_5)_2$ N-$NC_6H_2(NO_2)_3$, is a black solid free radical. It has a narrow (2 gauss wide) resonance line at $g = 2.0036 \pm 0.0002$ and is quite widely used as a spectrum calibration point. I would like to thank Prof. C.H. Townes of Columbia University, N.Y. for the gift of a few milligrams of this material originally prepared by Prof. J. Turkevich of Princeton University, N.J.

TABLE I

Results for Gadolinium in Ceric Oxide at X Band

ν_e = 9365 mc H = 3400 gauss

Series	Number of runs	Concentration atom per cent	g_1	width gauss	g_2	$\|\Delta\|$ mc
I	1	0.29	1.969	49		
II	1	0.05	1.967	16		
III	4	0.02	1.970	10 ± 3	1.946	56 ± 2
IV	18	0.005	1.9703 ± 0.0002	$2 \pm \frac{1}{2}$	1.9468 ± 0.0002	56 ± 1

TABLE II

Results for Gadolinium in Ceric Oxide at K Band

ν_e = 24,100 mc H = 8600 gauss

Series	Number of runs	Concentration atom per cent	Temperature °K	g_1	width gauss	g_2	$\|\Delta\|$ mc
I	3	0.02	4.5	1.988	10 ± 1	1.984	31 ± 1
II	6	0.005	300	1.9894 ± 0.0003	6 ± 1	1.9838 ± 0.0003	26 ± 2
III	1	0.005	77	1.989	8	1.984	30
IV	4	0.005	4.5	1.9890 ± 0.0004	6 ± 2	1.9838 ± 0.0012	32 ± 4
V	3	0.001	4.5	1.990 ± 0.002	15 ± 7	1.981 ± 0.001	40 ± 20

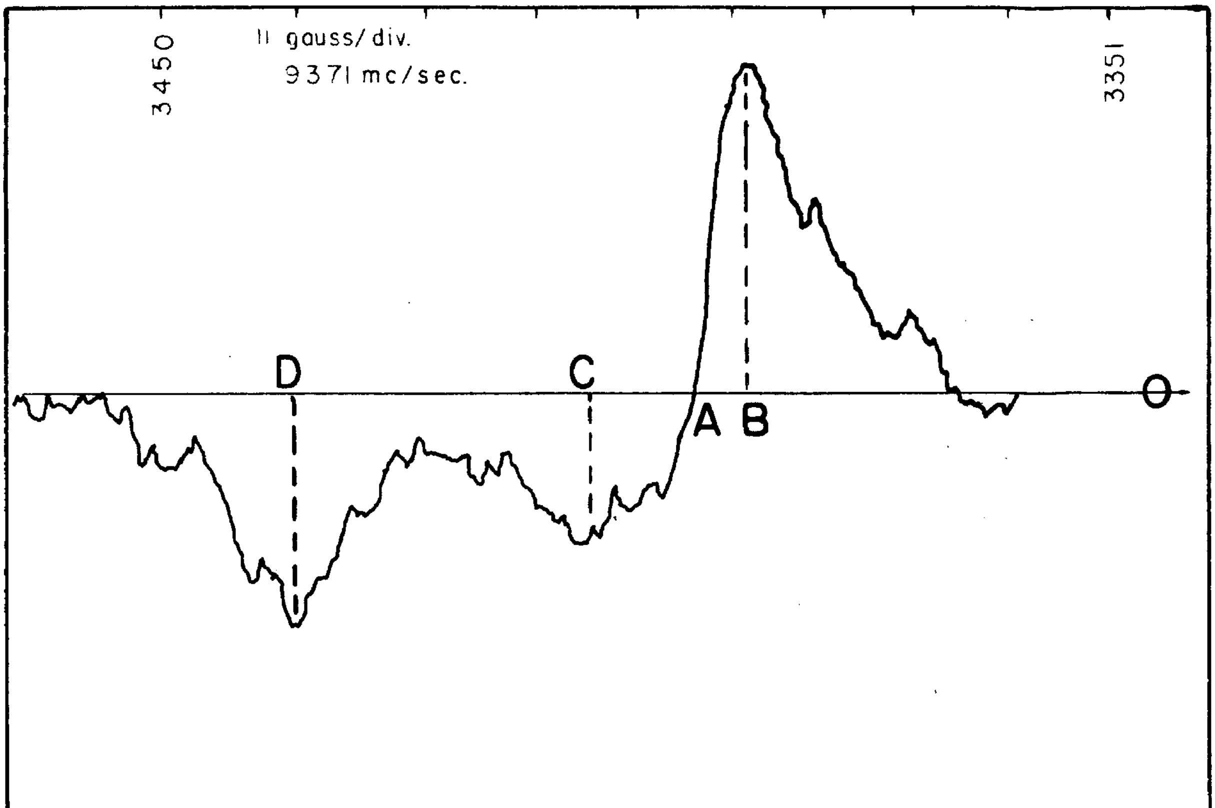
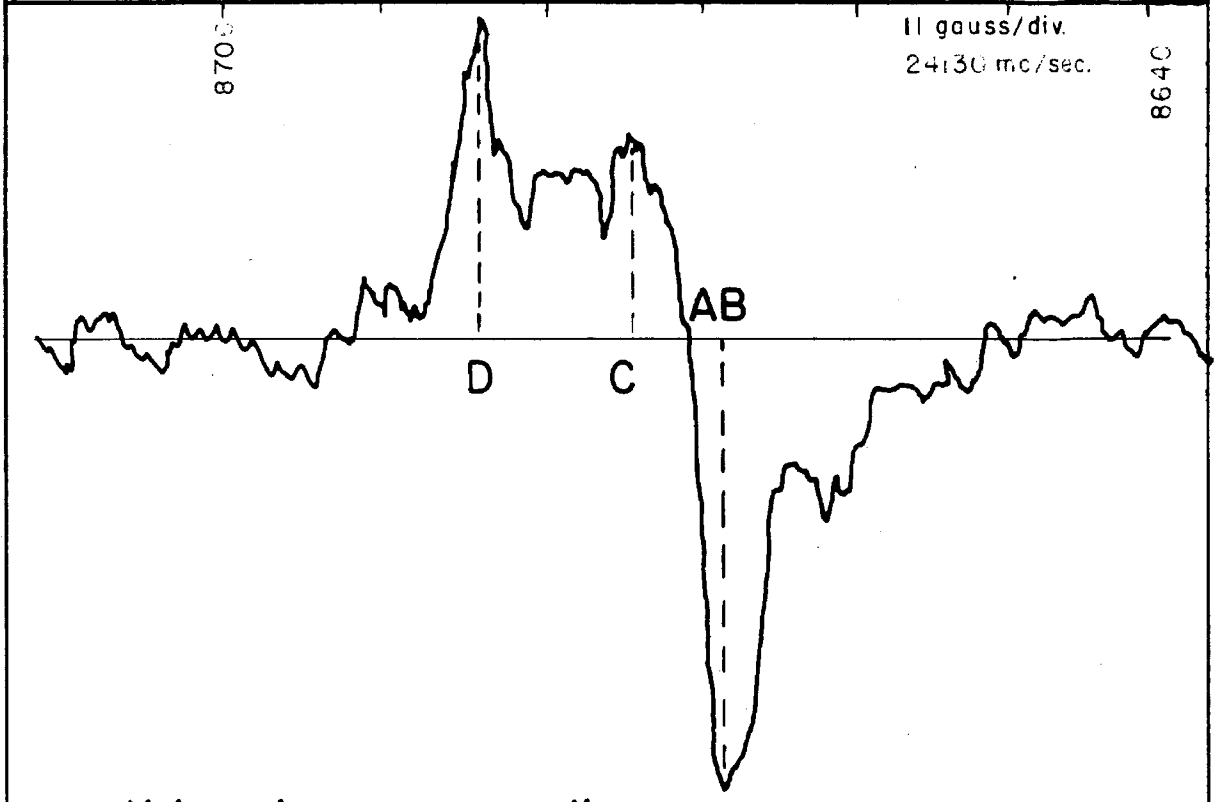


Figure 1 — X band resonance line.



— K band resonance line.

of the absorption line. The value of g_2 is calculated by formula (3) using the magnetic field at D. This is not the value of g for this resonance line if it were resolved since point D is the high-field point of inflection for such a line. This point is used as an indication of the line position to eliminate the errors in extrapolation or the necessity of estimating the width of the line. A systematic error of about one-half the line width is introduced in this manner. The zero-field splitting, Δ, was calculated using points B and D. Again, this is not quite correct since this takes the width of the splitting as the distance between the extreme points of inflection. It is felt that the gain in reproducibility warrants the introduction of the systematic error.

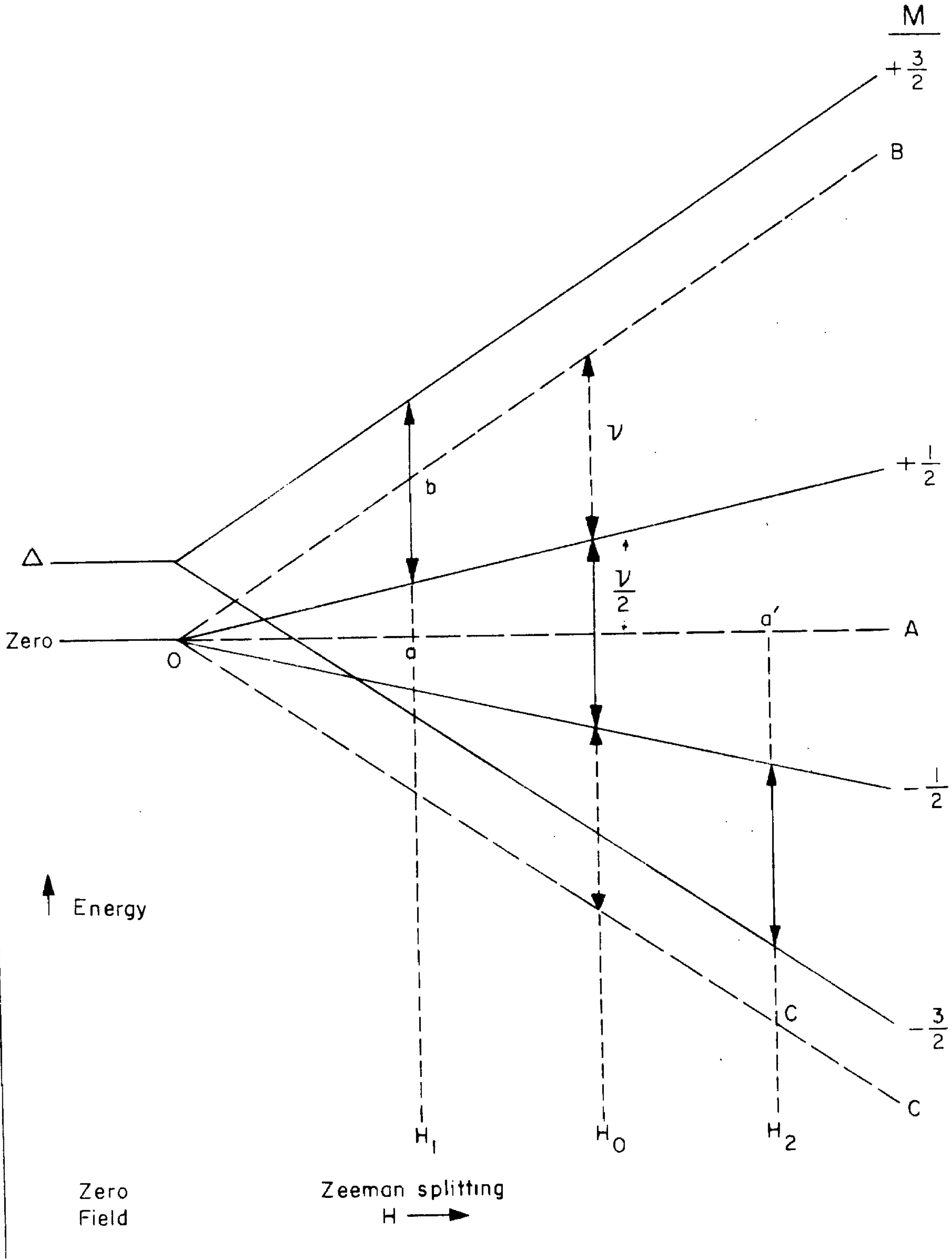
The zero-field splitting was calculated by a simple formula derived from similar triangles. Consider Figure 2, which illustrates the splitting of a fourfold degenerate ground state of, say, a ^4S state into two doublets by some mechanism other than a magnetic field. The magnetic field then splits each doublet.

There will be three possible values of magnetic field H_1, H_o and H_2 for a given energy interval ν (remembering the selection rule $\Delta M \pm 1$). It should be clear that for the case of $\Delta = 0$, $H_1 = H_o = H_2$. Dotted line OA is the bisector of the ± 1/2 level; OB and OC are the levels $\pm 3/2$ when $\Delta = 0$. In triangle Oab

$$ab = \frac{\nu}{2}\,\frac{H_1}{H_o} + \nu - \Delta = \left(\frac{\nu}{2} + \nu\right)\frac{H_1}{H_o},$$

similarly in triangle Oa'c

$$a'c = \frac{\nu}{2}\,\frac{H_2}{H_o} + \nu + \Delta = \left(\frac{\nu}{2} + \nu\right)\frac{H_2}{H_o}$$



Zero Field Splitting

Figure 2

eliminating H_o and solving for Δ

$$\Delta = \nu \frac{(H_2 - H_1)}{H_2 + H_1} = \nu \frac{(g_1 - g_2)}{(g_1 + g_2)} \quad .$$

The accuracy of these measurements is very difficult to evaluate. The two frequency measurements (ν_e and ν_p) are accurate to 5 significant figures. The accuracy of these readings does not constitute the accuracy in this experiment, however, since errors can arise from the identification of the various points on the line. The exact point of inflection and the exact point of zero slope must be estimated. Umfortunately this depends on such intangibles as the shape and strength of the line, the amount of noise and the zero drift and the health of the observer. A reasonable estimate of the accuracy is the average absolute deviation from the mean. If the number of runs included in this average is sufficiently large and under different conditions as in series IV Table I, then this is a good estimate. When, however, the number of runs included is small as in series III, Table I, the estimate is less satisfactory. The average absolute deviation from the mean is indicated in Tables I and II and also the number of runs included in the average.

The salient features of the resonance data can be summarized as follows:

(1) For a powder sample, there is some sort of structure which cannot be resolved with either extreme magnetic dilution (1:100,000) or low temperature (4.5°K) or with both.

(2) The zero field splitting, Δ, (if such does indeed exist) is quite small compared to that observed in other salts.

(3) No hyperfine structure could be resolved.

(4) The spectroscopic splitting factor, g, is some function of magnetic field. It is nearer 2.0023 (the free ion value for g) when calculated from measurements made at 8600 gauss then when calculated from measurements made at 3400 gauss. Also Δ is smaller at the higher field.

Discussion.

The theory of gadolinium in a crystalline field is quite different in character from that of the other rare earth ions. The gadolinium ion is in an S state ($4f^7\ {}^8S$) which, to first order, is not split by a crystal field. Straightforward application of the theory as mentioned in the introduction would predict a one-line resonance spectrum. The single line would have $g = 2$. It is clear, from the results presented in Tables I and II, and the summary, that such an idealized model is not adequate in this case. It is interesting to explore the situation further to see what changes from the simple model are suggested.

The fact that there might be some splitting is not surprising. Bleaney, Scovil and Trenam(21) observed seven lines for gadolinium in lanthanum ethyl sulfate, as have other investigators (a summary of the results on gadolinium is given in Table III). There is an important difference between the two cases; lanthanum ethyl sulfate crystallizes in hexagonal, C_{3h}, symmetry whereas ceric oxide has cubic, O_h, symmetry. With cubic symmetry the splitting should be much less since it is a higher order interaction.

TABLE III

Other Investigators Results For Gadolinium in

$Gd(C_2H_5SO_4)_3 \cdot 9H_2O$

Band	g	Fine Structure No. lines	Δ in mc/sec	Ref.
X		7		22
X		7	2,500	23
X	1.994 ± 0.001	7	1,900	24
K	1.992 ± 0.002	7		24
X	1.990 ± 0.002	7	3,400	21
22 cm	1.990 ± 0.002	7	3,400	21
*	1.99 ± 0.01	7	8,400	25

* This result is for $Gd_2(SO_4)_3 \cdot 8H_2O$

Splitting for an S state by a cubic crystalline field was first suggested by Bethe.(26) Using the methods of group theory he was able to show that the eight-fold degeneracy of an ^8S state could be partially removed by a cubic field,leaving two doublets and a quartet. Van Vleck and Penney(27) used Bethe's calculations to explain the magnetic anisotropy observed in manganous ammonium sulfate (here the manganous ion is a ^6S state so that the splitting is into three doublets). With the advent of paramagnetic resonance, more precise data could be obtained, and, in particular, a large isotropic hyperfine structure could be resolved.(28)

To account for this hyperfine structure, and also a smaller fine structure, Abragam(29) assumed that the electronic wave functions contained small admixtures of excited states with unpaired s-electrons.

For manganous ion ($3s^2\ 3p^6\ 3d^5\ {}^6S$) a 3s-electron would be promoted to the 4s orbital ($3s\ 3p^6\ 3d^5\ 4s\ {}^6S$) and Sachs(30) calculated that the fraction of excited state necessary to explain the observed hyperfine structure was 0.022.

For the case of gadolinium, the results reported here do not warrant the suggestion that a 5s-electron from the normal state ($4f^7\ 5s^2\ 5p^6\ {}^8S$) is promoted to a 6s orbital ($4f^7\ 5s\ 5p^6\ 6s\ {}^8S$) since no hyperfine structure was observed.* Since the hyperfine structure would be isotropic, it should be resolved even in a powder sample as in the case of Mn^{++} in ZnS powder.(31)

The fact that the structure was not resolvable strongly suggests that the splitting observed is anisotropic. Considering also that the splitting is very small, one is led to the conclusion that it is probably caused by the fifth-order process used unsuccessfully by Van Vleck and Penney to describe the anisotropy in manganese alum. Abragam and Pryce(34) estimate the splitting for manganese by this mechanism to be about 30 mc/sec, which certainly compares favorably with the observed splittings recorded in Tables I and II. Clearly, single crystal data are needed. With a single crystal it should be possible to resolve the lines and also to obtain the angular dependence. Only then could a conclusive argument be presented. All that can be

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[*] Natural gadolinium has five isotopes. Gd^{154}, Gd^{156} and Gd^{158} occur in, respectively, 2.15 per cent, 20.47 per cent, and 24.87 per cent(32) (total 67.49 per cent) natural abundance each with a nuclear spin of zero. They cannot produce hyperfine structure. Gd^{155} (14.73 per cent abundance) and Gd^{157} (15.68 per cent abundance) have a nuclear spin of either 3/2 or 7/2(33) and can produce hyperfine structure. If the case of the manganous ion, where the nuclear influence is very strong, is an indication of what can be expected with gadolinium, then hyperfine structure can be predicted with only one-third of the atoms contributing.

said now is that the evidence presented suggests that an illustration of fifth-order splitting via the cubic field has been observed.

As yet, the change in g and Δ with field has not been mentioned. The theories discussed above do not suggest such an effect. Although many investigators report their results for a particular compound at both K and X band; there is no case where the value of g changes outside the limits of experimental error.* Certainly further investigation of this effect is indicated. The value of g and Δ should be determined for a wide range of frequencies (fields) to determine an expression for g and Δ as a function of field. Experimentally, this is quite difficult. With the present data, all that can be said is that the changing value of g and Δ represent an interesting yet anomalous result.

