# VI. MICROWAVE SPECTROSCOPY*


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## RESEARCH OBJECTIVES

Work in the Microwave Spectroscopy Laboratory may be characterized as both pure and applied paramagnetics. We have been interested in the properties of paramagnetic materials, gases, liquids, and solids, and in the application of paramagnetic materials in quantum-mechanical or paramagnetic amplifiers. In general, the work involves an understanding of, and the development of a description for, the physical behavior of paramagnetic materials from a quantum-mechanical point of view. We are interested in energy transfer between the nearly uncoupled degrees of freedom in a system, such as the spin and the lattice, or between the lattice degrees of freedom themselves, or between the lattice degrees of freedom and the surrounding temperature bath. This interest involves not only an understanding of the dynamic properties of matter such as its saturation characteristics in the presence of electromagnetic energy, but also its more static characteristics such as the linewidth of the paramagnetic resonance lines themselves, and its variation with temperature, concentration of paramagnetic ions, and the amount of ordering within the magnetic system itself.

This laboratory is now actively engaged in research that comes under the following classes: the hyperfine structure of paramagnetic atoms, atomic recombination measurements, relaxation within electron paramagnetic liquids, problems of spin-spin and spin-lattice relaxation in solid paramagnetic materials, properties of paramagnetic amplifiers, and their design and application.

M. W. P. Strandberg

## A. RUBY FREQUENCY STANDARD

The development of atomic and molecular frequency standards has been centered chiefly around the use of quantum transitions of very narrow bandwidth. This report concerns the possibility of using a ruby maser oscillator as such a standard. It has been held generally that because of the relatively broad resonance lines in solids, such materials would prove unsatisfactory in this application. There is reason for believing that this conclusion is unduly pessimistic.

It has been indicated (1) that the precision of the frequency determination of an oscillator is given by

$$P = R\left(\frac{P_{signal}}{P_{noise}}\right)^{1/2} \ln\left(\frac{P_{signal}}{P_{noise}}\right)^{1/2}$$

where P is the ratio of the resonant frequency to the width of the frequency probability


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curve, R is the ratio of the resonant frequency to the resonant linewidth, and $P_{signal}$, $P_{noise}$ are signal and noise powers, respectively.

The linewidth in ruby should be approximately $10^3$ times that for ammonia, but paramagnetic oscillators can be built to produce $10^6$ times the power from an ammonia maser oscillator. If extraneous effects on the frequency stability of solid-state devices could be minimized, similar performance for the two types of frequency standard might be expected.

The origin of the anomalous linewidth (minimum width, 14 gauss) of the paramagnetic centers in ruby is still uncertain. We should be able to achieve a linewidth of 2 gauss arising from the aluminum magnetic moments alone because, as we have shown in previous reports, the crystalline field inhomogeneity is negligible. Experiments imposed on the magnetic field can be minimized by employing a field-independent signal transition frequency. For push-pull pumping in ruby, with the c-axis oriented 54.8° with respect to the magnetic-field direction, this frequency is approximately 5.7 kmc, and a magnetic field of approximately 2 kilogauss is required. Such a field is readily obtained from an Alnico permanent magnet, and by controlling the temperature of the magnet at 1°C, the frequency-stability degradation caused by magnetic-field changes can be reduced to 1 part in $10^{10}$ when the oscillator is operated as we have indicated.

To examine the frequency stability of a ruby maser oscillator experimentally, two units with a nonreciprocal cavity structure (2), and with pink ruby crystals entirely filling the resonant cavities, have been built to operate at 8.4 kmc. Other workers have found that serious frequency pulling may result from changes in the load as seen by the oscillator. The present design employs a cylindrical cavity operating in the $TE_{111}$ mode, excited in two spatially orthogonal degenerate modes that are driven $\pi/2$ radians out of phase. The unidirectional properties of this cavity should minimize frequency pulling caused by load variations.

