IV. MICROWAVE SPECTROSCOPY*

Prof. M. W. P. Strandberg
Prof. R. L. Kyhl
Dr. B. W. Faughnan
Dr. B. V. Gokhale
Dr. R. D. Mattuck
Dr. G. J. Wolga

J. M. Andrews, Jr.
P. C. Clapp
W. J. C. Grant
J. G. Ingersoll
J. D. Kierstead
D. W. Oliver

D. J. M. Park, Jr.
W. J. Schwabe
J. D. Stettler
Winifred F. Tank
S. H. Wemple
R. M. White

A. PHONON-SPIN ABSORPTION IN PARAMAGNETIC CRYSTALS

In order to obtain more information about the bandwidth of the spin-phonon inter-action in F-center quartz, an experiment was performed at a phonon frequency of 13 mc, with spin resonance at 189 mc. At the maximum phonon power input of 0.2 watt the size of the absorption signal decreased by a factor of 0.6. This is to be compared with a saturation of 0.5 at spin-resonance frequency of 13.7 mc, and of 0.3 at 19.1 mc. The conclusion is that the bandwidth of the saturation effect is larger than 160 mc. This agrees with the results of microwave phonon experi-ments by Jacobsen, Shiren, and Tucker (1), which revealed a minimum bandwidth of 1000 mc.

An acoustic experiment was also conducted on Cr^{+++}-doped magnesium oxide. Microwave spectra have indicated that because of the nearly perfect cubic symmetry of the crystalline field, the zero-field splitting is negligible. Hence it was predicted (2) that the acoustic saturation, S/S_O (ratio of signal with phonon power on to signal with phonon power off), would be detectable in this material. The bandwidth of the saturation effect should be equal to the spin linewidth, that is, approximately 10 mc. The acoustic saturation was observed, but it was somewhat anomalous. When the spin-resonance frequency was approximately equal to the phonon frequency of 13 mc, the saturation was maximum, with S/S_O = 0.38. At a spin-phonon frequency difference of ±2.0 mc, the saturation was S/S_O = 0.48, while at +7.0 mc, it appeared to reach a constant value of S/S_O = 0.57. Theoretically, we would expect that at this distance from resonance, the phonon-spin interaction should be much weaker, and S/S_O should be much closer to 1. We could account for such behavior by assuming that in addition to the direct interaction, the phonons cause thermal heating of the crystal. This would result in an S/S_O ratio that is independent of frequency. To test this hypothesis, an experiment will be performed with phonon frequency at 13 mc and spin frequency at 189 mc. If the S/S_O factor is still equal to 0.57, this experiment would constitute strong evidence in favor of a thermal-heating assumption.

R. D. Mattuck

References

1. E. H. Jacobsen, N. F. Shiren, and E. B. Tucker, Phys. Rev. Letters $\underline{3}$, 81 (1959).

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

B. PHONON TRANSPORT IN MAGNESIUM OXIDE

More experiments have been performed on phonon transport in magnesium oxide (MgO). The purpose of these experiments was to give measurements that have been reported (1) elsewhere a firm experimental foundation.

Paramagnetic-resonance spectra were run on the available MgO crystals at room temperature, liquid-nitrogen temperature, and liquid-helium temperature. At room temperature the most intense line arises from Cr^{3+} ions in a cubic crystal field. Other lines occur that can be ascribed to Mn^{2+} and Fe^{3+} impurities. At liquid-nitrogen and liquid-helium temperatures still another line appears that is slightly more intense than the chromium line and has a g-value of approximately 2.00. Since an attempt was made to diffuse titanium into these crystals, this line could be attributed to the Ti^{3+} ion. However, no hyperfine structure was observed, as would be expected from the two isotopes of titanium which have nuclear spin. These two isotopes are Ti^{47} with nuclear spin 5/2 and a natural abundance of 7.7 per cent, and Ti^{49} with nuclear spin 7/2 and a natural abundance of 5.5 per cent. These isotopes should give rise to hyperfine lines of approximately 1 per cent of the intensity of the central Ti^{3+} line. It may be that the hyperfine coupling constant is too large or too small, which would make the observation of hyperfine structure difficult. In the former case, the hyperfine lines would be widely separated and could be confused with lines from other impurities in the crystal. In the latter case, the hyperfine structure would merely contribute to broadening of the main line.

Phonon excitation experiments were tried only on the resonances arising from the chromium ion and the unidentified ion. There is some evidence that the phonon effect that was observed (1) in an experiment in which resonances with short relaxation time $(10^{-3}$ sec) were used, is really caused by direct coupling of the microwave field between the pump and monitor cavities. The measured saturation parameter for this line was found to be smaller than was previously thought. We found that $P_{sat} = 10^{-6}$ watt, approximately. The small amount of power required for saturating the resonance makes it possible for a small microwave-leakage field to give rise to an observable effect in the monitor cavity. Runs were tried on a broken crystal, and a signal caused by microwave leakage between cavities was observed.