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* It should be noted however, that few investigators are able to measure the value of g with sufficient accuracy to notice a shift of the same magnitude as reported here.

III. MANGANESE IN CALCIUM CARBONATE

Manganous ion in a single crystal of calcite has been investigated extensively by Hurd, Sachs and Hershberger(35) using the method of paramagnetic resonance. They were able to resolve thirty lines and, from this data, make a precise comparison between the predictions of theory and experimental observations. The agreement was good although small deviations greater than experimental error were found.

Since calcium carbonate crystallizes as both calcite, D_3 symmetry, and aragonite, D_{2h} symmetry, measurements on single crystals of aragonite containing Mn^{++} could be exceedingly interesting. Some effort was expended in obtaining such a sample.* Unfortunately, no such aragonite crystal could be found. It is possible, however, to prepare synthetic micro-crystals of aragonite. Less information can be obtained in this way but since the terms associated with the hyperfine structure in the hamiltonian of Hurd, Sachs and Hershberger are isotropic, it should be possible to compare that portion of the hamiltonian for the two cases.

Sample Preparation.

Keyser and Degueldre(36) have investigated the precipitation of calcium carbonate in considerable detail. Using x-ray methods, they have been able to construct condition diagrams showing how the temperature and method of mixing affects the micro-crystalline product.

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* Neither calcite or aragonite have been prepared synthetically in the form of large (5 mm on a side) single crystals. Crystals must be found in nature that contain about 0.01 per cent manganese.

Areas of 100 per cent calcite, aragonite and vaterite* are indicated. Samples of aragonite and vaterite were prepared using the conditions indicated by these areas except a small amount of manganese was added.

The stock solutions were: 1F $CaCl_2$, 1F Na_2CO_3 and 1F $MnCl_2$. All were made with reagent grade chemicals.

Aragonite. 250 ml. of 1F Na_2CO_3 were placed in a beaker. For 0.1 per cent Mn, 0.25 ml. 1F $MnCl_2$ solution was added to 250 ml. 1F $CaCl_2$ solution. This mixture was then added to the vigorously boiling Na_2CO_3 solution at a rate of 13 ml./minute with constant stirring. The resulting solution was filtered and the precipitate was washed with boiling water, then dried at 140°C for 2 hours.

Vaterite. 250 ml. 1F Na_2CO_3 were placed in a beaker in an ice bath. A solution was added the same as for aragonite, after precooling it in an ice bath. The mixture was filtered and the precipitate washed with ice water, then dried in a vacuum desiccator** for 6 hours.

X-ray powder pictures were taken of the samples using a Philips powder camera. For aragonite, the lines matched within experimental error with the values reported by Keyser and Degueldre. Several tries were made with vaterite. The best that could be obtained was a vaterite series with a weak calcite series also present.

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* Vaterite is an unstable form of calcium carbonate with hexagonal, C_6 symmetry. Its existence is in some doubt. Results on vaterite will be contained in a later section.

** The procedure of Keyser and Degueldre called for drying at 140°C. When this was tried, the solid "melted" and after drying, only calcite was found.

<u>Experimental Results</u>.

The results on aragonite micro-crystalline powder containing 0.1 per cent Mn^{++} can be found in Table IV. An effective value of g, g_{eff}, has been calculated for each line using the formula

$$g_{eff} = 3.0419 \times 10^{-3} \frac{\nu_o}{\nu_p}$$

The actual value of g for this group of lines lies between lines 3 and 4. The observed splitting, ΔH, is also included. To facilitate comparison of the experimental data and the theory, values of effective g and ΔH calculated using the energy level schemes indicated below are listed next to the observed values. The eigenvalues calculated by Hurd, Sachs and Hershberger using first-, second- and fourth-order perturbation theory are

$$E^{hfs}_{M_m} = K'Mm + \frac{A'^2}{2g\beta H_o} \quad M[I(I+1) - m^2] - m[(S(S+1) - M^2)]$$

$$+ \frac{A'^4}{(2g\beta H_o)^3} \quad [m^3\,\alpha(S) - M^3\,\alpha(I) + M^2m^3\,\Gamma(S) - M^3m^2\,\Gamma(I)$$

$$+ M^4m\,\varepsilon(I) - Mm^4\,\varepsilon(S) + m\,\Psi_S(I) - M\,\Psi_I(S) + Mm^2\,\phi_S(I)$$

$$- M^2m\,\phi_I(S) + M^3m^4 - M^4m^3]$$

where

$$\alpha(x) = x(x+1)\,[4 - 3x(x+1)]$$

$$\Gamma(x) = [6x(x+1) - 9]$$

$$\varepsilon(x) = [3x(x+1) - 1]$$

$$\Psi_x(y) = [3x^2(x+1)^2\,y(y+1) - x^2(x+1)^2\,)\;4x(x+1)\,y(y+1) + 2x(x+1)]$$

$$\phi_x(y) = [6x(x+1)\,y(y+1) - 11x(x+1) - 2y(y+1) + 5]$$

$$K' = (1/g)\,[A'^2\,g_{\parallel}^2\,\cos^2\theta + B'^2\,g_{\perp}^2\,\sin^2\theta]^{1/2}\;.$$

TABLE IV

Results for Manganous Ion in Calcium Carbonate

Aragonite
$\nu_o = 9365.8$ mc

Hurd, et. al.
$\nu_o = 9300$ mc $M = 1/2$

	Observed		Calculated		Observed		Calculated	
	Effective g $\pm .0005$	ΔH gauss ± 1	Effective g	ΔH gauss	Effective g $\pm .001$	ΔH gauss ± 2	Effective g	ΔH gauss
1	2.1545		2.1475		2.1567		2.1488	
		86.7		88.7		89.1		88.7
2	2.0959		2.0881		2.0959		2.0890	
		92.0		91.2		91.6		91.2
3	2.0373		2.0303		2.0374		2.0307	
		95.4		93.9		94.1		93.9
4	1.9797		1.9741		1.9803		1.9741	
		96.0		96.6		95.7		96.6
5	1.9250		1.9194		1.9250		1.9190	
		100		99.2		98.8		99.2
6	1.8711		1.8663		1.8711		1.8655	

Aragonite

$\nu_o = 25,039$ mc

$H_o = 8935.6$

	Observed		Calculated	
	Effective g $\pm .0005$	ΔH gauss ± 2	Effective g	ΔH gauss
1	2.0549		2.0550	
		90.9		91.9
2	2.0336		2.0336	
		93.2		92.9
3	2.0123		2.0123	
		93.5		93.9
4	1.9914		1.9913	
		96.1		94.9
5	1.9703		1.9705	
		95.1		95.9
6	1.9499		1.9499	

Assuming $g_{\parallel}$ and $g_{\perp}$ are nearly equal and that $A' = B'$, the values as given in the table can be calculated; details of this calculation are given in the appendix. It should be noted that Table IV includes results at both X band and K band. The experimental results of Hurd, Sachs and Hershberger have been converted to effective g values and included along with the corresponding theoretical values to compare them with the single crystal data.

Discussion.

The assumption that $g_{\parallel} = g_{\perp}$ seems justified since $g_{\parallel} = 2.0022 \pm 0.0006$ and $g_{\perp} = 2.0014 \pm 0.0006$ for calcite. Also $A' = B'$ in the case of calcite so that this too is a reasonable assumption for the aragonite case. Further evidence for the validity of these assumptions comes from the striking agreement between the theoretical values and the experimental ones. The comparison was made to the data for $M = 1/2$ since itare the most nearly isotropic (3 gauss shift from 0 to 90°).

Clearly the hyperfine energy level scheme for manganese stands the test of another crystalline lattice. The value of $A = 93.90 \pm 0.05$ gauss fits the experimental data for aragonite, at both K and X band, very well.

IV. OTHER COMPOUNDS WHICH HAVE BEEN INVESTIGATED.

In cases where a resonance is expected yet where none is observed, it is generally futile to postulate the reasons. Relaxation times and spin interactions can seldom be estimated; they can broaden the line to such an extent that the derivative is essentially zero. The spectroscopic state may be considerably different from that of a free ion and hence outside the range of investigation.

Several investigations are included here in which a reasonable search for a resonance was made with no observable results. They are included to record the fact that they were made and to illustrate the general use of paramagnetic resonance in chemistry; little effort will be made to guess the reasons for failure. It should be mentioned that continual checks were made on the operation of the equipment. Generally diphenylpicrylhydrazyl was included with sample so that in each case it was clear that the equipment was working properly.

<u>Manganese</u> <u>in</u> <u>Vaterite</u>.

A micro-crystalline powder of manganous ion in calcite gives an 18-line spectrum. The spectrum of manganous ion in aragonite gives a 6-line spectrum. A spectrum of at least 6 lines would be expected for vaterite with possibly the widths being different than that of aragonite. Since the existence of this unstable form of calcium carbonate is open to question, the possibility of confirmatory evidence by the use of paramagnetic resonance exists. A vaterite sample was prepared as discussed previously. A spectrum which seemed to be a superposition of calcite and aragonite was obtained.

Rare Earths in Ceric Oxide.

Since ceric oxide proved to be such a good matrix for gadolinium, it was of interest to see if the spectra of other rare earths could be observed. Samples of 0.01 atom per cent rare earth were prepared from the following oxides in the same manner as gadolinium was prepared; 99.9 per cent Sm_2O_3, pure Eu_2O_3, 99.8 per cent Yb_2O_3, 99.92 per cent Dy_2O_3,* 99.95 per cent Ho_2O_3.* Each sample was observed in the neighborhood of its free ion value of g; no resonance spectrum was recorded.

Free Radicals in Organic Glass.

Dr. Ronald Sowden(37) has found that the irradiation with ultraviolet light of a frozen (77°K) dilute solution of Bromal (CBr_3CHO) in a 3-methylpentane, isopentane mixture produces an absorption band in the ultraviolet which is not present in the glass before irradiation. A possible explanation for this behavior is the formation of CBr_3 and CHO radicals in much the same manner as acetaldehyde gas, which forms CH_3 and CHO radicals when irradiated. If such free radicals exist, there should be a paramagnetic resonance line in the neighborhood of $g = 2$.

With the help of Dr. Sowden, a sample was prepared and irradiated. The resonance spectrum was run from $g = 1.8$ to $g = 2.2$ while the temperature was maintained at 77°K. No absorption line was observed.

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* These samples were loaned by the Atomic Energy Commission through the kindness of Dr. Spedding of Iowa State University.

Further investigation by Dr. Sowden has indicated that the absorption band is caused by a more complicated process which may not involve the formation of free radicals.

Free Radical: Phenylcyclobutenedione.

Dr. Smutny[**] prepared a sample of phenylcyclobutenedione, $C_6H_5\underline{CCHCOCO}$. This compound is a yellow solid which could be free radical in nature. The paramagnetic resonance spectrum was run in the neighborhood of $g = 2$. No absorption line was observed.

Bis-cyclopentadienylnickel (II).

The cyclopentadienyl ring is unusual in the number of metals with which it forms organometallic compounds. One such compound is bis-cyclopentadienyl nickel (II), $(C_5H_5)_2Ni$, or nickelocene. Wilkinson, Pauson, Birmingham and Cotton(38) have reported that magnetic susceptibility measurements indicate two unpaired electrons but it is not clear as to the exact nature of the bonding. Paramagnetic resonance could shed some light on this problem.

The resonance spectrum of nickelocene was observed from $g = 2.8$ to $g = 1.8$ on a sample obtained from Dr. Hedberg.[**] The solid was run in an inert atmosphere. Two saturated solutions of nickelocene were run, one with tetrahydrofuran as a solvent and the other with ligroin as a solvent.[*] No resonance could be observed.

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[*] It should be noted that Wilkinson et. al report that nickelocene will decompose slowly even in the absence of air and light.

[**] Personal contact at the California Institute of Technology.

Hemocyanin.

In hemocyanin, copper is centered in a prophyrin ring. This compound is of considerable biological interest because in many ways it is like hemoglobin. Klotz and Klotz(39) use circuitous chemical means to establish the oxidation state of the copper as both cupric and cuprous. Since the compound is magnetically very dilute, susceptibility measurements lack the required sensitivity. For paramagnetic resonance, the magnetic dilution is an asset; hence the spectrum might shed some light on the oxidation state.

The paramagnetic resonance spectrum of both oxygenated and non-oxygenated hemocyanin was taken. No resonance line was observed for either case. Klotz and Klotz(40) report that similar results were obtained by the paramagnetic resonance group at the University of Chicago.

V. SPECTROMETER

The paramagnetic resonance spectrometer to be described is an extremely versatile, wide range, high resolution instrument. The principle of operation is analogous to that of more familiar types of absorption spectrometers. There is a radiation source which irradiates a sample and a detector that indicates the amount of transmitted power. It is different from the general spectrometer in that the sample must be in a magnetic field. Just as other spectrometers can be characterized as working in the ulta-violet or infrared, this spectrometer works in the very far infrared or high frequency radio wave region (microwave region). Figures 3 and 4 show the general appearance of the instrument. The block diagram, Figure 13, and following schematic diagrams represent the electronic details of the apparatus. The division into three units as mentioned above is indicated on the block diagram by dashed lines.

Either 9360 mc/sec (X band) or 24,000 mc/sec (K band) microwave sources are available for use in the spectrometer. Controlled magnetic fields from 2,500 gauss to 10,000 gauss permit the observation of resonance lines with a value of g ranging from $g = 0.7$ to $g = 7.5$. The field can be varied at rates of 1/2 to 50 gauss per minute allowing the observation of lines varying in width from a fraction of a gauss to about 1000 gauss. Spectra can be observed at temperatures from room temperature to liquid helium temperature using single crystals, powders, or solutions as samples. The sensitivity is difficult to estimate because of its dependence on line shape,

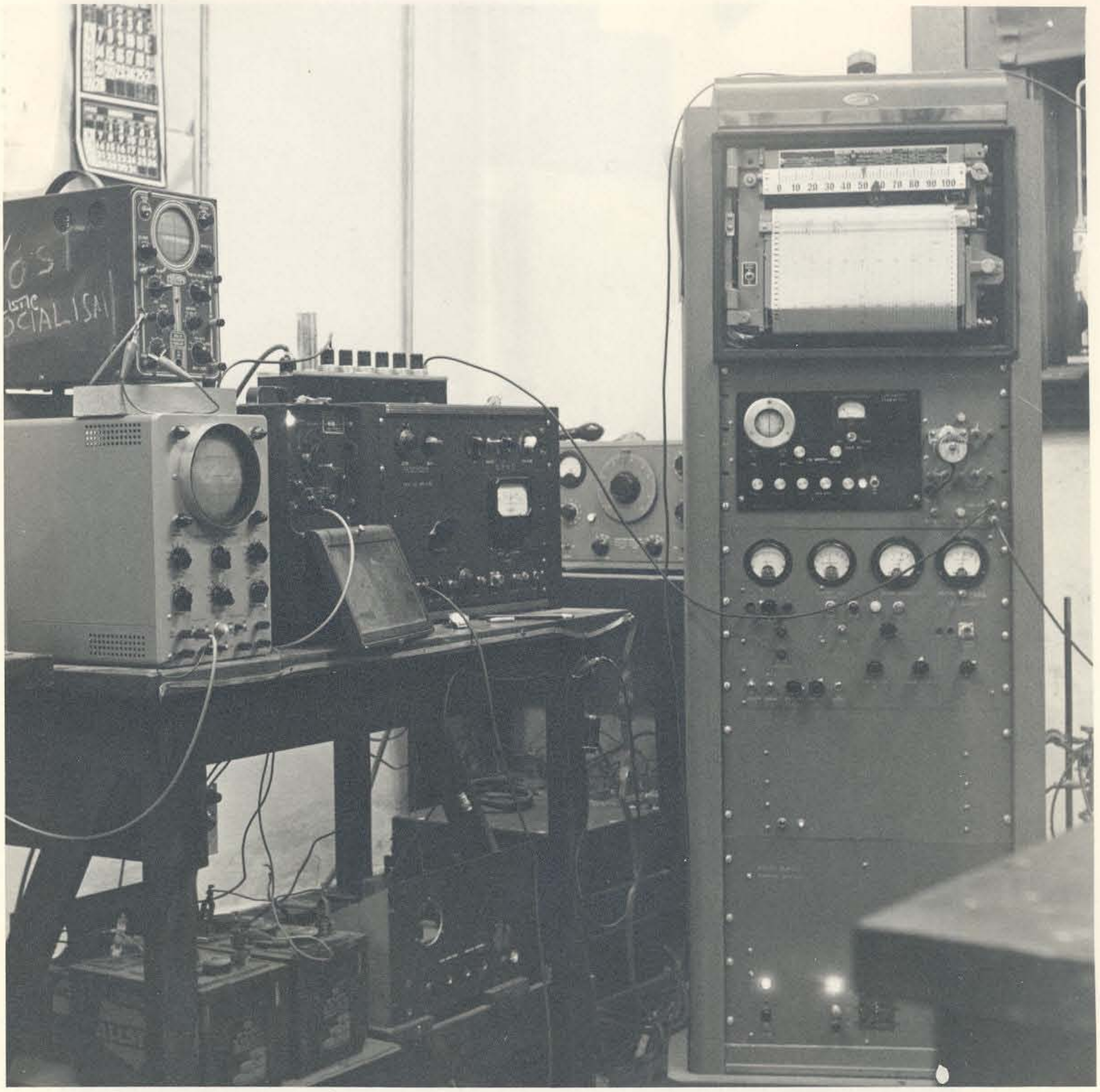


Figure 3. -- The detection system and magnet control system for the paramagnetic resonance spectrometer.