At the present time, the two oscillator units are being cold-tested. Preliminary measurements will be made to determine the relative frequency stability when the oscillators are operated simultaneously in the same magnetic field. The effect of magnetic-field variations on the frequency difference should thus be removed. More work, with the use of superconducting solenoids to provide the stable magnetic field that is required for operation as a frequency standard, is planned. Push-pull pumping at 21,660 mc will be employed, and the signal transition will be between the two center levels of the four energy levels that are being used. Pumping at 34,600 mc between the two outside levels is also being considered.

R. A. McFarlane

References

1. M. W. P. Strandberg, a paper presented at the Symposium on Generation, Frequency Stabilization, and Amplification of Electromagnetic Oscillations by Atomic and Molecular Resonances, Asbury Park, New Jersey, Feb. 29, 1956.

2. M. W. P. Strandberg, Unidirectional paramagnetic amplifier design (to be published in Proc. IRE).

## B. SPIN-LATTICE RELAXATION

As other members of this group have pointed out (1, 2), in a multilevel system there is no one-to-one correspondence between spin-lattice relaxation times, as measured by the rf saturation method or by relaxation methods, and the spin-phonon transition probabilities calculated from theory. The pertinent relations have been calculated for a four-level system, with the assumption that it can be represented by a system of rate equations (3).

With the relaxation method we have to solve the matrix equation

$$\dot{N} = WN$$

with the constraint $\sum_{i=1}^{4} N_i = \text{constant}$. Here, N is a column matrix, with $N_i$, the concentration of particles in the $i^{th}$ state; $W_{ij} = w_{ij} + V_{ij}$ $(i \neq j)$, with $w_{ij}$, the lattice-induced transition probability of a particle going from state j to state i, and $V_{ij} = V_{ji}$, the transition probability associated with an external field; and $W_{ii} = -\sum_{j} w_{ji}$ $(j \neq i)$.

Observe that any one of the rate equations is the negative sum of the other three. Therefore if we pick any three rate equations, and then eliminate the odd concentration by using the conservation equation, we obtain, in general, a system of three linearly independent coupled equations which gives the matrix equation

$$\dot{X} = A_o + AX$$

where $X_i$ is a concentration, and the elements of $A_o$ and A are dependent upon the total number of particles, the $w_{ij}$'s and $V_{ij}$'s. To remove the constant term, let

$$B = X - X_o, \quad AX_o = -A_o$$

The components of $X_o$ can easily be found by Cramer's method. This yields the equation

$$\dot{B} = AB$$

Whence we have an ordinary eigenvalue problem. First, we find the eigenvalues $\lambda_i$ (i=1, 2, 3) of A:

$$|A-\lambda| = 0, \quad \lambda_{ij} = \lambda_i \delta_{ij}$$

Then the solution is

$$B = DC$$

where C is a column matrix, with $C_i = e^{+\lambda_i t}$, and D is a matrix that is such that

$$D\lambda = AD$$

The three independent components of D can be determined by the concentrations given for t = 0. If these conditions require that $N_i(t=0) = N_j(t=0)$, then their rate equations cannot be used to determine the independent components of D.

The rf solution is the solution obtained by using the procedure discussed above for t = 0. We shall give the solution explicitly for an important case.

For $E_4 > E_3 > E_2 > E_1$, and $E_4 - E_1 \ll kT$, we use the approximation

$$\exp[(E_j-E_i)/kT] \approx 1 - \frac{E_i - E_j}{kT}$$

and for i > j,

$$w_{ji} n_i \approx w_{ij}\left(1 - \frac{E_j - E_i}{kT}\right) n_i \approx w_{ij} n_i - \frac{E_j - E_i}{kT}\frac{N}{4}$$

because

$$n_i = \frac{N}{4}\left[1 + 0\left(\frac{E_j - E_i}{kT}\right)\right]$$

Then let

$$w(ij) \equiv \begin{cases} w_{ji} & \text{for } j > i \\ w_{ij} & \text{for } i > j \end{cases}$$