The small value of the saturation parameter for the two resonances studied means

that the monitor power should be smaller than that previously used, that is, it should not be greater than 10^{-6} watt. Then the results of phonon transport might be observable for small amounts of pump power, and could be distinguished from the signal caused by saturation from direct microwave leakage, which decreases in a known way with pump power. Performing the experiment in this manner may give results similar to those observed by using the resonance with the long relaxation time previously reported. In that case a small persistent signal, attributable to phonon transport, was observed after the microwave-leakage field had decreased beyond the limit of observation. Experiments of this kind are now being carried out.

B. W. Faughnan

References

1. Research on Paramagnetic Resonances, Seventh Quarterly Progress Report on Signal Corps Contract No. DA36-039-sc-74895, Research Laboratory of Electronics, M.I.T., Feb. 15, 1959 - May 15, 1959, p. 2.

C. ADIABATIC FAST-PASSAGE EXPERIMENTS

Equipment has been assembled for the study of the adiabatic fast-passage mechanism in an electron-spin system. Our interest is in the "slow AFP" region, in which the time required to sweep through the linewidth of the transition is long compared with T_2 but short compared with T_1.

Theoretical analysis indicates (1) that spin inversion is possible under these conditions, provided that the rf field strength is strong enough. Experimental investigation of this process should provide additional information on the spin-relaxation mechanism.

The present equipment achieves a magnetic-field sweep rate of 40 gauss per millisecond by discharging a capacitor through the existing magnet modulating coils. This value is not too large, but is probably adequate. It will be possible to increase the sweep rate if the need arises. The rf excitation is provided by a 500-mw Varian V-58 klystron that is pulsed to keep down the average dissipation in the sample.

The Smith-chart plotter will be used for the observations.

R. L. Kyhl

References

1. See B. V. Gokhale's report, Section IV-E.

D. CASCADED CAVITY MASER

The physical structure for a four-cavity cascade maser incorporating the unidirectional gain feature described, for example, by M. W. P. Strandberg (1), has been
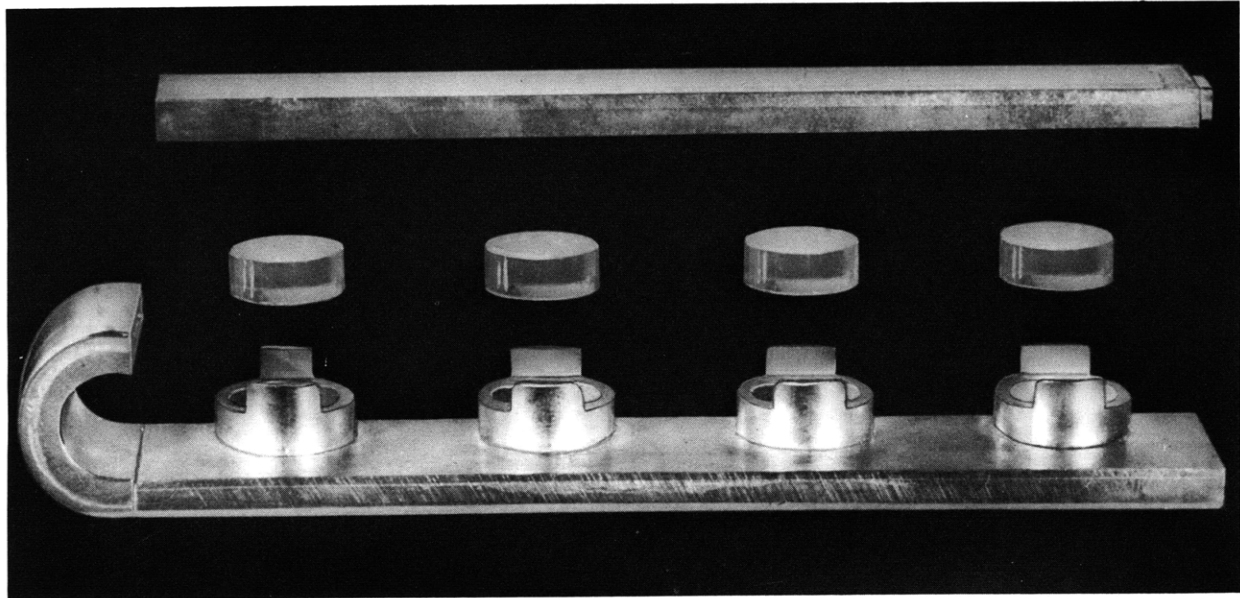
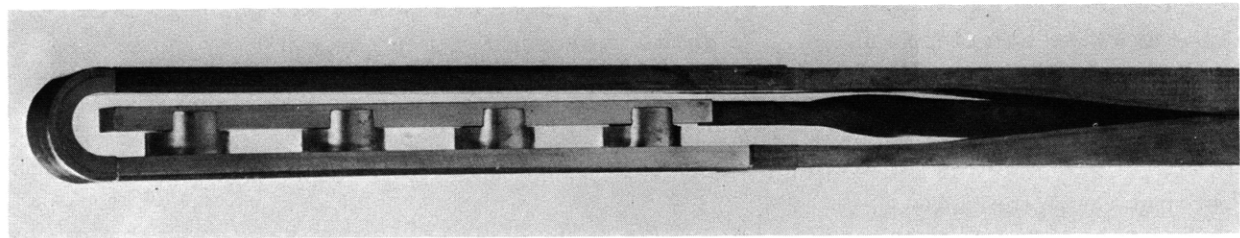Fig. IV-1. Traveling-wave amplifier cavity assembly.