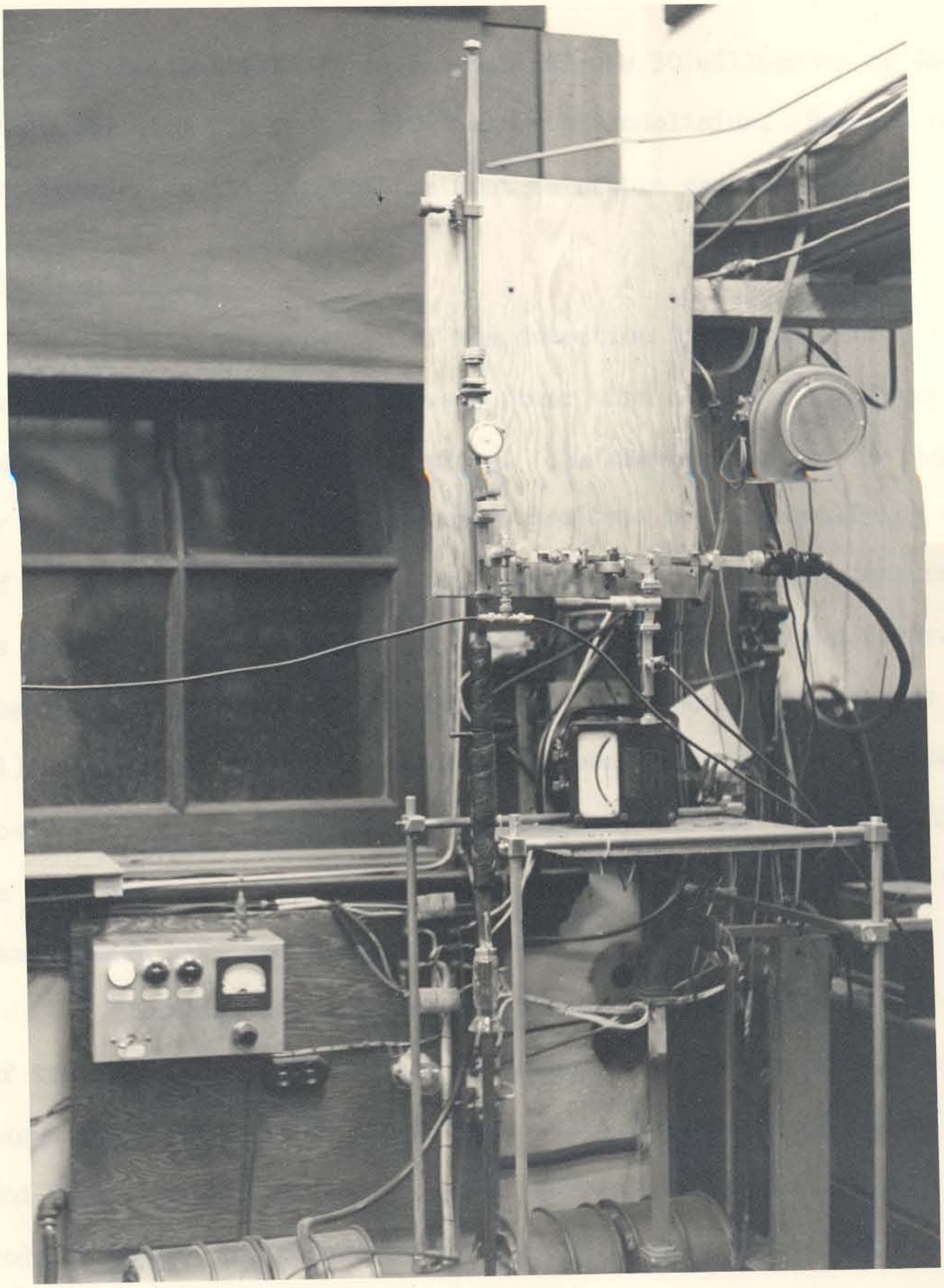


Figure 4. -- The waveguide system, K band, for the paramagnetic resonance spectrometer.

however, the smallest sample encountered was 30 milligrams of CeO_2 with 0.001 atom per cent or 10^{15} atoms of gadolinium. Because of some broadening this is not the most favorable case.

Detection System.

It is the function of the detection system to record the very slight reduction in microwave power when absorption of energy by the paramagnetic sample takes place. The microwave power is indicated by measuring the small D.C. current produced by the rectifying action of a crystal detector. The most direct way to make this measurement is with a galvanometer, as has been done by Lancaster and Gordy.(41) The use of a galvanometer suffers from two major disadvantages: (1) changes in microwave power for reasons other than resonance absorption are detected as resonance lines; and (2) high sensitivity is not possible. To overcome these difficulties the nature of the measurement has been changed.

Instead of measuring the direct absorption line, the derivative of the line is recorded. This is accomplished by modulating the main magnetic field by a few gauss at an audio frequency (509 c.p.s.), and detecting the change in crystal current at this frequency. As the modulation amplitude becomes small compared to the line width, the variation in crystal current becomes proportional to the derivative of the absorption line. The advantages of measuring the derivative are fourfold: (1) high gain audio amplification can be used with the resulting increase in sensitivity, (2) the power stability of the microwave source becomes unimportant because only changes occurring at 509 c.p.s. are detected, (3) the center of the absorption line can be estimated accurately since the derivative is changing rapidly at the center of the line, and, (4) the line width is more conveniently measured because the points of inflection are evident on the derivative curve.

With this in mind, it is possible to state the function of the detector more explicitly. The detector must amplify the 509 c.p.s. component of the crystal current and correlate it in frequency and phase to the field modulation. The result of this correlation must produce a derivative curve.

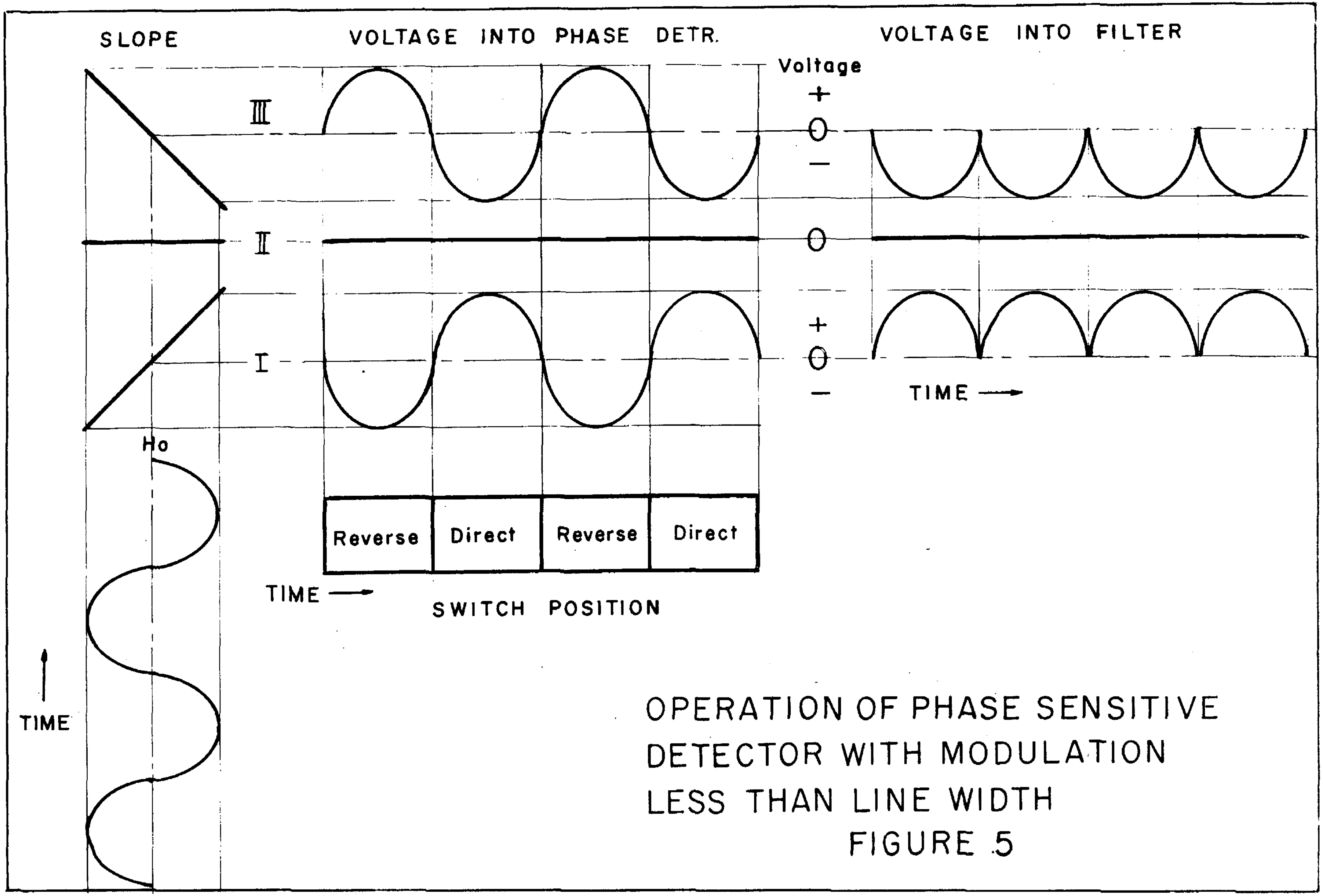
High Gain Amplifier (A). This unit was designed to have an overall voltage gain of about 2×10^6 at 509 c.p.s. The first stage uses a 12AY7, which is a tube designed particularly for audio amplification with low noise introduction. The circuit is the one recommended by the manufacturer(42) for this application. The input impedence is 470 ohms,which is the proper impedence match(43) for a type 1N26 crystal diode. The next three stages were designed for high amplification. They are resistance-capacitance coupled with frequency selective characteristics.(44) The high-pass portion was designed to eliminate 60 c.p.s.; the response is down 4.5 db from 509 c.p.s. to 60 c.p.s. The low-pass portion was designed to eliminate high frequency noise; the response is down 2 db at 1,300 c.p.s.(45) The stages are series-decoupled in pairs to eliminate low frequency oscillation via the power supply.

Narrow Band-Phase Sensitive Detector (B). The narrow-band stage is a cascode amplifier with a twin tee filter in a feedback circuit. Low-frequency feedback amplifiers of this type are discussed in considerable detail by Valley and Wallman.(46) Since the twin tee filter network is a rejection filter, all frequencies, except the frequency of interest, are fed back 180° out of phase with the input signal, hence the feedback tends to cancel out the signal. A cascode circuit has the following advantages: the input is of high impedence and isolated from the feedback; and even with triodes of moderate mu, amplifications comparable to those of pentodes can be obtained. Since the effective Q (a figure of merit for a filter circuit) of a twin tee circuit is $Q_{TT} = \frac{A + 1}{4}$, where A is the overall gain without feedback, correspondingly high Q results from this increase in gain. Tube type 6BK7A is especially designed for cascode circuits. Three types of filters are made available by the selectivity switch. Position one is a wide band position. Position two uses a fixed twin tee filter tuned to 509.3 c.p.s. ± 0.1 per cent. An effective Q of about 40 can be obtained with this filter. Position three is a variable frequency twin tee filter. The frequency can be set at any value from 400 c.p.s. to 10,000 c.p.s. An effective Q of about 20 can be obtained. Both twin tee filters have $n = 1$.(47)

The addition of the cathode follower to the feedback loop isolated the high-impedence plate load from the input of the twin tee filter and provides a source of low impedence for the filter. It also acts as a buffer to isolate successive stages. The cathode follower uses one-half of a 12AU7 tube, the second half is used as a low impedence source for the phase sensitive detector.

Phase sensitive detectors are sometimes called demodulation detectors, homodynes, or lock-in detectors. The function of this circuit is to correlate the 509 c.p.s. signal plus noise with a 509 c.p.s. synchronizing signal in such a way as to eliminate the noise and respond only to the 509 c.p.s. signal. In this application, the output is a voltage which is proportional to the derivative of the absorption line.

The phase sensitive detector may be considered as a synchronized switch, which reverses the polarity of the signal. The output is fed into a filter. This is indicated diagramatically in Figure 5. Two cycles of field modulation about some steady field magnetic H_o are indicated in the lower left hand corner. Let H_o correspond to some idealized point at the beginning of an absorption line when the slope is 45° and constant for the width of the modulation as indicated at I. This condition could be realized only with a vanishingly small modulation amplitude. The amplified voltage going into the reversing switch will vary with time as indicated. Below this is indicated the position of the switch on the same time scale. The rectified output or voltage into the filter will have an average positive value. If the slope of the absorption curve is zero, as in II (either away from or at the center of a resonance line), no output is noticed. If the slope is in the opposite direction as in III, then the voltage into the filter will have an average negative value. It is clear that the average voltage at the filter will be proportional to the slope of



OPERATION OF PHASE SENSITIVE DETECTOR WITH MODULATION LESS THAN LINE WIDTH

FIGURE 5

the resonance line. Noise, being random pulses, will occur with equal probability for either position of the synchranous switch so that the average output caused by the noise will be zero.

The synchronized switching operation can be done in a number of ways. Various methods are described in considerable detail by Chance.(48) A vacuum tube switch is the most sensitive. The tube is driven to cutoff at the proper time by a signal applied to the suppressor grid. Such a system was used here for some time. It was found that long time (20 minutes) stability, even with no input signal, was very poor. The system was finally discarded in favor of a mechanical chopper. This is truly a synchronized switch. Its main disadvantage is that it only maintains contact for 145° of each half cycle requiring 35° to perform the switching operation. The added stability of the mechanical chopper more than compensated for the loss in signal strength.

The chopper used is a Stevens-Arnold type 314 high frequency chopper with an 18 volt r.m.s., 600 ohms driver coil.

<u>D.C. Amplifier (C)</u>. The function of the D.C. amplifier section is to perform the time averaging of the correlation and amplify the derivative signal enough to drive the Brown recorder. A switch provides four different time constants for the filter (averaging network). The response is such that the output is down 13 db at 0.1 c.p.s. for position (4), 0.2 c.p.s. for position (3), 0.4 c.p.s. for position (2), and 0.8 c.p.s. for position (1). Tantalum electrolytic capacitors were selected for use in the filter because of the high capacity that could be obtained with a **low** leakage rate.* Two mercury

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* The leakage of a 320 mf tantalum electrolytic is about the same as an ordinary paper capacitor.

batteries are connected in such a way as always to keep the capacitors polarized properly.

The grounded grid differential amplifier is discussed by Valley and Wallman.(49) The differential output voltage from such a circuit is independent of both plate supply voltage and heater voltage fluxuations. The voltage gain of this stage is 20.

A cathode follower is used to provide a low output impedence to drive the Brown recorder.

<u>(D)</u>. A Brown Electronik Stripchart recorder is used to make a permanent record of the resonance line. The sensitivity and range have been adjusted so that it records from 0 to 10 millivolts. Since the derivative signal varies about zero, a constant potential is added by a battery and helipot to make the Brown recorder a zero-center device. A gain control is also provided for the recorder; each step of the control doubles the gain.

<u>Phase Control and Audio Amplifier</u> (E). The 509 c.p.s. synchronizing voltage from the house generator passes through a conventional 0 to 180^{o} phase control network. The phase relationship between the field modulation and chopper operation can be adjusted to the condition illustrated in Figure 5.

A conventional audio power amplifier was used to drive the chopper.

Magnet Control System.

The magnet control system was designed to give precise control of the magnetic field over a wide range of fields. Proton magnetic resonance is used as a reference both for controlling and for measuring the field. At any instant, the field can be measured to five significant figures by simply measuring the frequency of the proton resonance oscillator. For those unfamiliar with the old flip coil field measurements, it can be said that this method is a considerable advance in the art of magnetic field measurement.

Magnet (F). The magnetic field is produced by a large electromagnet of the low-voltage, high-current variety. It was originally designed and built by Safonov(50) and used for cosmic ray measurements. Waugh(51) replaced the pole pieces and used it for nuclear resonance studies. The pole faces are six by fourteen inches with a gap of one and one-half inches. Waugh investigated the field homogeneity, which is good enough for paramagnetic resonance where the lines are usually at least 2 gauss wide.

There are eight independent water-cooled windingsand two high resistance auxiliary windings. Four of the main windings were connected in series and supplied with 150 volts, 30 amperes by a 25 kilowatt generator (G-1). For short periods of time (15 minutes), 40 amperes can be used and a field of 10,000 gauss obtained, but such high current for a longer time will overheat the windings. The other four main windings were connected in series and supplied with 3 to 25 amperes by a 5-kilowatt generator. The field of this generator is excited by a bank of storage batteries (120v) in series with a motor-driven rheostat for control. The two auxiliary coils were constructed by Waugh.(51) One coil is driven by a 25 kilowatt 509 c.p.s. house generator;* the field can be modulated to ± 2 gauss in this manner. The other coil is driven by the control coil driver and can correct the field to ± 5 gauss.

R.F. Oscillator (G). The function of the radio-frequency oscillator section is to detect the proton resonance absorption signal when the frequency of the oscillator and the magnetic field satisfy the proton resonance conditions. A transitron oscillator circuit as described by Knoebel and Hahn(52) was chosen for this purpose because with this type of circuit the oscillation amplitude changes only slightly as the frequency is changed. Since Knoebel and Hahn have discussed this circuit in great detail, it seems appropriate to mention only the relatively minor differences between theirs and the one used here.

In the Knoebel and Hahn circuit, the radio-frequency tank circuit consists of a condenser, a length of coaxial line (the probe), and the coil for the proton sample at the end of the probe. The coaxial line, with its associated inductance and capacitance, makes frequencies much higher than about 40 mc difficult to obtain. Even at lower frequences this arrangement requires that the tuning condenser and oscillator tube be close (one foot) to the proton sample. This is

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* The frequency, 509.3 c.p.s., was chosen because of the availability of a generator. Actually any frequency reasonably low but well away from 60 c.p.s. would be satisfactory. The problem of eliminating pickup becomes acute near 60 c.p.s. At high frequencies (> 1000 c.p.s.)it takes too much power to modulate the magnetic field. 500 c.p.s. is a reasonable and convenient compromise.

quite inconvenient from an operational standpoint. As is indicated in the schematic, a link coupling(53) arrangement was used to overcome this difficulty.

With such an arrangement, the coil for the radio frequency oscillator tank was mounted directly on the tuning condenser and is actually a tightly coupled transformer with the secondary winding connected to a coaxial cable about six feet long. A coil containing the proton sample (0.1F $MnSO_4$ solution) was attached to the end of the cable. The proton sample is, of course, in the gap of the magnet. The absorption of energy by the protons is reflected back to the main oscillator via the link. Proton resonance frequencies up to 42 mc were used for control. Presumably higher frequencies are possible but were not used because of the maximum field limitation of the magnet.

The frequency modulation system of Knoebel and Hahn was found to introduce considerable amplitude modulation. A more satisfactory system was found to be that of modulation of the magnetic field.

To facilitate sweeping the magnetic field, the oscillator tuning condenser is equipped with a clock motor drive. By using different combinations of condensers and motors, various sweep speeds can be obtained. To sweep the entire range, it is necessary to change coils and probes. Table V gives the proper combinations.

The R.F. oscillator unit contains also an audio amplifier stage and a broad band radio-frequency amplifier. The output of the latter goes to the frequency meter to determine the frequency, hence the magnetic field.

TABLE V

Coil and Probe Combinations.

Frequency				Added capacity	Field	
lower mc.	upper mc.	Coil	Probe		upper K gauss	lower K gauss
11	13.4	1	Low	150	2.5	3.1
13.4	16	1	Low	20	3.1	3.8
16	17.6	1	High	0	3.8	4.2
17.6	22	2	High	0	4.2	5.4
22	28	2	Med.	0	5.2	6.6
28	35	3	Low	0	6.6	8.2
35	42	4	High	0	8.2	10

Coil	Primary No. 14 wire	Secondary No. 18 wire
1	7 turns, 10 turns/inch	7 turns, closed spaced
2	6 turns, 10 turns/inch	7 turns, closed spaced
3	7 turns, 8 turns/inch	7 turns, closed spaced
4	5 turns, 5 turns/inch	6 turns, closed spaced

Monitor Control and Power Supply (H). This unit is conventional in design. It contains a small oscilloscope to monitor the proton signal and the power supply and oscillation level control for the R.F. oscillator.