$$\sum_i{}' (ij) \Rightarrow i \neq j$$

$$\beta(ij) \equiv w(ij)\frac{E_i - E_j}{kT}$$

If there is a small rf field-induced $V_{ij}$, then it follows that $w(ij) \rightarrow w(ij) + V_{ij}$, but $\beta(ij)$ does not change; that is, there is no $V_{ij}$ term included in $\beta(ij)$. For saturation between levels n and m, we have

$$n_\ell = \frac{N}{4}\left\{1+\frac{1}{4}A_{\ell k}B^{-1}\right\}$$

$$n_k = \frac{N}{4}\left\{1+\frac{1}{4}A_{k\ell}B^{-1}\right\}$$

$$n_m = \frac{N}{4}\left\{1-\frac{1}{8}(A_{\ell k}+A_{k\ell})B^{-1}\right\}$$

where

$$A_{\ell k} = \left[3\sum_i{}' w(ik) - w(\ell k)\right]\sum_j \beta(j\ell) + \left[3w(\ell k) - \sum_i{}' w(i\ell)\right]\sum_j \beta(jk)$$

$$B = \left[\sum_i{}' w(i\ell)\right]\left[\sum_j{}' w(j\ell)\right] - w^2(\ell k)$$

The experimental results can now be related to the $w_{ij}$'s, for they give values for either $n_i - n_j = f(t)$ or $(n_i-n_j)_{saturated}/(n_i-n_j)_{equilibrium}$.

J. D. Stettler

## References

1. B. W. Faughnan, Investigation of lattice-phonon models by interaction with parametric spin levels, Ph.D. Thesis, Department of Physics, M.I.T., September 1959.

2. R. D. Mattuck, Phonon-spin absorption in paramagnetic crystals, Ph.D. Thesis, Department of Physics, M.I.T., May 1959.

3. N. Bloembergen, Phys. Rev. 104, 324 (1956).

## C. MASER CIRCUITS WITH NEGATIVE L AND C

The physical mechanisms that restrict bandwidth in electronic circuits can often be represented by equivalent lumped reactive circuit elements. The shunt capacitance of tubes is, in fact, such an element. The finite linewidth of paramagnetic resonance lines can be represented by an equivalent RLC circuit. Such a representation is accurate for Lorentz-shaped lines but is only an approximation in the central region for Gaussian lines.

There is, of course, a large literature on networks for achieving desirable bandpass characteristics in the presence of these limitations, by means of cascading, coupled circuits, stagger-tuning, or more sophisticated means. Fano (1), and others, have discussed the basic theoretical limitations on such networks.

The interesting point about masers is that the natural equivalent circuit for an inverted paramagnetic resonance line contains not only negative R but also negative L

and C properties, in the sense that the change of reactance with frequency is reversed. This fact opens up new possibilities for coupling networks, and permits gain-bandwidth products in a given situation that are in excess of values to be expected from the line-width.

The reactance reversal arises from the solution of the equations of motion of the spin system. For any doubters, it can be readily observed experimentally.

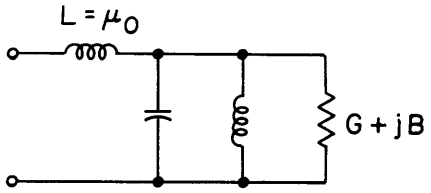
The permeability of a region containing paramagnetic material is given in terms of the complex susceptibility

$$\mu = \mu_o(1+\chi'-j\chi'')$$

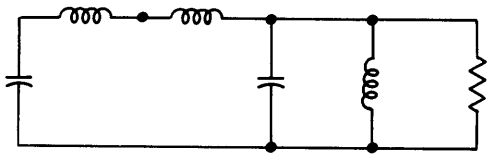
In the frequency range of a paramagnetic resonance line (if a Lorentzian line is assumed) the susceptibility can be given in terms of the peak absorption $\chi''_{max}$ and the linewidth $1/T_2$. Hence

$$\mu = \mu_o\left(1 - \frac{j\chi''_{max}}{1 + jT_2\Delta\omega}\right)$$

If, for equivalent circuit purposes, we set $\mathscr{H} \rightarrow$ I, and $-\nabla \times \mathscr{E} \rightarrow$ V, the resonance can be diagrammed as




where $G = 1/(\mu_o\chi''_{max}\omega_o)$ and $jB = j[T_2\Delta\omega/(\mu_o\chi''_{max}\omega_o)]$. If the paramagnetic material is in a resonant cavity, the circuit becomes