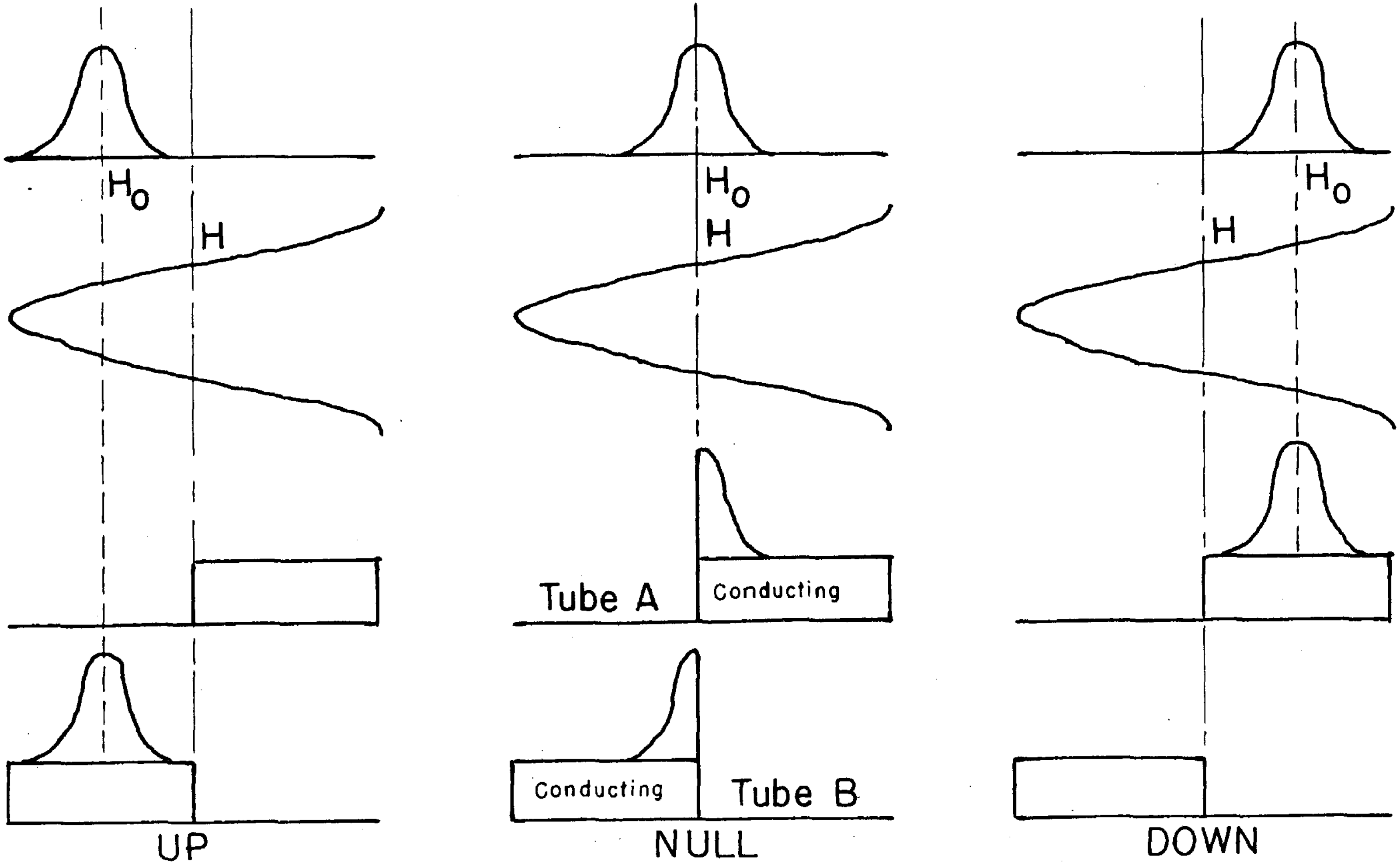
This unit is arranged so that it can be removed from the rack; the section fronted by the black panel is easily removed. The section can be put into a separate case and combined with a frequency-modulated R.F. oscillator to form a portable fluxmeter as described by Knoebel and Hahn.(52) Their circuit has been modified by the addition of a self-contained oscilloscope and by using a crystal modulator since the modulators as described would not operate in a strong fringing magnetic field. A crystal modulation unit that would operate in fields of about 1000 gauss was constructed by evaporating a thin coating of aluminum onto the diaphram of a crystal earphone. This diaphram was then arranged to be the ground plate of a condenser attached to the tank circuit.

Phase Sensitive Detector (I). The function and design considerations of a phase sensitive detector have been discussed in the detector section. Since the controller is essentially a null device, any drift or erratic operation will be compensated for automatically. Nearly any type of phase sensitive detector is suitable. The unit used by Thiene(54) happened to be available and was used with slight modification.

In the detector section, operation of the phase sensitive detector was discussed in the detector section for the case when the modulation was small compared to the line width. Here, the modulation is always greater than the line width and the operation of the phase sensitive detector is different.

Figure 6 illustrates the operation in this case. At the top is indicated a proton resonance line. The value of the field at resonance for some particular frequency, ν_o, of the R.F. oscillator is indicated as H_o. One cycle of field modulation is indicated in the center. The gating of tubes A and B is shown at the botton. Also the resonance line is shown as it occurs when a tube is conducting.

At the null condition (center) tube A is conducting during one-half the resonance and off for the other half, as is tube B; the



Operation of the phase sensitive detector with the modulation greater than the line width.

Figure 6

average current for both tubes is the same. Suppose the main field drifts up slightly to a value H. Since ν_o has not changed, the resonance is still at H_o, slightly lower than H. The resonance will always occur at the time during the cycle when tube B is conducting and never when tube A is conducting. The average current passed by tube B is now higher than tube A. If the field drifts down as on the right, the opposite effect is observed and tube A will conduct more than B. If the remaining circuitry is so arranged that when B conducts more than A the main magnetic field is decreased and vice versa, the null condition will essentially be maintained. Actually an error signal is required to maintain a correction, so that the field is held between the limits of the two points of inflection of the proton resonance line.

The signal is amplified in a conventional way by a 6SJ7 pentode and fed into a 6J6 triode. This tube is connected as a phase inverter. Signals, equal in amplitude but out of phase by 180^o are taken from cathode and plate. The out of phase signals are then connected to the control grids of the gate tubes. The synchronizing voltage enters this unit through a $0-180^o$ phase control network. The output is then amplified, with feedback through a twin tee filter network to improve the wave form, and used to control the suppressor grid of the gate tubes. The output of the gate tubes is filtered and amplified in a balanced system.

Control Coil Driver (J). The function of the control coil driver section is to transform the small voltage change from the phase sensitive detector into a magnetic field correction by driving the auxiliary coil. The system used is a conventional balanced D.C. power amplifier. The schematic is self-explanatory except for possibly three points.

Since it is impossible to find two tubes such as the type 211 which have identical operating characteristics over a wide range, it was necessary to include a variable bias control (Balance No. 3) to keep the grids of the 211's at about the operating potential when the control switch is on manual.

A dual potientiometer, marked antihunt, feeds a portion of the signal back to the beginning of the D.C. amplifier. This is a very important circuit as it adjusts the response time of the field correction. It is necessary for the field correction to be slow compared to the time necessary to sense an error in fields, yet fast enough to keep up with any drifts or fluctuations in the magnetic field.

The neon bulb, NE-51, is used to protect the rectifiers against the voltage surge from the control coil when the main magnetic field excitation is turned off.

Main Generator Control (K). The function of the main generator control unit is to correct the magnetic field when a correction of more than ± 5 gauss is needed. If the current through the control coil reaches 100 ma, relay K-1 is closed. This activates K-2, the relay which controls the motor operating the field control rheostat of G-9. The motor will run until the current through the control coil is essentially zero. Manual operation is provided, as are limit switches at either end of the field rheostat.

Power Supply (L). This unit includes two conventional electronically regulated power supplies. The low voltage supply for the phase sensitive detector and associated audio amplifier tubes delivers + 300 volts DC, 100 ma, regulated. The high voltage supply for the D.C. amplifier sections delivers + 550 volts D.C., 40 ma regulated. Various filament supplies are also included.

1000v Power Supply (M). This 1000 volt, 0.3 ampere supply furnishes power for the 211's driving the control coil. It is essentially an Army Rectifier RA-34-H. The physical appearance has been considerably changed but its electrical characteristics are as described in detail in the instruction book.

It should be noted that the high voltage switch also turns on and off the filaments of the 211's. This is to avoid a situation in which the plate voltage is off and the 211's are on. Such a condition would result in excessive grid current because of the high positive potential (+ 350v) on the grids of the 211's.

R.F. Amplifier (N). The function of this unit is to amplify the R.F. from the proton oscillator until it is detectable by the frequency meter. The amplifier consists of a war surplus 6 tube, I.F. amplifier strip. It was found that 105v, 10 ma per tube resulted in reasonable operation. The R.F. coils were rewound to facilitate stager tuning. With stages 1, 3 and 5 tuned to 30 mc/sec, stages 2 and 4 tuned to 38 mc and stage 6 tuned to 33 mc, the response was flat from 32 mc/sec to 45 mc/sec, dropping off slowly below 32 mc. A voltage gain of 154 was obtained in the flat region.

Frequency Meter (O). An Army type BC-221-N frequency meter was used to measure the frequency of the R.F. oscillator. Although this meter was designed by the manufacturer to measure frequencies up to 20 mc/sec, no trouble was encountered in its operation at 42 mc/sec when used in conjunction with the R.F. amplifier mentioned above.

The meter consists of a variable R.F. oscillator with an accurately calibrated dial. The oscillator frequency can be easily compared to a self-contained crystal controlled oscillator. The crystal controlled oscillator frequency was occasionally compared to the frequency of radio station WWV. The unit also contains a mixer stage so that the difference beat note between the proton R.F. oscillator and the BC-221-N R.F. oscillator can be compared.

Amplifier (P). It is more convenient to watch the zero beat than to listen as is usually done with this type of frequency meter. To facilitate oscilloscope display, additional amplification was needed. A conventional audio amplifier of two stages served this purpose.

Microwave System.

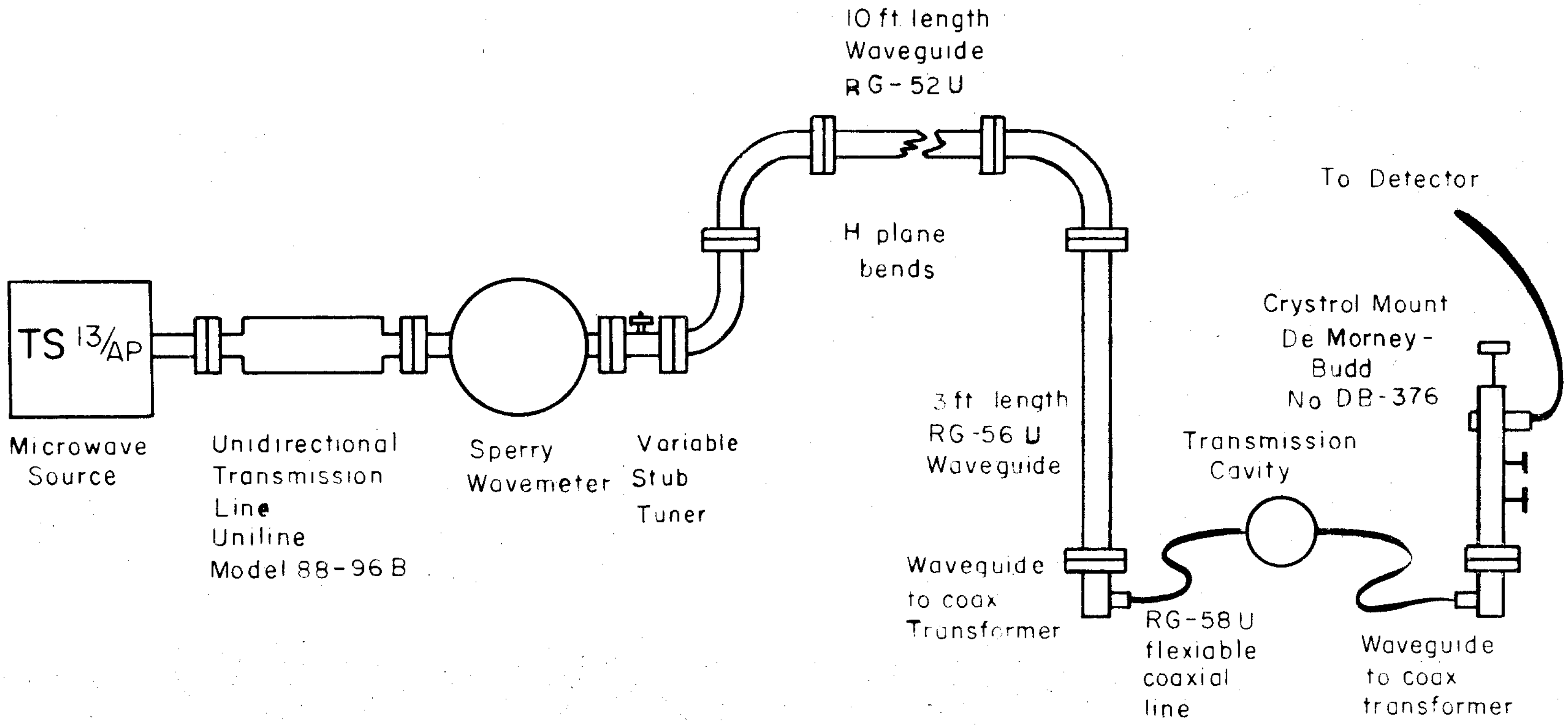
The microwave system supplies the electromagnetic energy for the spectrometer. In general terms, this system consists of two monochromatic microwave sources with suitable systems for transmitting and detecting the microwaves. The higher frequency (24,000 mc/sec) is known as K band and the lower (9,360 mc/sec) is known as X band. The two systems are independent and are used separately.

Waveguide (Q) and Klystron Power Supply (R); X band. A pictorial diagram, Figure 7, illustrates the general plan of the X band waveguide system.

An army surplus test unit known as TS-13/AP was used as a microwave source. The only modification necessary was the removal of tubes V102 and V103. After about 6 hours of operation under conditions of limited ventilation, no noticeable drift in frequency could be detected for 2 to 3 hours. A frequency control device, therefore, was not needed. Maximum power available was about 25 milliwatts in a frequency range 8,500 mc/sec to 9,660 mc/sec.

The output of the TS-13/AP was fed into a unidirectional transmission line section. This unit has a forward attenuation of less than 1 decibel and a reverse attenuation of > 13 decibels. With such characteristics, the transmitted power is unaffected while reflected power is essentially eliminated; the klystron sees an infinite length of waveguide. The frequency of the klystron will, therefore, be unaffected by mismatching components further along in the system.

The output of the Uniline attenuator is fed into a Sperry calibrated wavemeter. This unit indicates frequency directly on a calibrated dial. The absolute accuracy(55) is ± 2.5 mc/sec at 60 per cent relative humidity and 25°C, the relative accuracy is ± 1 mc/sec, and the calibration point is 9,310 ± 1 mc/sec. The unit was obtained from war surplus.



Microwave system – X band
Figure 7

From the wavemeter, the power goes through a variable stub tuner, used to optimize the impedance as seen by the signal source, and through a system of waveguide bends to a coaxial line to waveguide transformer. A short section of flexible coaxial transmission line couples the waveguide to a coaxial cavity.

This cavity is situated between the poles of the magnet and contains the sample under investigation. A Helmholtz coil, used to modulate the magnetic field, surrounds the cavity. About 10 gauss peak to peak (inside the cavity) field modulation can be obtained by this method. Figure 8 is a photograph of the cavity and helmholtz coil.

A portion of the microwave power is coupled out of the cavity and into a waveguide section by a coaxial line and appropriate transformer. The waveguide feeds a tunable crystal mount using a type 1N27 crystal to detect the microwave power. Changes in crystal current are detected by the detector system.

Waveguide (Q); K band. The waveguide system for K band is slightly more complicated than that of X band because provision is made for operating at reduced temperature. The microwave path is illustrated in Figure 10 and starts with a low voltage, thermally tuned klystron type 2K50. After a flap attenuator, a portion of the microwave power is taken from the main waveguide with a directional coupler. This portion was used to measure the frequency of the source. A galvanometer registers the crystal current when the calibrated wavemeter is tuned to the microwave frequency. Next along the main waveguide is a

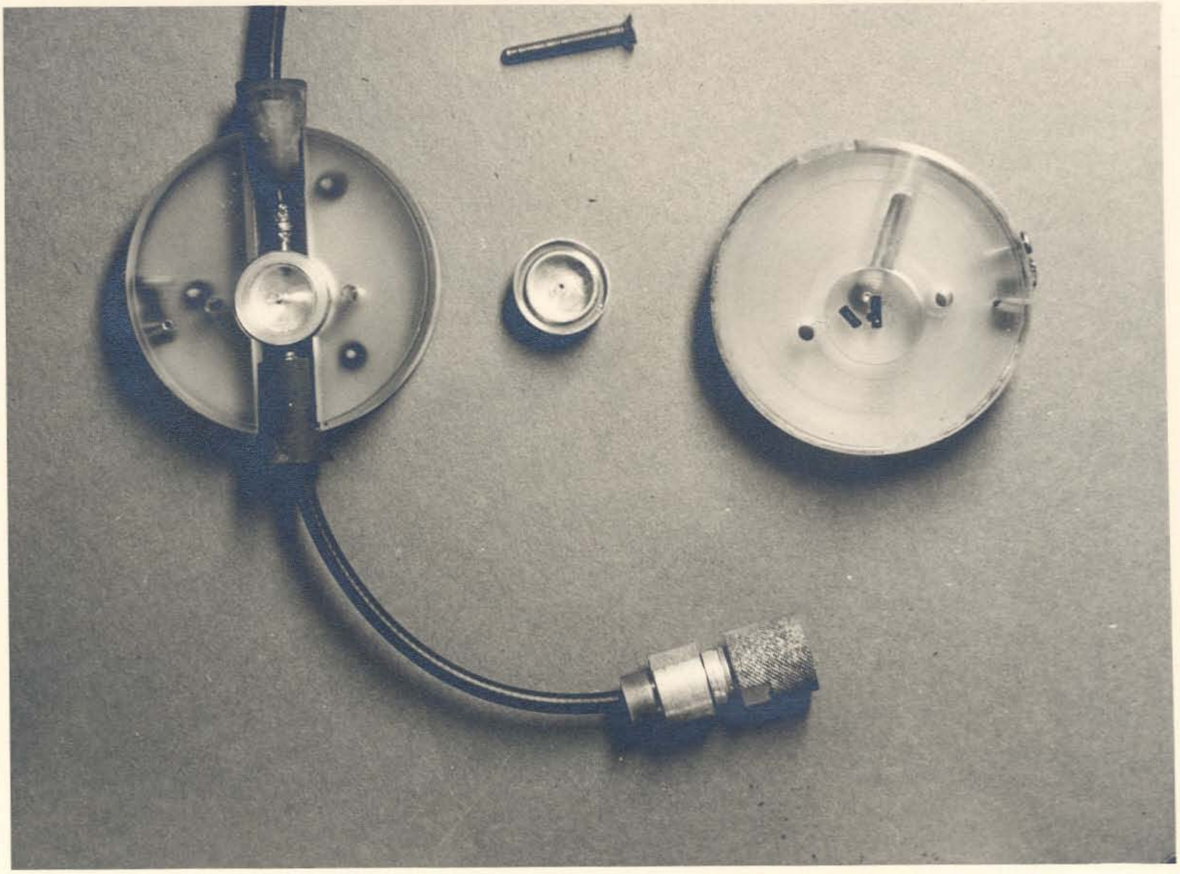


Figure 8. -- X band coaxial cavity and Helmholtz coil.