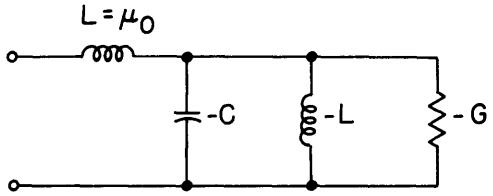


in which the added capacitance, of course, represents electric-field energy, and the added inductance represents magnetic-field energy in any additional cavity volume outside the paramagnetic sample.

If the resonance is inverted by three-level pumping or other means, the permeability becomes

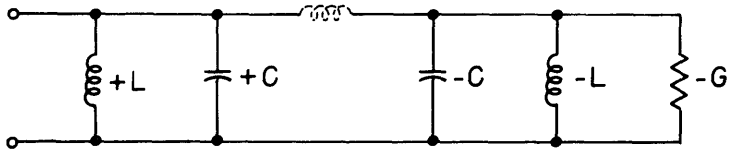
$$\mu = \mu_o\left(1 + \frac{j\chi''_{max}}{1 + jT_2\Delta\omega}\right)$$

and the equivalent circuit becomes

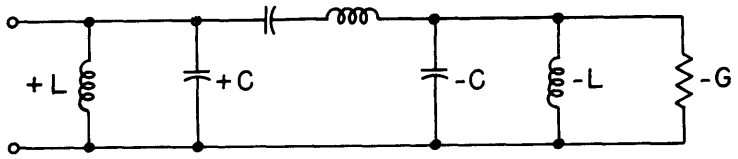



where $\chi''_{max}$ is still taken positive.

If it were not for the $\mu_o$ term, one could achieve very large bandwidth by tuning out the negative L and C with positive L and C as indicated in the following diagram:




As it is, something can still be achieved by resonating the L and adding a second cavity coupled to the first. With suitable choices of impedance level, the equivalent circuit for such a two-cavity circuit can be represented as follows:




SECOND CAVITY | MASER CAVITY | PARAMAGNETIC RESONANCE

It is intuitively evident that the largest gain-bandwidth product will be achieved if the series-L term representing $\mu_o$ is minimized relative to the maser material. This means that the filling factor and the value of $\chi''_{max}$ must be kept as large as possible. For significant use of the negative reactance properties we need $XG \leq B/G$, where G and B refer to the paramagnetic material, and X is the cavity reactance. If we can achieve a unity filling factor, this expression reduces to

$$\chi''_{max} \geq \frac{1}{\omega_o T_2}$$

or in terms of the resonance linewidth, $\Delta\omega_{para}$, we have

$$\chi''_{max} \geq \frac{\Delta\omega_{para}}{\omega_o}$$

For "pink" ruby at 4°K under optimum conditions, this requirement is just about met.

$$\chi''_{max} \approx \frac{\Delta\omega_{para}}{\omega} \approx \frac{1}{200}$$

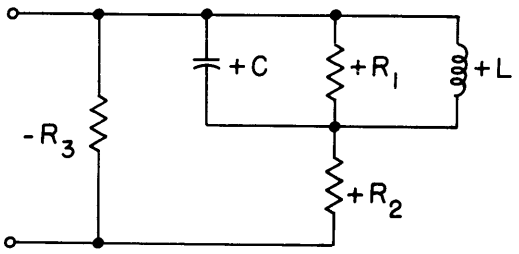
Changing the chromium concentration does not give much improvement. Lowering the concentration reduces $\chi''_{max}$, but raising the concentration increases $\Delta\omega_{para}$. The increase is all to the good because it increases the intrinsic bandwidth, but it does interfere with the types of schemes discussed here.

It is to be expected that advances in maser materials will result in higher $\chi''_{max}$ values for a given bandwidth, and hence significance will be given to these circuit considerations. For materials available now, improvements should result from using higher operating frequency and lower temperature.

Figure VI-1 shows the gain versus frequency that is to be expected from a circuit of the type shown above with B/G = XG. Figure VI-2 shows a similar plot for a hypothetical material for which B/G = 2XG.

It is to be expected that if the second cavity also contains an inverted paramagnetic resonance, the over-all performance will be still more improved. Experimental work along these lines has already been done by F. E. Goodwin, G. E. Moss, and coworkers (2). Traveling-wave networks utilizing these properties are another possibility.

It would be interesting to obtain basic network theorems concerning the limitation on circuits containing elements of this kind. The negative L and C properties are reproducible when only negative R is used in a circuit of the following type:




$|R_2| = |R_3|$

but such a circuit is not realizable with maser materials. Incidentally, these negative L and C properties do not appear in parametric amplifiers. The broadbanding

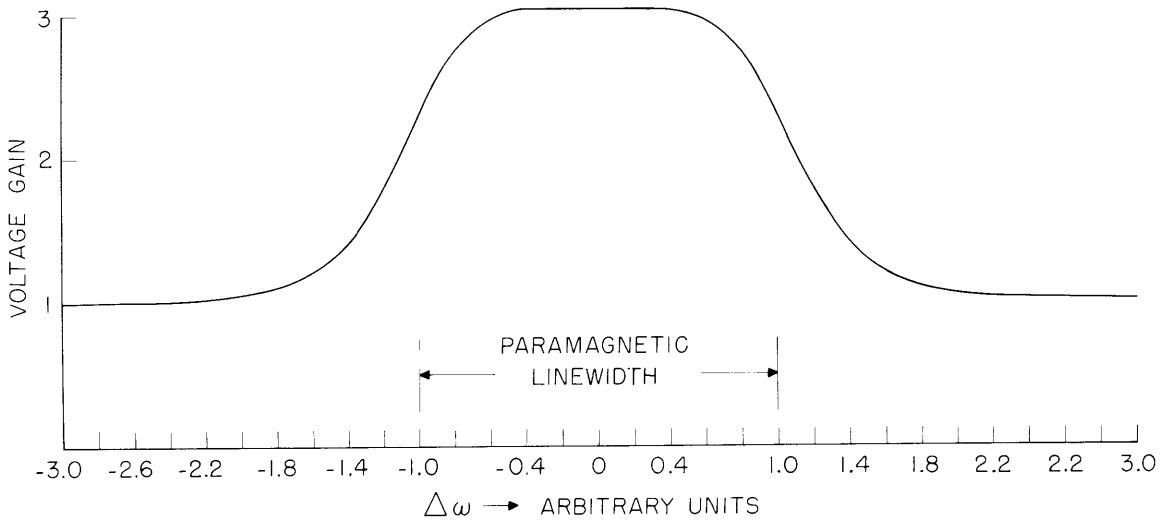



Fig. VI-1. Gain versus frequency characteristic for a reactance-compensated paramagnetic amplifier with $X = B/G^2$, or $\chi''_{max} = (\omega_o T_2)^{-1}$.