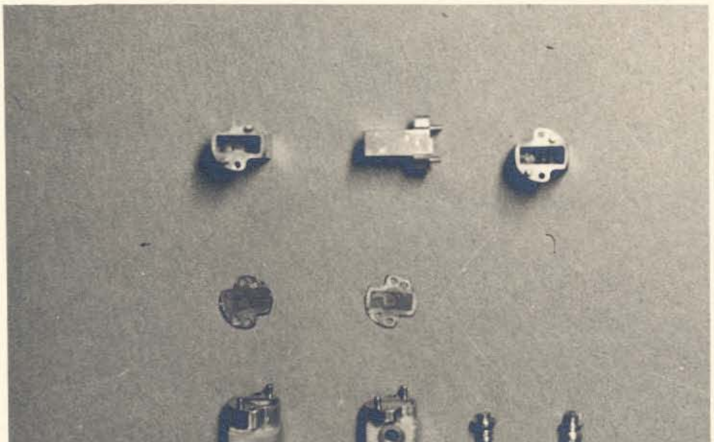
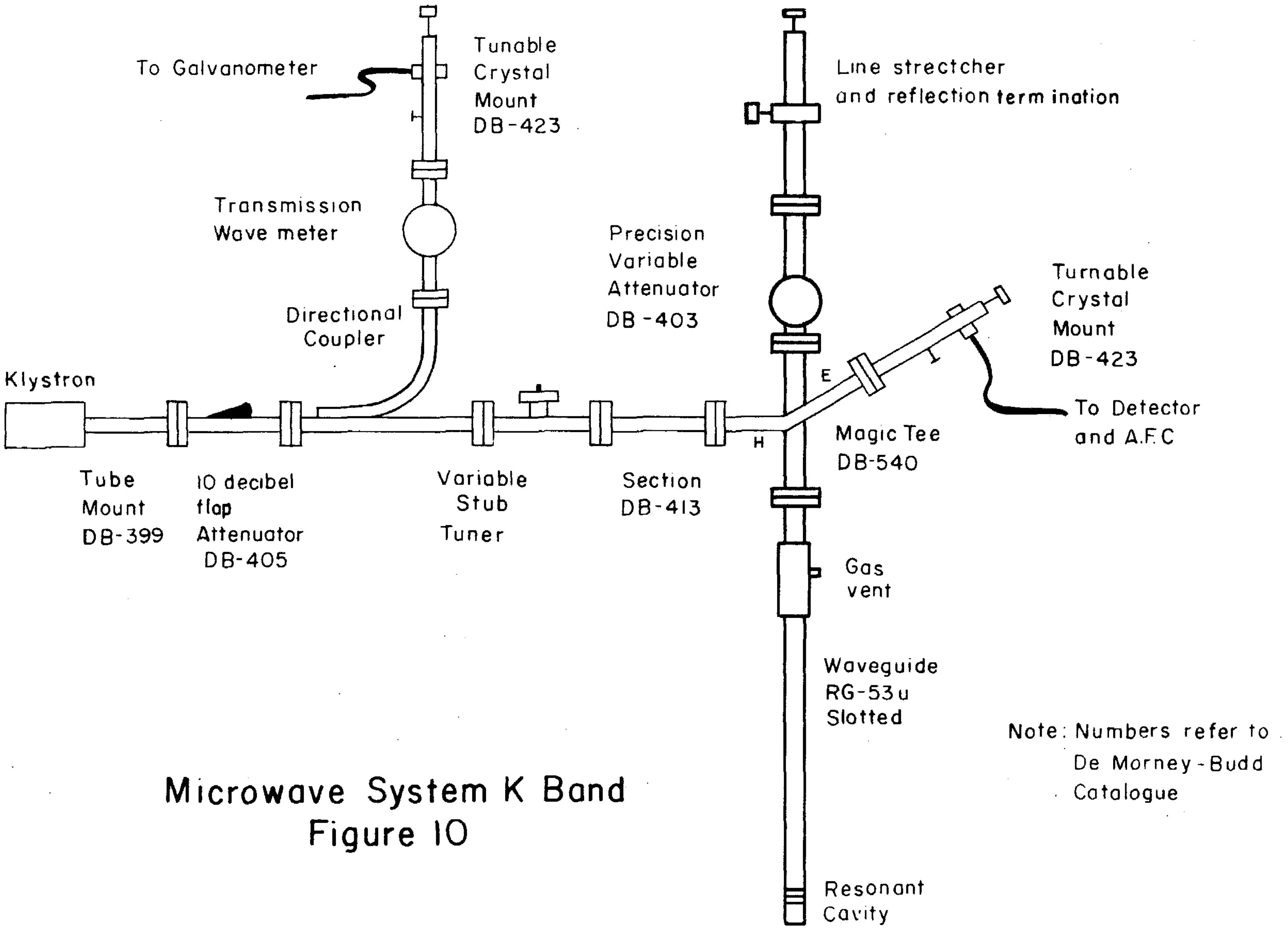


Figure 9. -- K band rectangular cavities.



Note: Numbers refer to De Morney-Budd Catalogue

Microwave System K Band
Figure 10

variable stub tuner similar to that used at X band and for the same purpose. Finally the microwave power is fed into a magic tee arranged as a microwave bridge.

A magic tee has the property that microwave power does not go straight through but is always split into the two opposite arms. For example, power entering H (the H-plane arm) will not go into E (the E-plane arm) but rather divide equally between the arm going up and the one going down. Similarly, power going up (or down) will divide equally between the E and H-plane arms.

To construct a microwave bridge using this unit, a tunable crystal mount was attached to the E-plane with the crystal detector output going both to the A.F.C. and Detector unit. Microwave power was fed into the H-plane arm. A variable attenuator, line stretcher and reflection termination were attached to the upper arm of the magic tee. With this combination the amplitude and phase of the reflected power coming down that arm could be controlled. A section of waveguide was placed between the lower arm of the magic tee and a rectangular cavity situated between the poles of the magnet. This cavity, shown in Figure 9, was designed to operate in the TE_{210} mode and to contain the sample under investigation. The operation of this type of bridge is as follows. Power, entering the H-plane arm, divides equally into the upper and lower arms and is reflected back towards the center by either the cavity or the reflection termination. If phase and amplitude of the reflected power entering the E-plane arm from the top is carefully adjusted to be 180° out of phase and equal in amplitude to the signal entering the E-plane arm from below, the power at the crystal detector will be zero as will the crystal current. Any loss of power in the lower section will disrupt this balance and produce crystal current.

The main advantage of a bridge system such as this is that the crystal detector can be operated under low current conditions yet a reasonable amount of power can be used to irradiate the sample. Low crystal current is desirable because crystal noise is directly proportional to crystal current; high power is desired at the sample because a fraction of the incident power is absorbed at resonance. Such a system suffers a severe limitation at low temperature because the balance of the bridge is dependent upon the length of the lower section of waveguide. If there is an extreme temperature gradient up the waveguide (say, from $4.5^{\circ}K$ to $300^{\circ}K$) the length will be changing and the bridge will not stay balanced. For this reason, it was found impossible to use the bridge at low temperature. Instead, the attenuator in the upper arm was set at maximum and the lower arm used alone. The crystal current then indicates one-half the reflected power from the cavity.

High sensitivities can be obtained by this system, especially if the Q (a figure of merit) of the sample cavity is made high. The rectangular cavity was gold plated to increase the Q. A high Q cavity has a very narrow resonance curve so that the frequency stability of the klystron was a serious problem. For Kband, an automatic frequency control (A.F.C.) system was required.

A.F.C. System.

The purpose of this system is, as mentioned, to keep the frequency of the klystron at exactly the resonant frequency of the cavity even though the latter may change. The general operation of this unit is as follows. A 4kc/sec sine wave modulation was applied to the klystron repeller electrode. The output of the klystron was no longer monochromatic at a frequency of ν_0, but frequency modulated* about ν_0 at this 4kc/sec rate. Assume that this modulation is small compared to the width of the cavity resonance curve. When ν_0 is the cavity resonance frequency also, the output is just frequency modulated and, when detected by a non-frequency sensitive device such as a crystal, no signal at 4kc/sec is observed. When ν_0 drifts to one side or the other of the cavity resonance, the output as detected by the crystal will be amplitude modulated at 4kc/sec. There will be a phase shift of 180° in this amplitude modulation depending upon the direction of this drift. Enough information is contained in this signal to control a servo system that adjusts the klystron frequency back to the cavity resonant frequency. It should be noted that the 4kc/sec is not detected in the detector section because of its narrow band character.

<u>Selective Amplifier (S)</u>. The output of the crystal was fed into a narrow band high gain amplifier of essentially the same design as that of the detector system. A twin tee electronic filter section the same as in the detector system was used, except, here, the filter passes only 4kc/sec. Schematic diagrams of these units are not included because of the similarity.

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* It is important that the amount of modulation, when calculated in gauss, be small compared to the width of the resonance line to eliminate distortion caused by the frequency modulation.

Phase Sensitive Detector (T). Phase sensitive detectors have been discussed previously. One special characteristic is required here; the unit must operate with a floating D.C. ground. A crystal diode array as shown on the schematic diagram was selected as best suited for this purpose. The main point in the operation of such a circuit is that the reference signal is large compared to the information signal, so that the resistance of the crystal diodes, as seen by the information signal, will be the resistance as determined by the reference signal.

Output from the phase sensitive detector is filtered slightly and amplified with a balanced D.C. amplifier with a gain of about 20. This correction is applied to a resistor between the bias control and the grid of the tuning triode section of the 2K50 klystron. With the unit on automatic, any correction will change the bias of this triode, therefore, the frequency of the microwave source.

Klystron Power Supply (R). The 300v power supply used to power the 2K50 klystron was constructed by Shoolery(56) and used here with slight modification. A diode rectifier type 6H6 was added from the grid of the tuning triode to ground to prevent the grid from becoming positive in case the correction signal was larger than the bias voltage.

4Kc Generator (U). A Heathkit audio oscillator was used as a 4Kc/sec generator.

Operation.

Magnetic Field Controller. The proper coil and probe are selected for the magnetic field of interest by reference to Table V, page 44. Grid 3 of the R.F. oscillator is adjusted in conjunction with the oscillation level until that point is found where the oscillation level control can be turned the furthest in a counterclock-wise direction yet still maintain oscillation, as indicated by "grass" (noise) on the monitor oscilloscope. The tuning condensers are set to the desired frequency as indicated by the frequency meter (BC-221-N). The oscillation level is then adjusted to the point where the detector current meter indicates one small division above the no oscillation value. Balance controls 1, 2, and 3 are adjusted in turn to give a zero reading on the vacuum tube voltmeter when the selector switch is on 1, 2 or 3 respectively. With generator G-1 delivering the proper current and the 500 c.p.s. generator set at 115v, the manual-automatic switch is turned to automatic. The current from the control generator is slowly increased with the manual control switch until the proton line is seen on the monitor oscilloscope. The manual field control must then be turned to the off position immediately.[*] The field controller should be operating automatically. To change the field, the tuning condensers can be turned (at a reasonably low rate) manually or with a clock drive motor.

To measure the strength of the magnetic field, the oscillator frequency of the BC-221-N is changed until a zero beat is observed on the oscilloscope. From the reading of the oscillator dial and associated calibration book, the magnetic field, H, can be calculated using the formula:

$$H(\text{gauss}) = 234.836 \quad {}_p(\text{mc})$$

where ${}_p$ is the frequency of the oscillator.

---

[*] When the proton line is seen on the monitor oscilloscope, automatic control starts immediately. If the control generator is slowly increasing, the current in the correction coil increases in such a manner as to keep the field constant. When this current reaches 100 ma, the relay system will operate in such a manner as to make the control generator decrease the field but with the control generator already increasing, a fuse will be blown.

Microwave System X Band. The sample should be placed in the cavity at the point where the microwave magnetic field is maximum; this point is at the bottom of the removable section of the cavity (see Figure 8, page 54) midway between the center post and the cavity wall. A single crystal can be cemented in place, or, for powder samples, a concentric trough was constructed of lucite into which the powder can be pressed and the trough cemented to the proper place. Samples in capillary tubes can be used by putting the capillary tube through the hole in the side of the cavity provided for this purpose. The end of the capillary should not touch the center post.

The TS-13/AP microwave source should be turned on at least 6 hours before it is used. With the cavity in place, a 0-200 microammeter is connected to the output of the crystal detector. The cavity tuning, repeller, variable stub tuner, and tunable crystal mount are adjusted (in that order) for a maximum meter reading. The attenuator in the TS-13/AP is then adjusted for about 50 microamperes crystal current. When the meter is removed and the crystal detector attached to the Detector unit, the system is ready for operation.

Microwave System K Band. The sample must be placed in the center of the cavity against a large wall. This will be the place (for the TE_{210} mode) where H is maximum. A single crystal can be glued to the wall with Duco cement (product Dupont Co.). Powders should be pressed into a lucite pillbox, 1/8th inch in diameter, 1/6th inch high with 0.002 inch wall. The pillbox can then be glued to wall of cavity.

Figure 9, page 54, shows several cavities; one of them has the sample in place. When more convenient the sample can be placed on the end of a stub that fits into the wall of the cavity. One stub shown has a sample in place. The cavity is assembled by connecting it to the end of the waveguide. An iris (two shown in figure) of appropriate size is placed between the cavity and the waveguide. The proper size is found by trial and error, but generally the hole in the iris will be about No. 34 drill gauge. The waveguide system is assembled as shown in various figures.

The klystron must be tuned to the resonant frequency of the cavity. This frequency will depend on the size of the cavity and the sample. To find the frequency of the cavity, a 0-200 microammeter is connected to the output of the crystal detector at E; the attenuator is adjusted to maximum attenuation. The microwave frequency is slowly changed by turning the bias helipot on the klystron power supply unit. The reading of the microammeter will change. At each low current point, the attenuator is turned to zero attenuation and the plug and line stretcher adjusted for zero reading on the meter. This process is continued until that point is found where phase control alone will not balance the bridge, but where the attenuator will also be needed. If the attenuator reads from 25 to 50 divisions at balance, the iris size is satisfactory, if not the iris should be changed. The attenuator is then advanced to maximum and the automatic-manual switch on the A.F.C. unit is turned to automatic position. Maximum power can be obtained by turning the repeller control slowly, while in the automatic position, until a maximum reading on the meter is obtained. The meter should then be removed and the detector system attached. The unit is ready for operation.

Low Temperature Operation - K Band. It is possible to operate the K band system at reduced temperature, either 77°K (liquid nitrogen) or 4.5°K (liquid helium). Figure 11 shows the two dewar vessels disassembled and figure 12 shows the system in place with helium storage vessel and transfer tube.

The system for helium consists of two glass dewar vessels constructed to fit between the poles of the magnet. With about 3 liters of liquid nitrogen in the outer dewar vessel, the inner vessel will be completely submerged. The waveguide enters the inner vessel through a ball and socket joint lubricated with silicone grease. The transfer tube enters through a ball socket joint also; the tube has a side arm to use as a vent. Liquid helium is placed in the inner dewar. About 2/3 of a liter of helium is needed to cool the inner dewar and waveguide. The vessel holds about 300 ml so that one liter of helium is required to fill the vessel. To minimize loss, the helium gas is vented through the inside of the waveguide. Maximum transfer of heat from the waveguide is obtained in this way. When cool, the loss is about 1 ml of liquid helium per minute.

The transfer tube was constructed of seamless, stainless steel tubing. The inner tube is 1/8th inch inside diameter, 0.005 inch wall. Concentric to this is a 3/8th inch tube. Teflon spacers, about 10 inches apart, separate the two tubes. The space between is evacuated. The general shape of the tube can be seen in Figure 10.

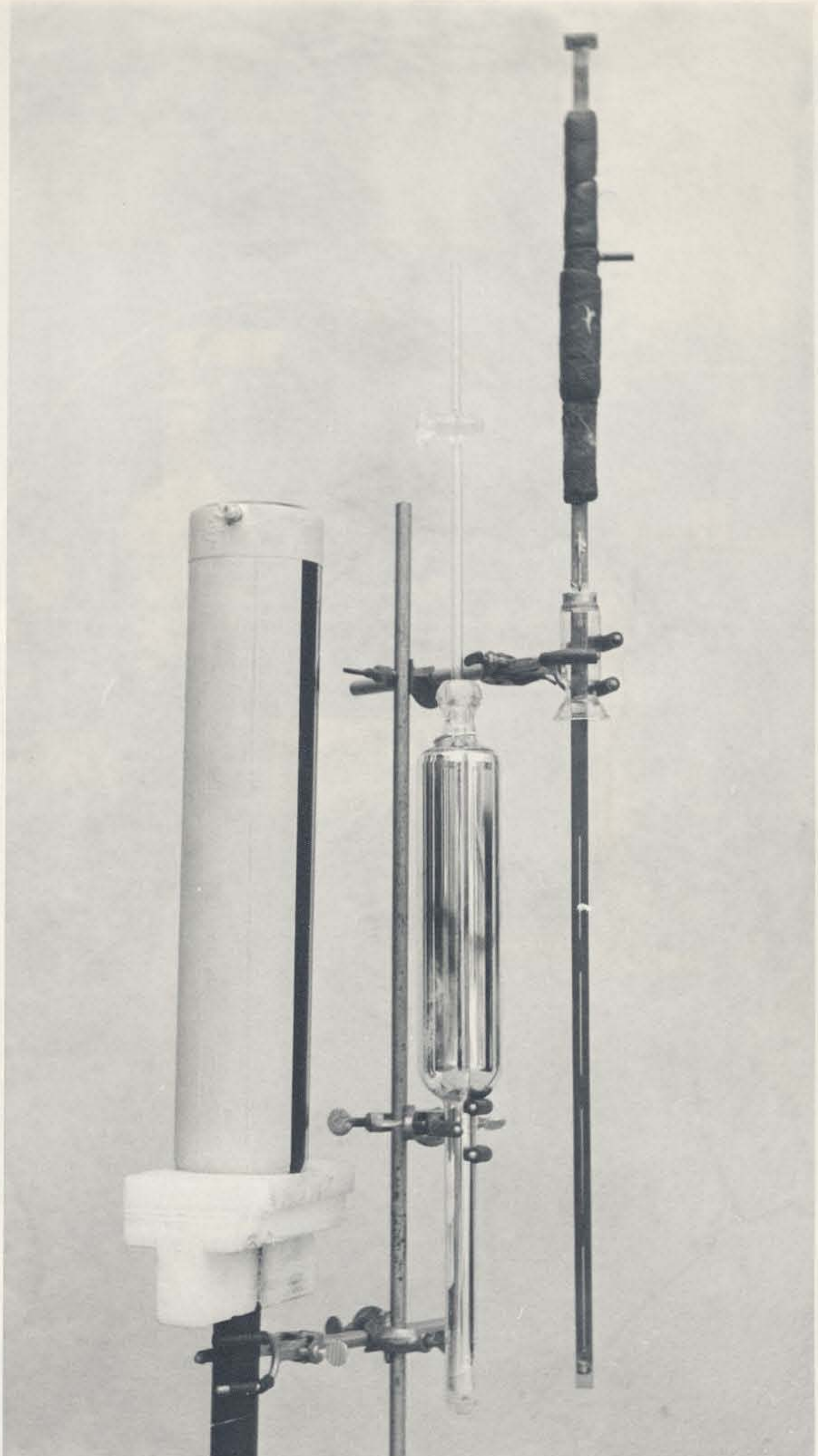

Figure 11. -- Dewar vessels.

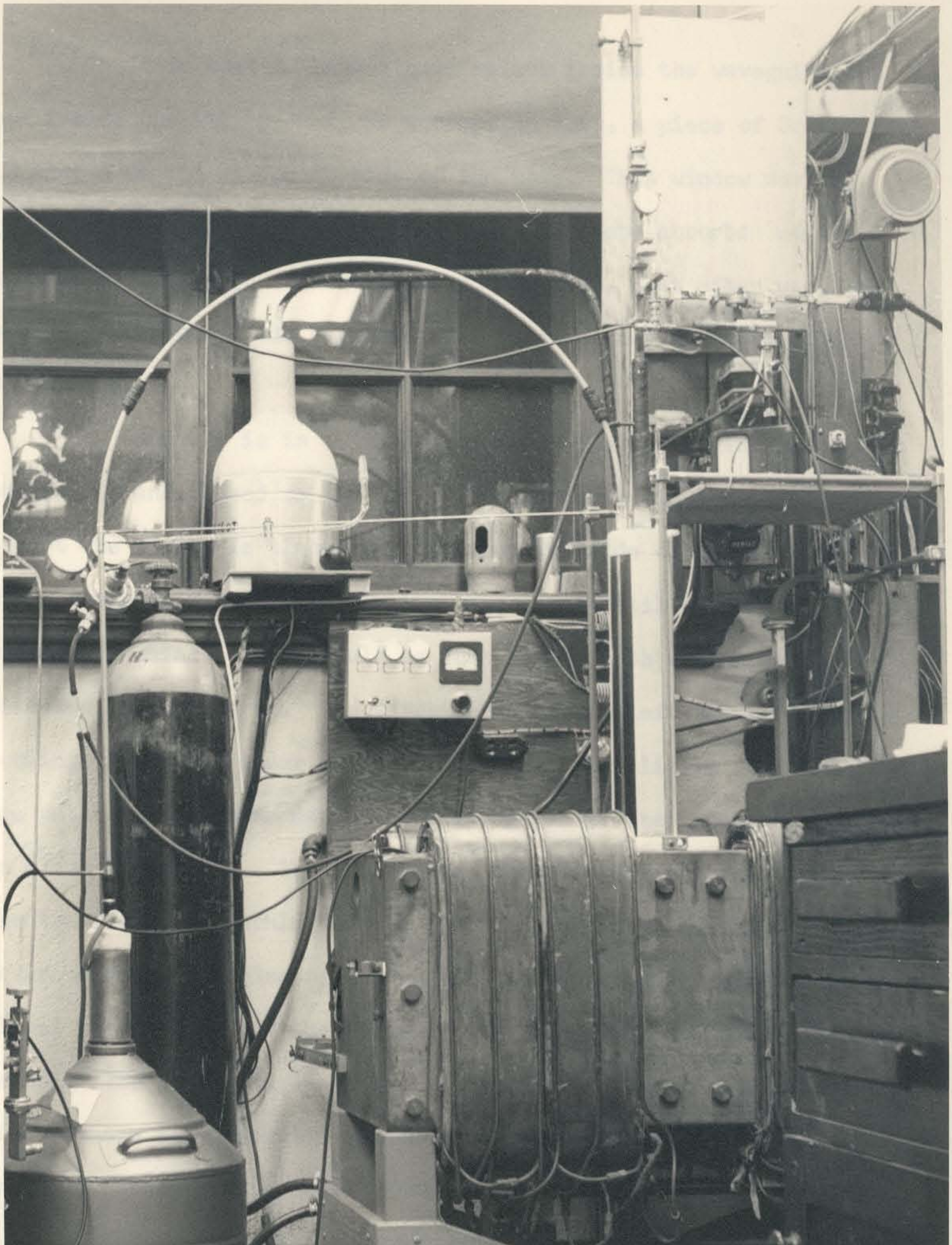

Figure 12

It is best to have liquid helium inside the waveguide but not inside the cavity.(57) To accomplish this, a piece of Scotch tape is placed on the waveguide side of the iris. This window must be replaced after each operation (probably, the tape absorbs moisture when it is warming). It should be noted, also, that after use, the waveguide inside should be dried with tissue since moisture collects on warming.

Assembly is in a logical manner. The cavity is filled with helium gas and placed on the end of the waveguide in the usual manner, except the window is placed on the waveguide side of the iris. The inner dewar is filled with air; then evacuated until about 1 mm Hg pressure remains. This should be done before each use, as helium diffuses through pyrex. The slight pressure is left to facilitate pre-cooling. With the inner dewar on its side, four little styrofoam floats are put into the inner dewar. The waveguide is then inserted and held in place by springs. The inner dewar should hang from the waveguide. The transfer tube should then be fitted into place. With the nitrogen dewar between the poles of the magnet, the inner dewar is lowered into place; the free end of the transfer tube goes into the helium storage vessel. The waveguide hangs in its usual place but with a thin teflon window where the waveguide attaches to the magic tee (this is to keep the cold gas out of the rest of the waveguide system).

It is advisable at this point to apply a little helium pressure on the storage dewar and check the waveguide vent to make sure the transfer tube is clear. With a slow stream of helium entering the waveguide vent and leaving through the side arm of the transfer tube, liquid nitrogen is placed in the outer dewar until it is 1 inch from the top. With this arrangement, the waveguide is in contact with liquid nitrogen. The system should be pre-cooled for about one hour.*

To transfer helium, the vent is cleared and the side arm opened. About 2 lb gauge pressure of helium from a helium tank is applied to the storage dewar. The end of the transfer tube should be visible (the dewar vessels are strip silvered) and the helium can be easily seen as it comes out of the tube. The inner dewar should be filled to about 1/2 full. Although the helium meniscus is very difficult to see, the styrofoam floats indicate the helium level very clearly. As soon as the transfer is finished, the side arm should be closed; all the helium gas must then go up the waveguide to the vent.

When the helium level becomes low, the side arm can be opened and pressure again applied to the storage dewar and the inner dewar refilled. This operation proceeds smoothly.

For operation at liquid nitrogen temperature, the system is similar. The inner dewar is replaced by a single wall tube that fits over the waveguide. The inside should be carefully purged with dry nitrogen, or helium before cooling to remove any moisture. Best results are obtained if a small positive pressure (1 lb gauge) of helium is maintained through the vent to prevent air from condensing on the inside of the tube.

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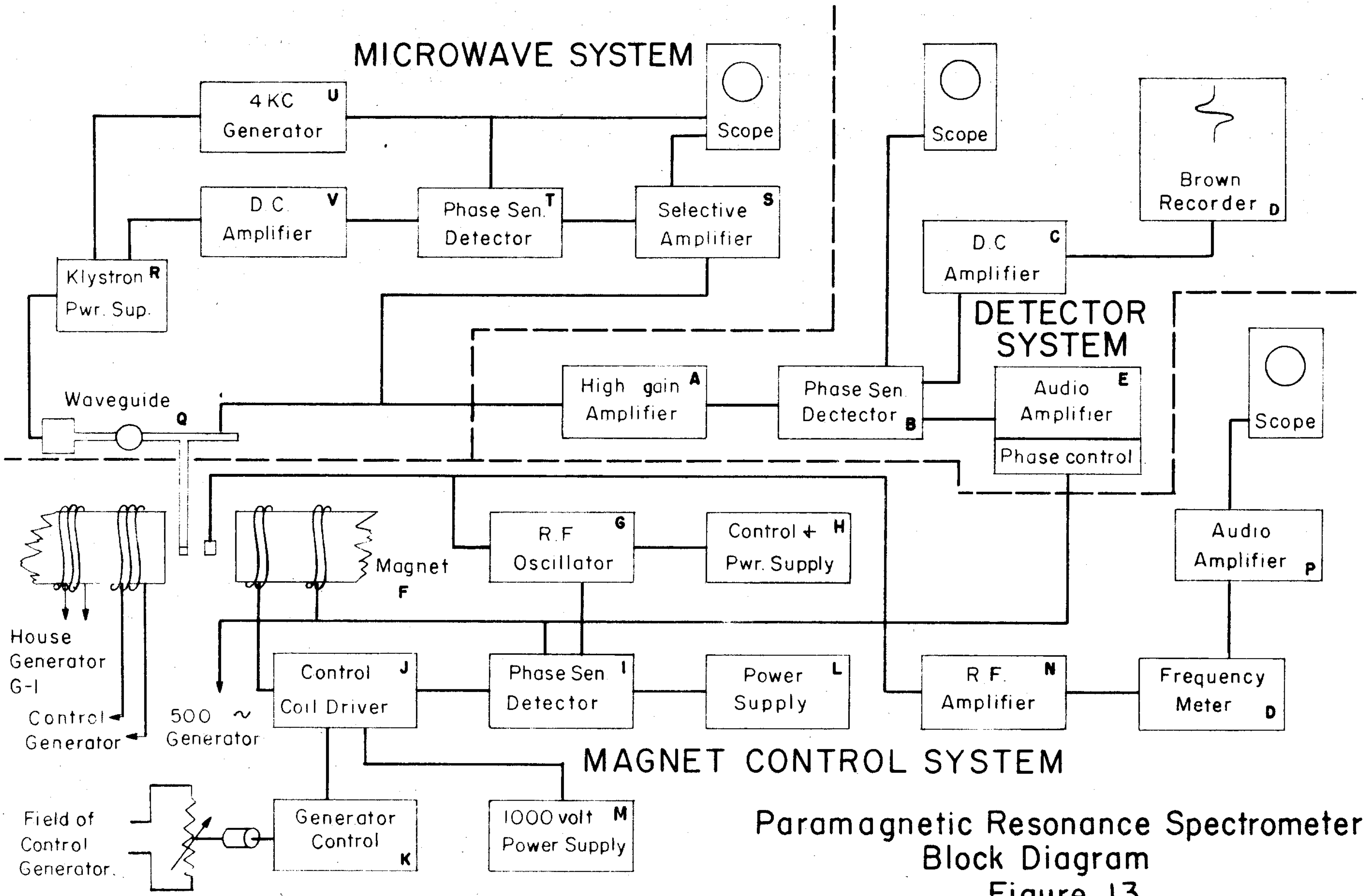
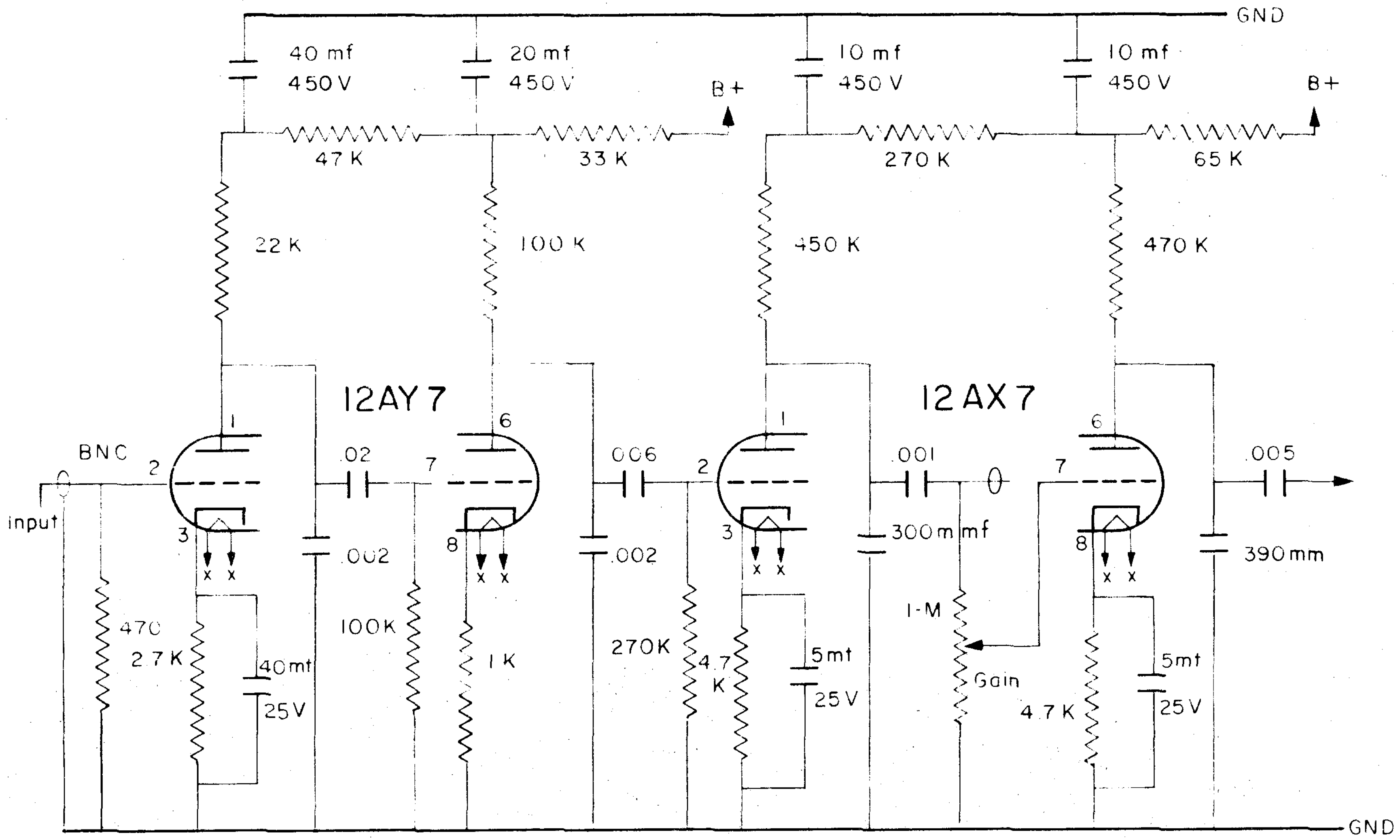
* It is best to find the cavity frequency and turn on the A.F.C. at this time. The A.F.C. can follow the change in cavity size when the temperature changes from 77° to 4.5°K.