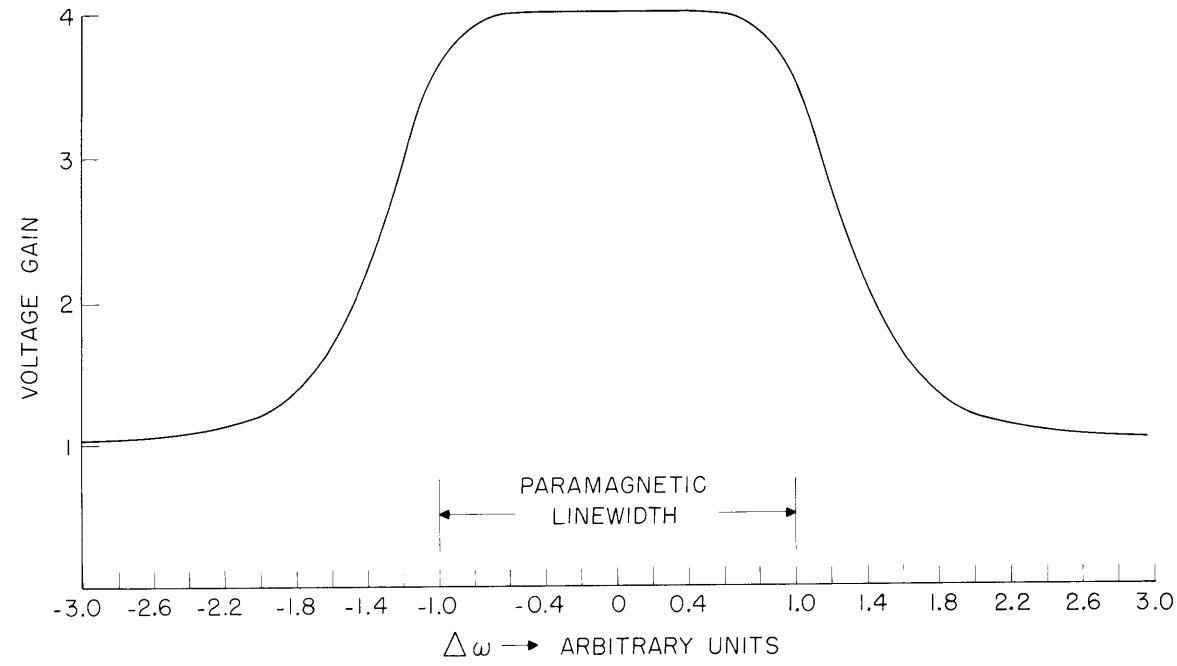



Fig. VI-2. Gain versus frequency characteristic for a reactance compensated paramagnetic amplifier with $2X = B/G^2$, or $\chi''_{max} = 2(\omega_o T_2)^{-1}$.

possibilities there, as discussed, for example, by H. Seidel (3), are of a more conventional type.

R. L. Kyhl

References

1. R. M. Fano, Theoretical limitations on the broadband matching of arbitrary impedances, J. Franklin Inst. 249, 57 (January 1950); 139 (February 1950).

2. F. E. Goodwin and G. E. Moss, Hughes Aircraft Company, Culver City, California (private communication, Nov. 12, 1959).

3. H. Seidel and G. F. Herrmann, Circuit aspects of parametric amplifiers, IRE WESCON Record, Part 2 (Circuit Theory), 1959, p. 83.

## D. A SECONDARY STANDARD FOR ELECTRON PARAMAGNETIC-RESONANCE EXPERIMENTS

A powdered sample of magnesium oxide (MgO) sealed in glass has been made for use as a standard in electron paramagnetic-resonance measurements. It has the advantage of being sufficiently compact (2.5 cm × 2 mm) to fit into any of the microwave cavities that are now being used in this laboratory, and it is also chemically stable. The standard has one absorption line, approximately 2 gauss wide, arising from the paramagnetic impurity ion $Cr^{+++}$ in a cubic environment. The narrowness of the line will interfere very little with any spectrum that is of interest and, since it is a powder, the line is also independent of magnetic-field orientation.

The standard was calibrated by comparing it with known lines of molecular oxgen, which was used as a primary standard.

The values of interest for the MgO standard are:

$$4\pi\chi'' = 8.0 \times 10^{-8}$$

$$n = 7.5 \times 10^{12} \text{ spins}$$

A discussion of the theory and experimental details has been given elsewhere (1).

J. D. Kierstead, P. C. Clapp, M. W. P. Strandberg

References

1. Research on Paramagnetic Resonances, Ninth Quarterly Progress Report on Signal Corps Contract No. DA36-039-sc-74895, Research Laboratory of Electronics, M.I.T., Aug. 15, 1959 - Nov. 15, 1959, p. 25.