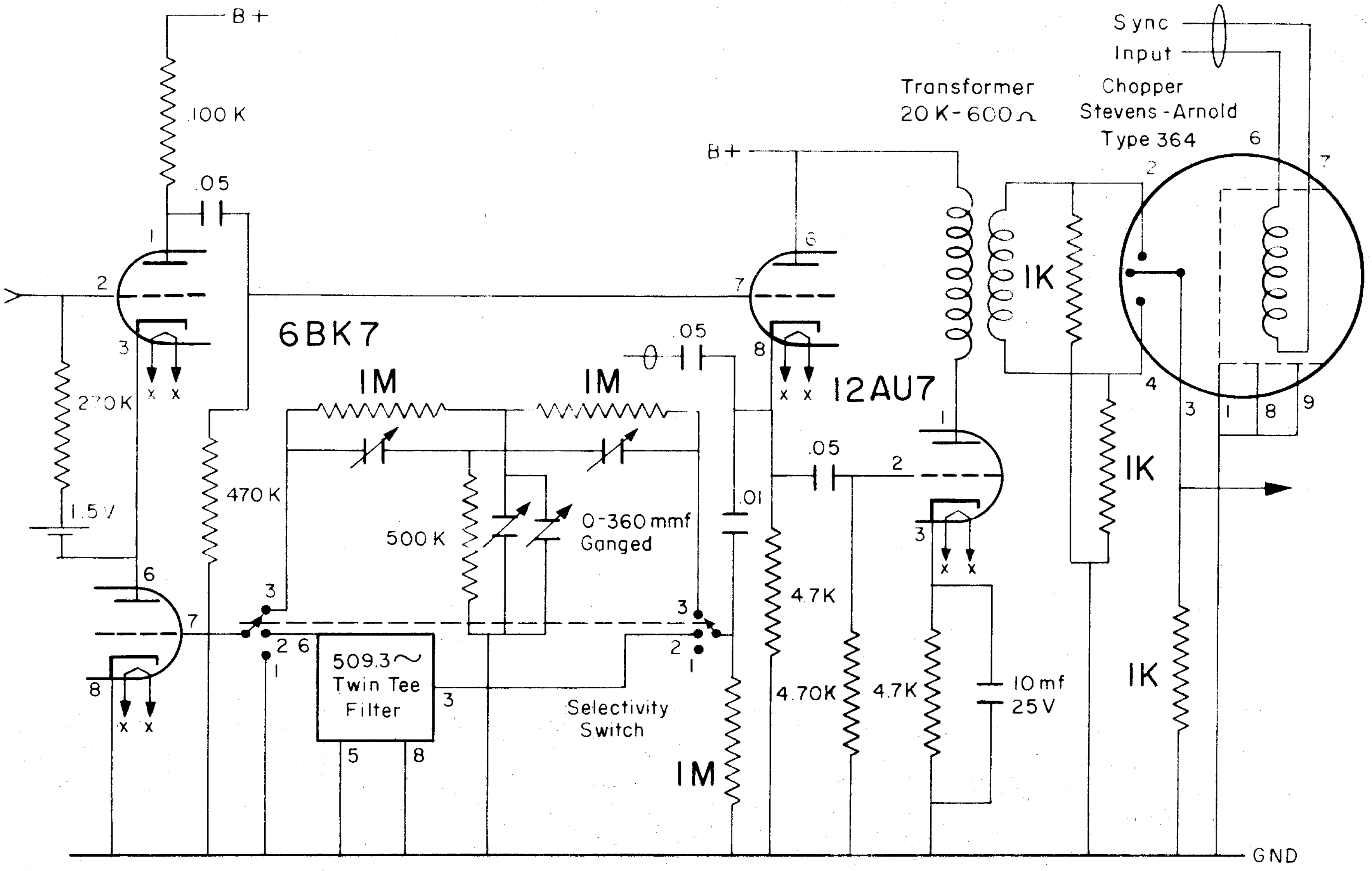


Paramagnetic Resonance Spectrometer
Block Diagram
Figure 13



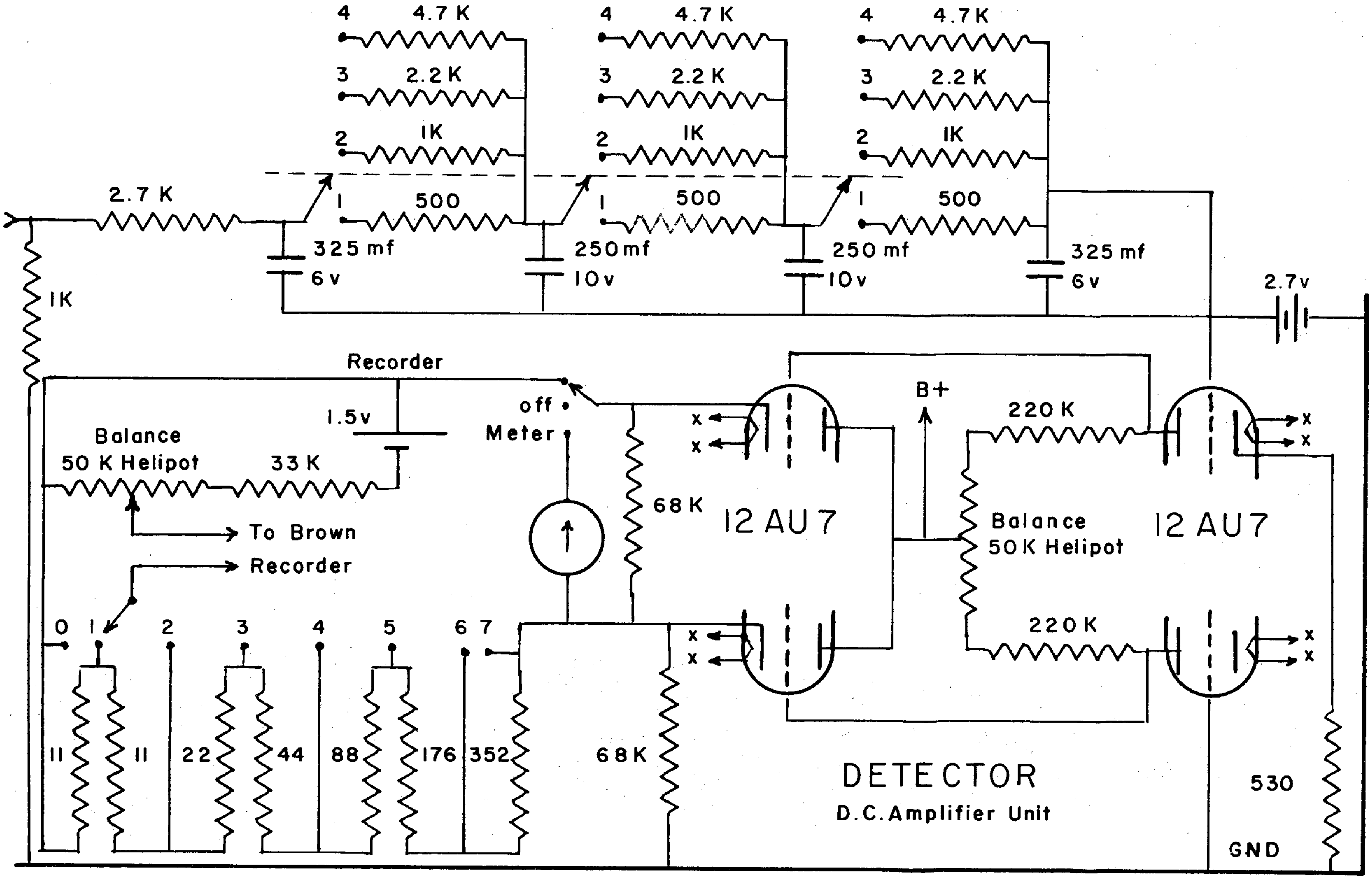
DETECTOR

High Gain Amplifier section



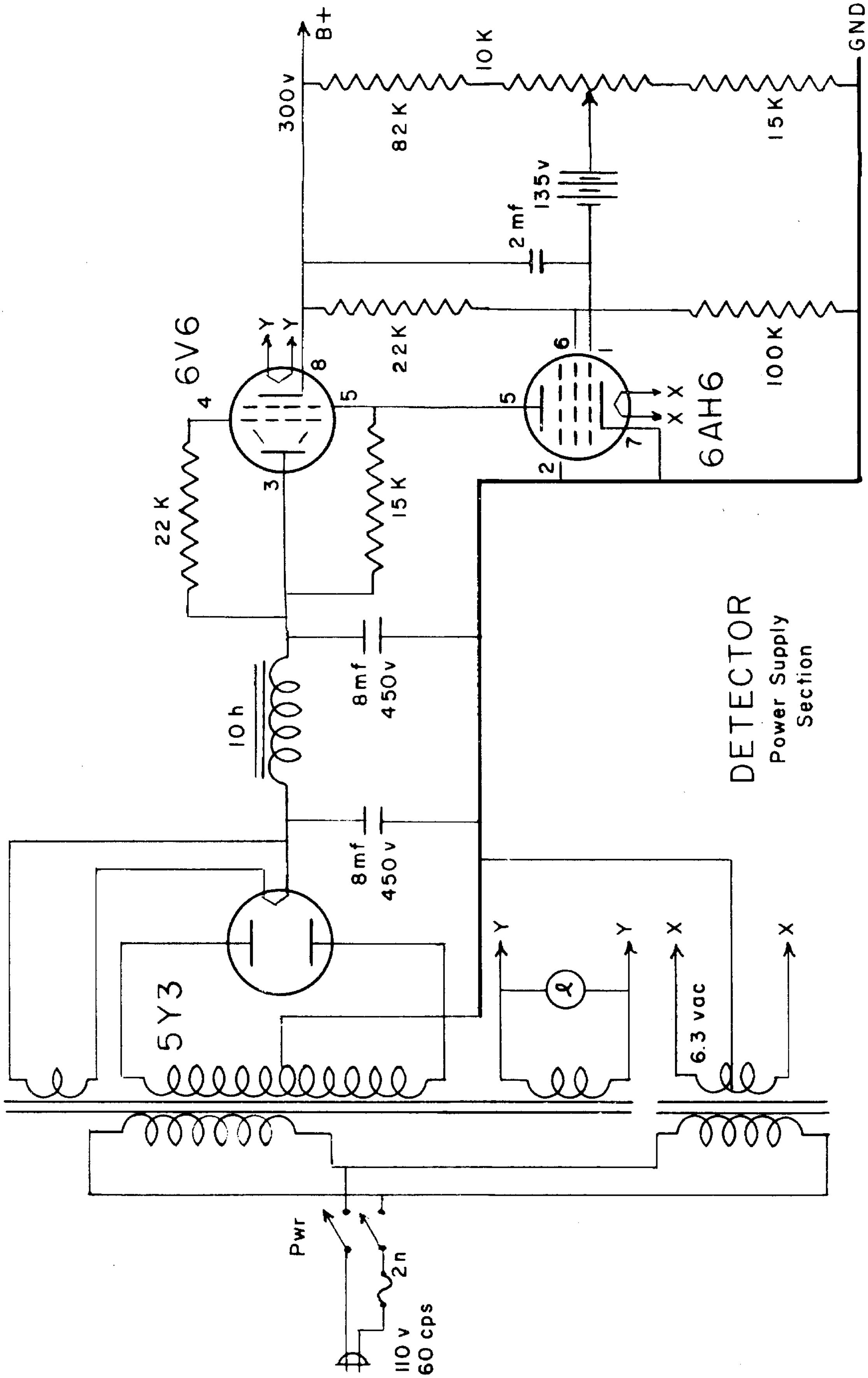
Detector

Narrow band phase sensitive section

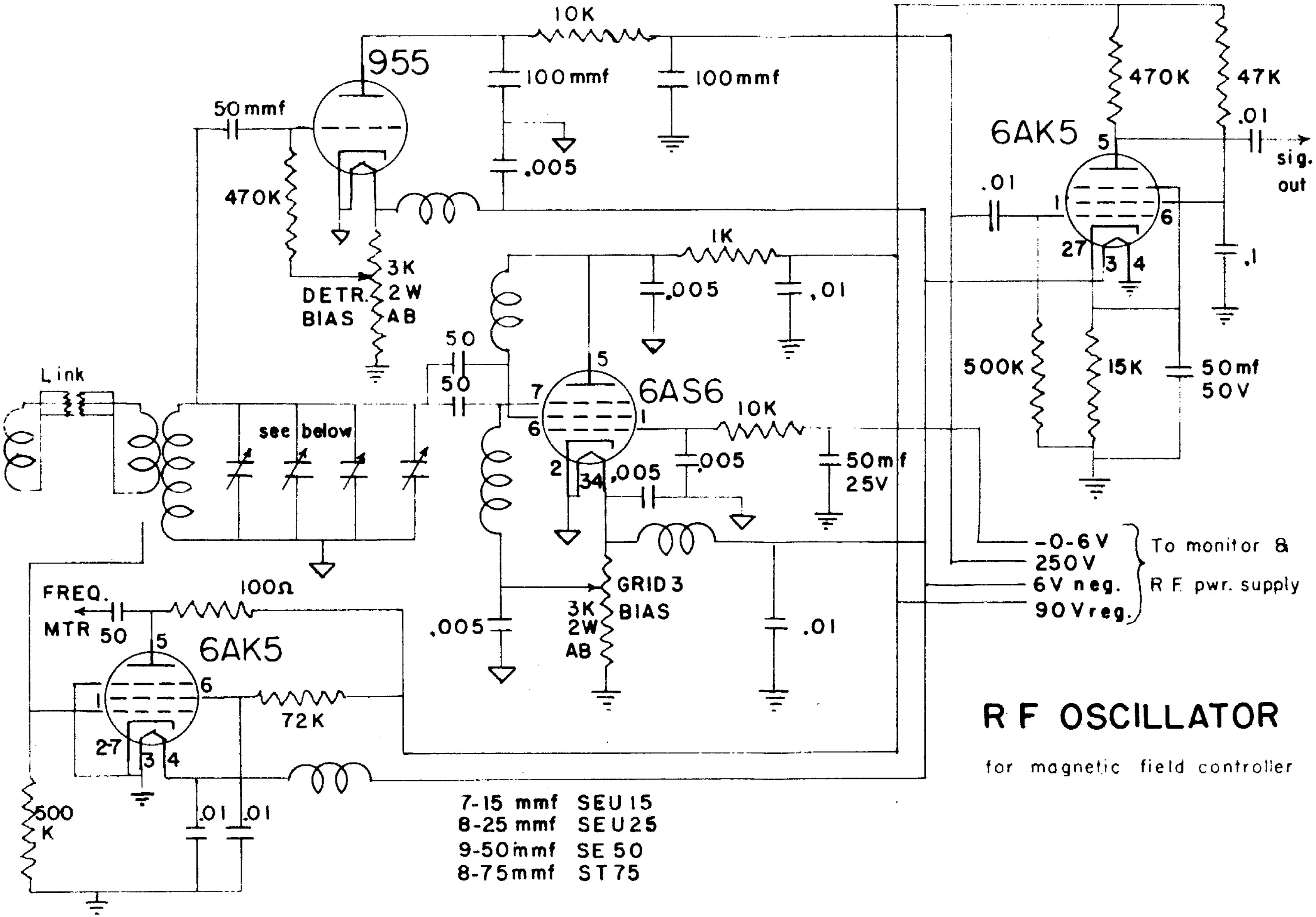


DETECTOR

D.C. Amplifier Unit



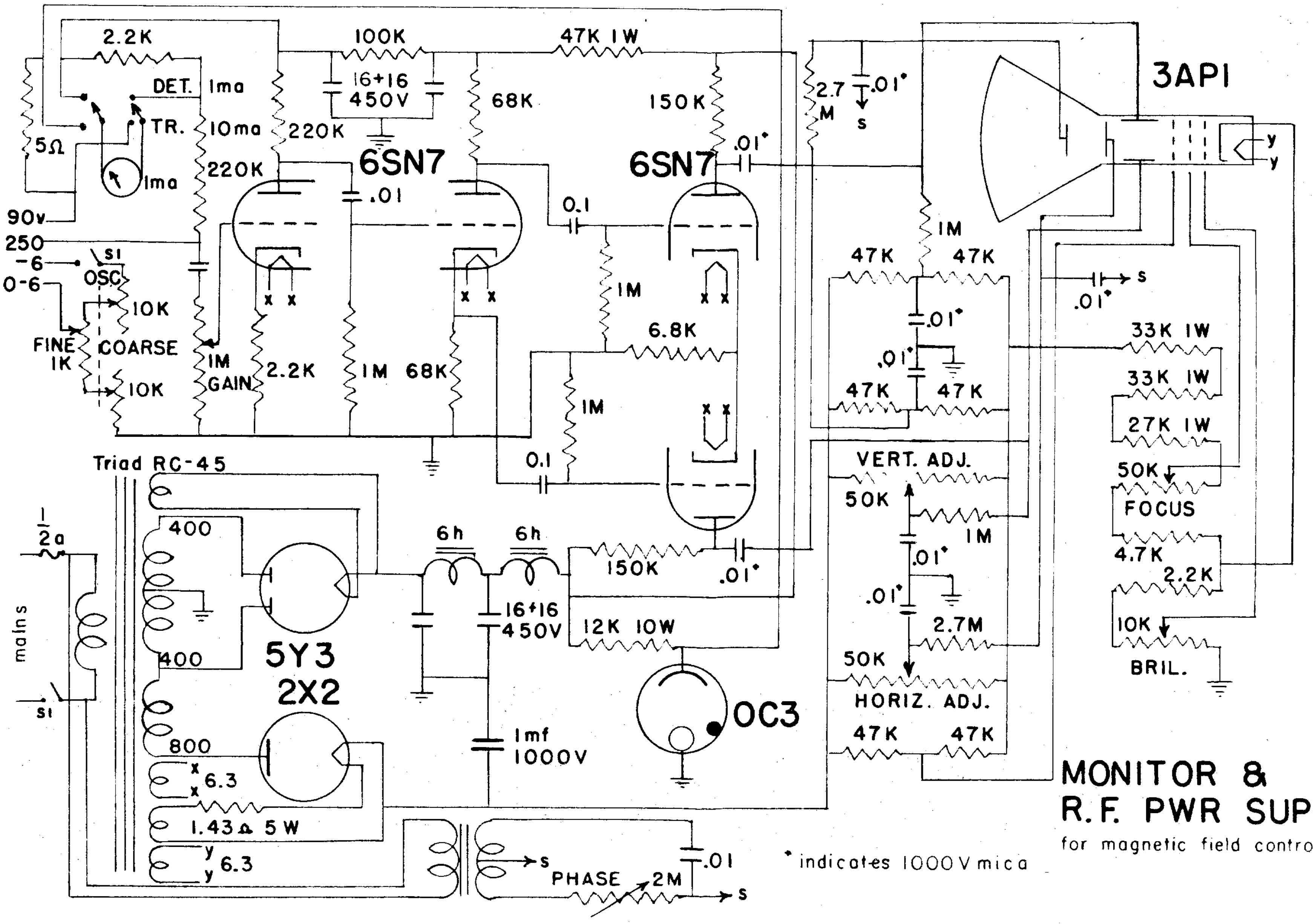
DETECTOR
Power Supply
Section



R F OSCILLATOR

for magnetic field controller

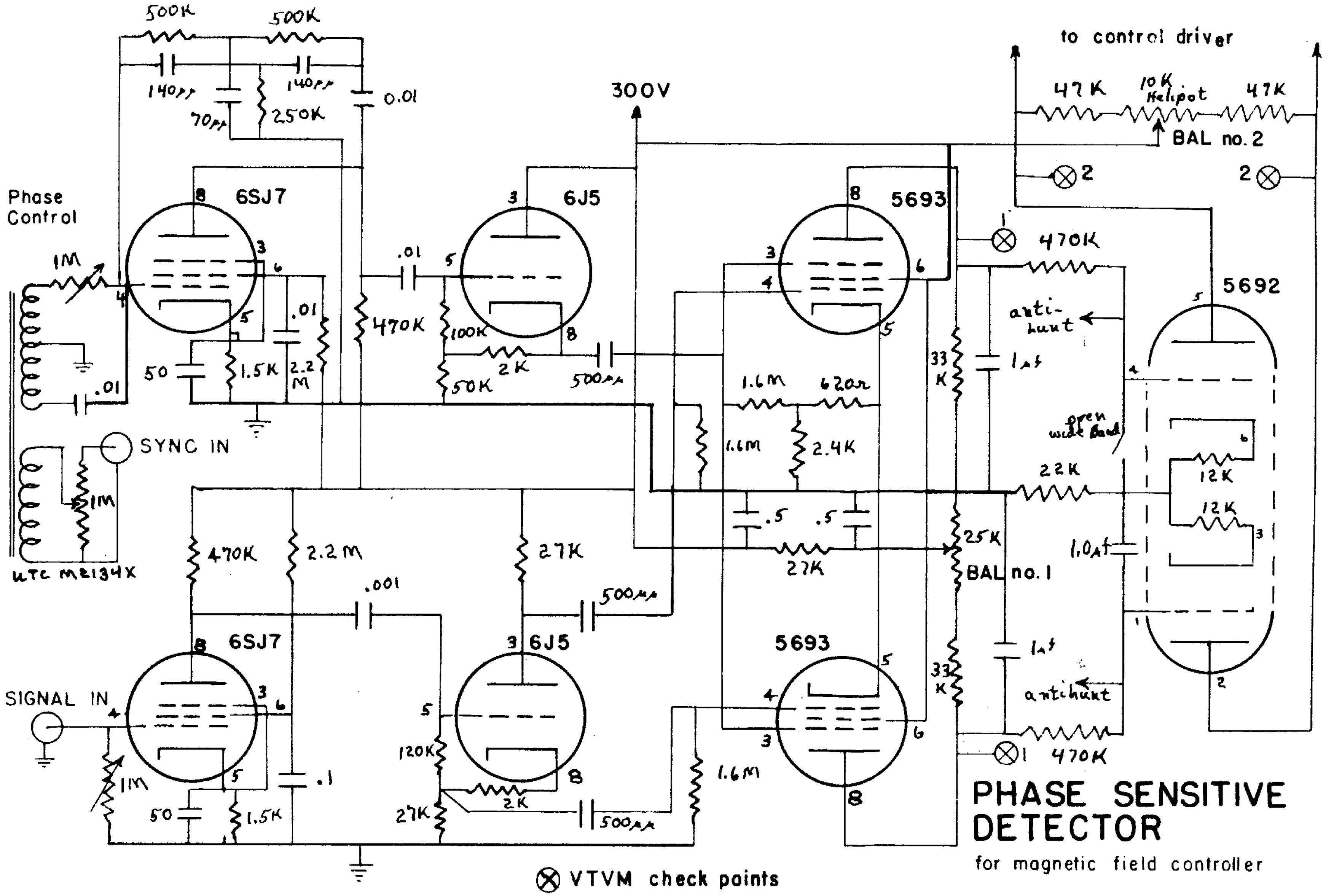
7-15 mmf	SEU 15
8-25 mmf	SEU 25
9-50 mmf	SE 50
8-75 mmf	ST 75



MONITOR &
R.F. PWR SUPPLY

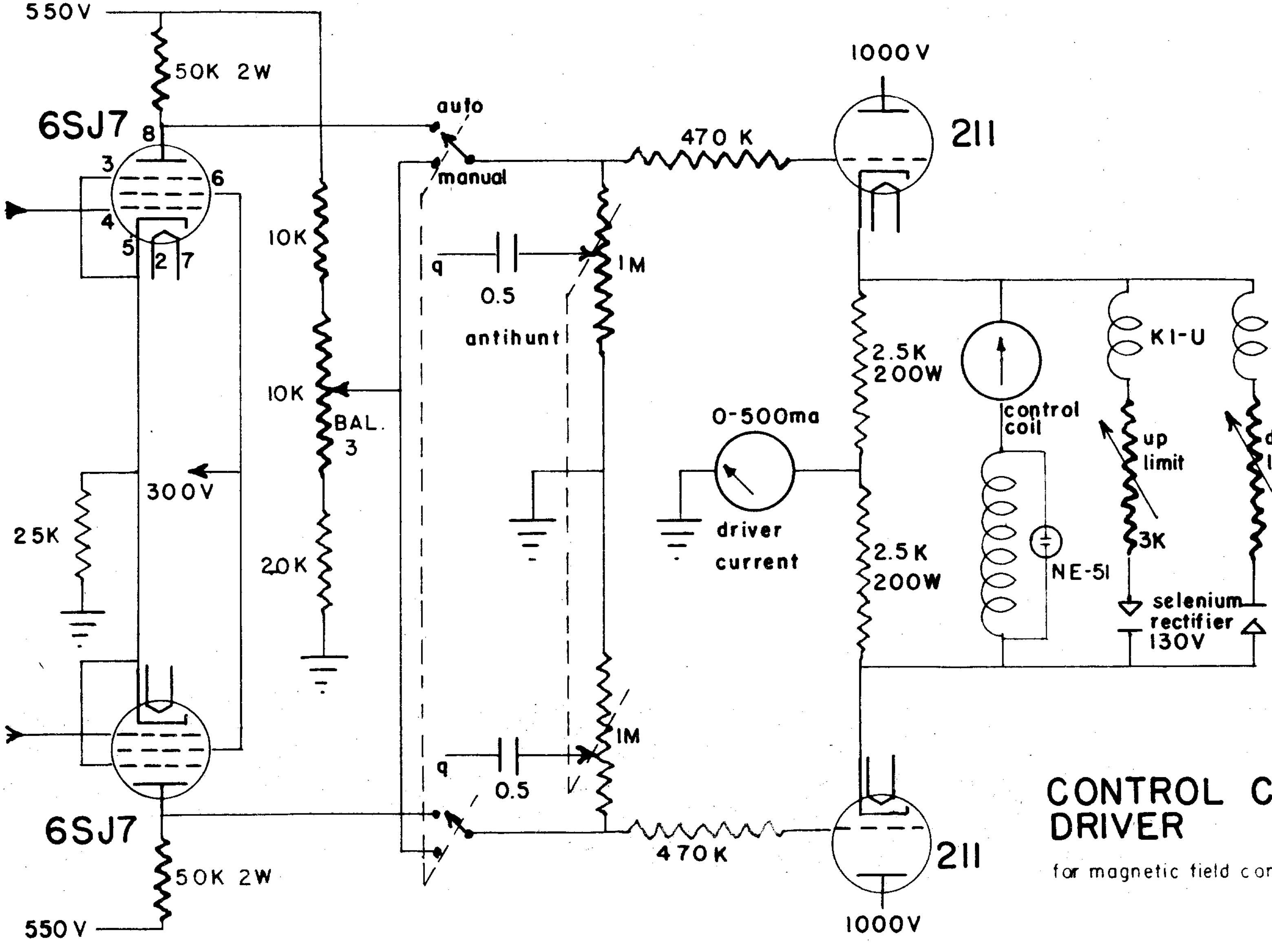
for magnetic field controller

* indicates 1000V mica



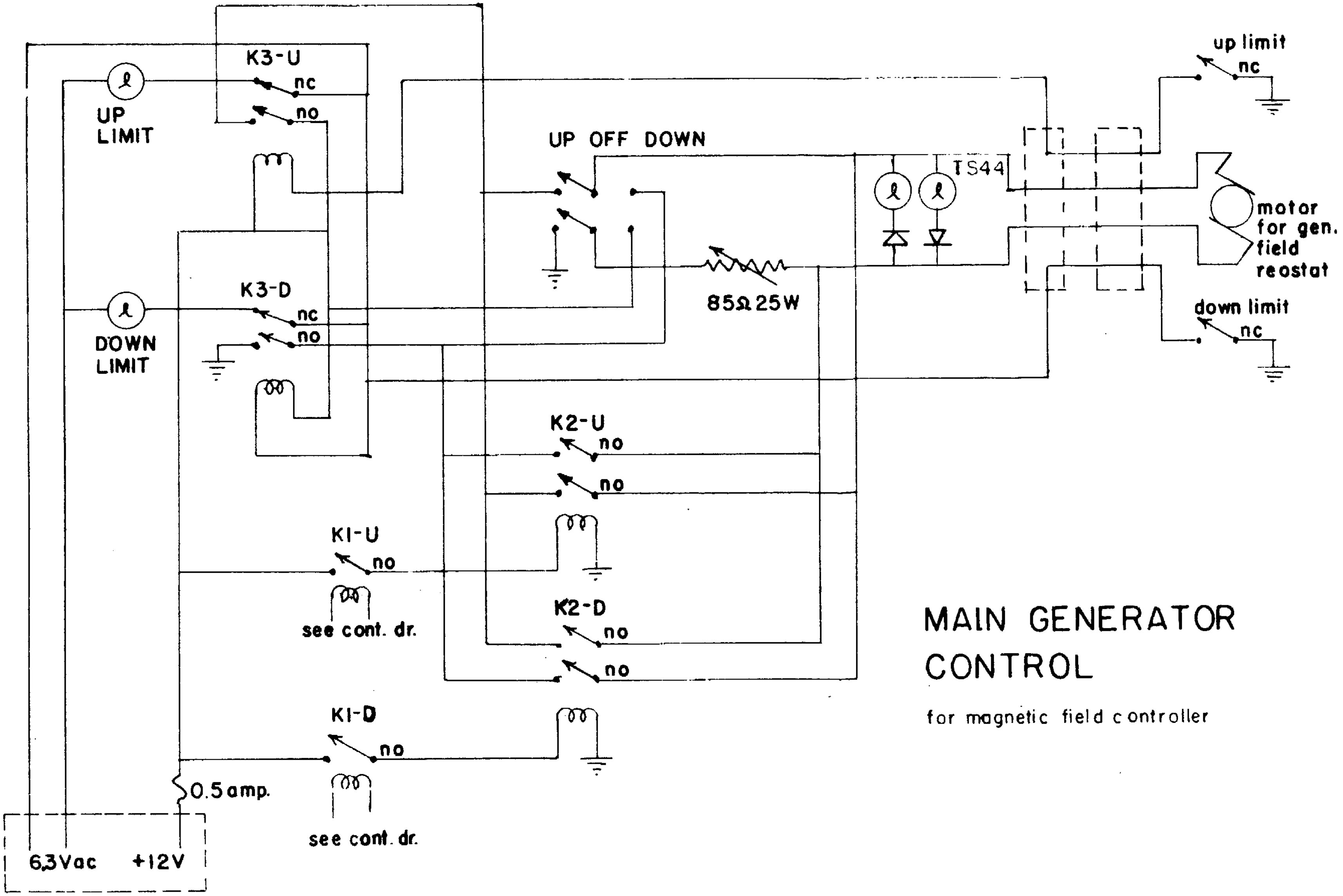
PHASE SENSITIVE DETECTOR

for magnetic field controller



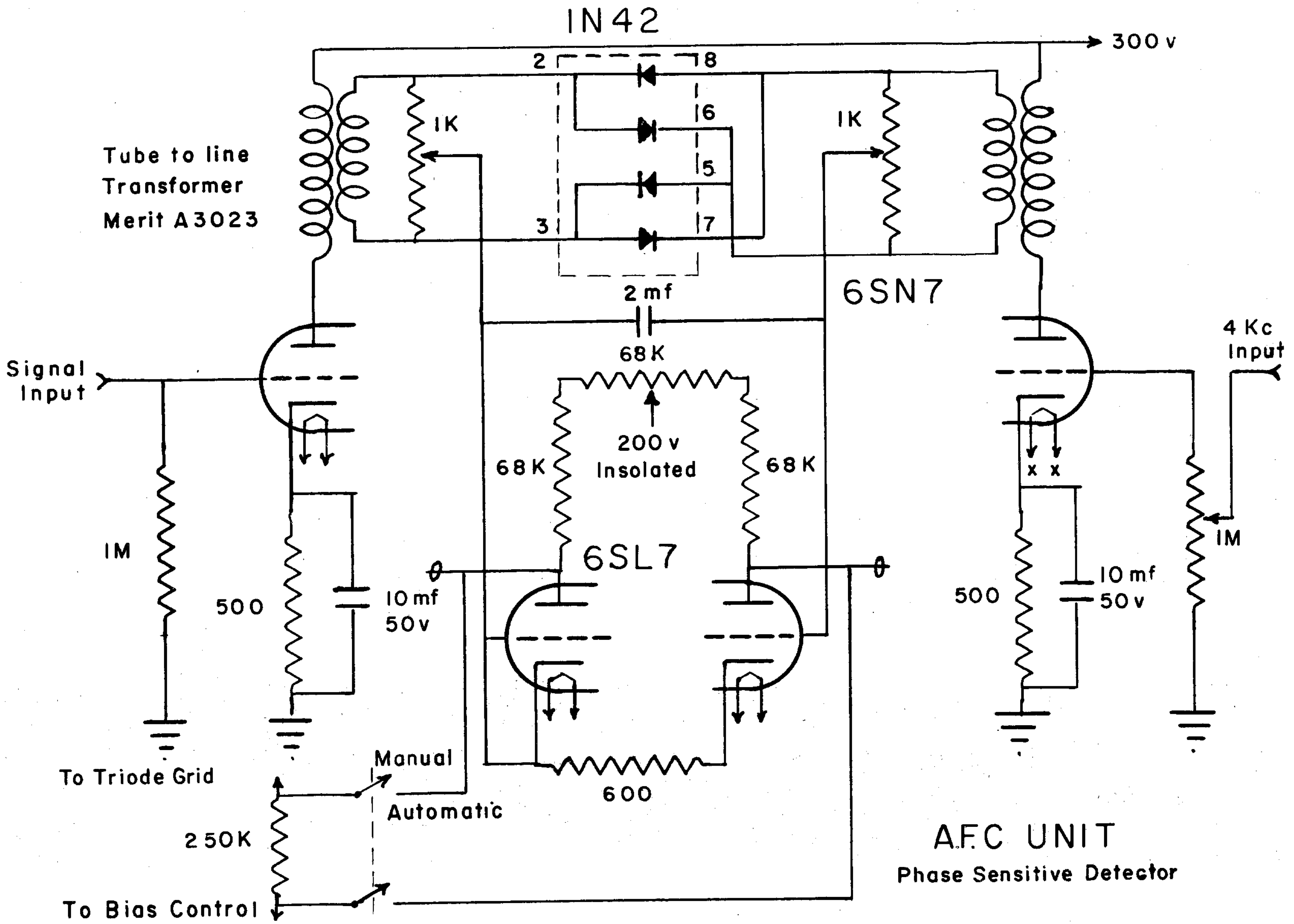
CONTROL COIL DRIVER

for magnetic field controller



MAIN GENERATOR CONTROL

for magnetic field controller



AFC UNIT
Phase Sensitive Detector

APPENDIX I

Calculation of the Resonance Condition

In a cyclotron resonance experiment, Gardner(58) carefully measured the ratio of ω_e, the cyclotron resonance frequency, to ω_p, the proton resonance frequency for the same magnetic field. His proton sample was water and the measured value of μ_p could be corrected if the free proton moment was desired. A water sample is used for operation of the magnetic field controller described herein, hence the uncorrected data are required for calculation of the resonance condition.

The cyclotron resonance condition is

$$\omega_e = \frac{eH}{mc} .$$

The proton resonance condition is

$$\omega_p = \frac{2\mu_p H}{\hbar} .$$

Their ratio is

$$\frac{\omega_e}{\omega_p} = \frac{eH}{mc} \frac{\hbar}{2\mu_p H} = \frac{\mu_o}{\mu_p}$$

where μ_o is the Bohr magneton $\mu_o = \frac{\hbar e}{2mc}$. Gardner reports the uncorrected value for this ratio as

$$\frac{\omega_e}{\omega_p} = 657.475 \pm 0.008,$$

so

$$\frac{2\mu_p}{\mu_o} = \frac{2}{657.475 \pm 0.008} = (3.04194 \pm 0.00004) \times 10^{-3}.$$

The paramagnetic resonance condition is

$$\hbar \omega_e = g \mu_o H = g \mu_o \frac{\hbar \omega_p}{2 \mu_p}$$

$$g = \frac{\omega_e}{\omega_p} \frac{2 \mu_p}{\mu_o} = \frac{\omega_e}{\omega_p} (30.4194 \pm 0.0004)$$

or

$$g = (3.04194 \pm 0.00004) \times 10^{-3} \frac{\nu_e}{\nu_p}$$

APPENDIX II

Calculation of Hyperfine Splitting.

The hyperfine structure hamiltonian used by Hurd, Sachs and Hershberger$^{(35)}$ is

$$H_{hfs} = AS_zI_z + \frac{1}{2}B(S_+I_- + S_-I_+)$$

where $S_\pm = S_x \pm iS_y$ and $I_\pm = I_x \pm iI_y$. S is the effective electronic spin and I is the nuclear spin. They calculated, using first-, second- and fourth-order perturbation theory, that the eigenvalues of H_{hfs} are

$$E^{hfs}_{Mm} = K'Mm + \frac{A'^2}{2g\beta H_o} \quad M[I(I+1) - m^2] - m[S(S+1) - M^2]$$

$$+ \frac{A'^4}{(2g\beta H_o)^3} \; [m^3\alpha(S) - M^3\alpha(I) + M^2m^3\,\Gamma(S) - M^3m^2\,\Gamma(I)$$

$$+ M^4m\;\varepsilon(I) - Mm^4\;\varepsilon(S) + m\;\Psi_S(I) - M\;\Psi_I(S)$$

$$+ Mm^2\;\emptyset_S(I) - M^2m\;\emptyset_I(S) + M^3m^4 - M^4m^3]$$

where

$$\alpha(x) = x(x+1)\;[4 - 3x(x+1)]$$

$$\Gamma(x) = [6x(x+1) - 9]$$

$$\varepsilon(x) = [3x(x+1) - 1]$$

$$\Psi_x(y) = [3x^2(x+1)^2\;y(y+1) - x^2(x+1)^2 - 4x(x+1)\;y(y+1) + 2x(x+1)]$$

$$\emptyset_x(y) = [6x(x+1)\;y(y+1) - 11x(x+1) - 2y(y+1) + 5]$$

$$K' = (\tfrac{1}{g})\;[A'^2\;g^2_{\parallel}\;\cos^2\theta + B'^2\;g^2_{\perp}\;\sin^2\theta]^{1/2} \approx A'.$$

M is the magnetic quantum number and m is the quantum number corresponding to the projection of I along in magnetic field.

The total eigenvalue is

$$E_{Mm} = g\beta HM + E_{M}^{fs} + E_{Mm}^{hfs}$$

Since the selection rule for transitions is $\Delta M = \pm 1$, the transition energy is

$$h\nu_{o} = E_{Mm} - E_{M-1,m} = g\beta H + (E_{M}^{fs} - E_{M-1}^{fs}) + (E_{Mm}^{hfs} - E_{M-1,m}^{hfs} - E_{M-1,m}^{hfs}).$$

Solving for the position of the line at constant frequency, one obtains

$$\begin{aligned} H = H_{o} &- (E_{M}^{fs} - E_{M-1}^{fs}) - Am - \frac{A^{2}}{2H_{o}}[I(I+1) - m^{2} + m(2M-1)] \\ &- \frac{A^{4}}{8H_{o}^{3}}[(4M^{3} - 6M^{2} + 4M - 1)(m\,\varepsilon(I) - m^{3}) \\ &+ (3M^{2} - 3M + 1)(m^{4} - m^{2}\,\Gamma(I) - \alpha(I)) \\ &+ (2M - 1)(m^{3}\,\Gamma(S) - m\,\phi_{I}(S)) + m^{2}\,\phi_{S}(I) - m^{4}\,\varepsilon(S) - \Psi_{I}(S)] \end{aligned}$$

where

$$H_{o} = \frac{h\nu_{o}}{g\beta} \qquad \text{and} \qquad A = \frac{A'}{g\beta} .$$

The splitting or distance between the lines for various changes in m are

$$\Delta = H_{Mm} - H_{M,m-1}$$

$$\Delta = -A + \frac{A^2}{2H_o} [(2m - 1) - (2M - 1)]$$

$$- \frac{A^4}{8H_o^3} [(4M^3 - 6M^2 + 4M - 1) \ (\varepsilon(I) - (3m^2 - 3m + 1))$$

$$+ (3M^2 - 3M + 1)(4m^3 - 6m^2 + 4m - 1 - (2m - 1) \ \Gamma(I))$$

$$+ (2M - 1)(3m^2 - 3m + 1) \ \Gamma(S) - \phi_I(S)) + (2m - 1) \ \phi_S(I)$$

$$- (4m^3 - 6m^2 + 4m - 1) \ \varepsilon(S)].$$

For $M = \frac{1}{2}$, $I = \frac{5}{2}$, and $S = \frac{5}{2}$

$$\Gamma(I) = \frac{87}{2} ; \qquad \phi_S(I) = \phi_I(S) = \frac{2805}{8} ; \quad \varepsilon(S) = \frac{101}{4}$$

and

$$\Delta = -A - \frac{A^2}{2H_o} (1 - 2m) - \frac{A^4}{8H_o^3} \left(\frac{1259}{4} + \frac{2318}{4} m + \frac{600}{4} m^2 - \frac{400}{4} m^3\right)$$

Hurd et. al give $A = 93.90 \pm 0.05$ gauss.

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PROPOSITIONS

1. A mechanism of migrating lattice defects has been proposed to explain the oxidation of nickel metal and also conductivity measurements made on NiO. (C. Wagner, Z. phys. Chem. 21, 25 (1933).) This model is the basis for a large group of mechanisms which can be substantiated in only a general way by the use of oxidation rate measurements. It is proposed that a precise study of the oxidation of nickel be made using the technique of paramagnetic resonance. Information obtained by this method would either put the present model on a firm foundation or would suggest the correct one.

2. Complexometric titrations have been used with considerable success to determine many metal ions, particularly those of the iron transition group. (R. Hara and P.W. West, Anal. Chim. Acta 12, 72 (1955).) It is proposed that this method can be considerably simplified by using a coulometric titration method. (D.D. DeFord, J.N. Pitts, and C.J. Johns, Chem. 23, 938 (1951).)

3. It is proposed that single crystals of $NaBH_4$ (W.H. Stockmayer, D.W. Rice, and C.C. Stephenson, J. Am. Chem. Soc. 77, 1980 (1955).) be used as scintillating crystals to form a simple, highly sensitive neutron scintillometer.

4. Chance and Fergusson assumed that the orbital contribution to the magnetic susceptibility of active peroxidase complex II is not completely quenched in order to account for the large deviations from

the expected value of the magnetic susceptibility which were observed. Such orbital contributions have also been assumed for the inactive cyanide complexes of catalase and peroxidase, but it is still not clear how the magnetic data should be interpreted in terms of bond types. (B. Chance and R.R. Fergusson, "A Symposium on the Mechanics of Enzme Action", McElroy and Glass Editors, Johns Hopkins Press, Baltimore, 1954, p. 389.) It is proposed that the method of paramagnetic resonance be used to investigate these compounds in order to determine the magnitude of the orbital contribution. Such an investigation should also give further insight into the valence states and bonding of the iron in these compounds.

5. A long, persistent after-glow has been observed in gaseous nitrogen. (Lord Rayleigh, Proc. Roy. Soc. 176, 1 (1940).) It is generally assumed that this after-glow is caused by the recombination of atomic nitrogen although reasonable doubt exists. (G. Boocock, H.O. Pritchard, and A.F. Trotman-Dickenson, Faraday Soc. Discussions 17, 104 (1954); G.R. Freeman and C.A. Winkler, J. Phys. Chem. 59, 371 (1955).) It is proposed that this effect can be studied by using the method of paramagnetic resonance.

6. Heat capacity measurements have been made recently for AsH_3 in the range around 32^oK. A gradual transition exists which is presumably due to the onset of molecular rotation. (R.H. Sherman and W.F. Giauque, J. Am. Chem. Soc. 77, 2154 (1955).) It is proposed that further study be done in this region using the method of nuclear resonance because the transition might be of an order-disorder type.

7. The rate of oxidation of cuprous copper by bromine has been observed to increase as the bromide ion concentration is increased. (G.M. Arcand, "Ph.D. Thesis", CIT, 1955.) At first glance, this is surprising since the cuprous bromide complex is known to be more stable than the cupric bromide complex. A model is proposed to account for this behavior.

8. The mechanism of vinyl polymerization involves the competition between radical-radical reactions and radical-scavenger reactions. (R.M. Noyes, J. Am. Chem. Soc. 77, 2042 (1955).) The characteristic times for these reactions are given as 10^{-13} sec and 10^{-11} sec respectively. It is proposed that paramagnetic resonance experiments can distinguish between the fragments involved in this reaction and indicate their ratio if such a model is the correct one.

9. The crystal structure of geranylamine-HCl has been determined by X-ray diffraction. (G.A. Jeffrey, Proc. Roy. Soc. 183, 388 (1945).) To explain the apparent anisotropic temperature factor observed in this determination, a model is used which involves one end of the molecule being fixed in space and the other end "wagging". It is proposed that additional information on this effect can be obtained from nuclear resonance experiments done at various temperatures.

10. A change in the stock room system for the Gates and Crellin Laboratories is proposed which would make the stock room more accessible and save the department money. A 24 hour serve-your-self system is suggested for graduate students which would require only one attendant per stock room for the undergraduates. Such a system

would make the stock available at hours outside the normal working day; the money saved in salary would more than compensate for any lack of cooperation on the part of the graduate students in checking out equipment.