Fig. IV-2. Traveling-wave amplifier waveguide assembly.

constructed. Figure IV-1 shows the cavity assembly. The four cylindrical cavities for operation in the TE_{111} circularly polarized mode are placed along the X-band signal waveguide. The narrow waveguide dimension provides tight coupling to the cavities and also saves space in the cryostat. The rubies, which fill the cavities, are approximately 15 mm in diameter and 6 mm high. They are now being ground. The c-axis will be parallel to the axis of the cavity. Coupling holes to the signal waveguide are located at the circularly polarized position (2). The K-band pump waveguide is shown in Fig. IV-2.

Preliminary rf tests have shown some residual reflections in the waveguide which may have to be tuned out.

R. L. Kyhl

References

1. M. W. P. Strandberg, Unidirectional paramagnetic amplifier design (submitted for publication, June 25, 1959, to Proc. IRE).

2. M. Tinkham and M. W. P. Strandberg, The excitation of circular polarization in microwave cavities, Proc. IRE 43, 734-738 (June 1955).

E. PROPOSED MODIFICATION OF BLOCH'S EQUATIONS

Redfield (1) has discussed the inadequacy of the Bloch equations (2) describing the time dependence of the magnetization of a system of coupled spins, and he suggested modifications that were necessary to describe his own observations on nuclear magnetic resonance with large radiofrequency power. Here we attack the problem in the same spirit but obtain an essentially simpler result.

A spin system subject to a steady field $H_z = H_o$ and an rf field $H_X = H_1 \cos \omega t$, but otherwise completely isolated from its surroundings, can be most easily discussed in a rotating coordinate system with the aid of an "effective Hamiltonian" $\mathscr{F}$.

The magnetic-moment operator $\vec{M}$ has components M_x, M_y, M_z in the rotating coordinate system which are related to the components M_X, M_Y, M_Z in the fixed coordinate system as

$$M_x = M_X \cos \omega t - M_Y \sin \omega t$$

$$M_y = M_X \sin \omega t + M_Y \cos \omega t \tag{1}$$

$$M_z = M_Z$$

The effective Hamiltonian operator $\mathscr{F}$ is given by

$$\mathscr{F} = -\vec{M} \cdot \vec{H}_{eff} + V_{sp-sp} \tag{2}$$

Here V_{sp-sp} represents the mutual interaction energy of the spins (including dipole and exchange energies) from which nonsecular terms are omitted. The effective magnetic field $\vec{H}_{eff}$ is defined by its components in the rotating coordinate system:

$$\left(H_{eff}\right)_x = \frac{H_1}{2}, \quad \left(H_{eff}\right)_y = 0, \quad \left(H_{eff}\right)_z = H_o - \frac{\omega}{\gamma} \tag{3}$$

where γ is the magnetogyric ratio.

The quantum-mechanical equations for the time variation of the expectation values of the components of the magnetic moment are:

$$\frac{d}{dt}\left\langle M_x \right\rangle = \gamma H_{eff_z}\left\langle M_y \right\rangle - \frac{i}{\hbar}\left\langle M_x V - VM_x \right\rangle$$

$$\frac{d}{dt}\left\langle M_y \right\rangle = \gamma H_{eff_x}\left\langle M_z \right\rangle - \gamma H_{eff_z}\left\langle M_x \right\rangle - \frac{i}{\hbar}\left\langle M_y V - VM_y \right\rangle \tag{4}$$

$$\frac{d}{dt}\left\langle M_z \right\rangle = -\gamma H_{eff_x}\left\langle M_y \right\rangle$$

Exact integration of these equations is quite difficult. If the quantities $i/\hbar\left\langle M_x V - VM_x \right\rangle$ and $i/\hbar\left\langle M_y V - VM_y \right\rangle$ are replaced by the simple damping terms $\left\langle M_x \right\rangle/T_2$ and $\left\langle M_y \right\rangle/T_2$, we obtain Bloch's equations for $T_1 \rightarrow \infty$.

It is easy to understand the asymptotic behavior of the solutions of Eqs. 4 for $t \rightarrow \infty$. Let us assume that the spin system is in thermal equilibrium at a certain (not too low) temperature T before the application of the rf field. The result of applying the rf field must be the establishment, after a sufficiently long time, of a Boltzmann distribution for a new temperature T' and the new Hamiltonian $\mathscr{F}$. The temperature T' can be calculated from the requirement for the constancy $\left\langle \mathscr{F} \right\rangle$ throughout the process (3). From these considerations, it can be seen that if the initial values (before the application of the rf field) of the magnetic moment are $\left\langle M_x \right\rangle_o = 0$, $\left\langle M_y \right\rangle_o = 0$, $\left\langle M_z \right\rangle_o = \left\langle M_z \right\rangle_o$, then the ultimate or final values predicted by Eqs. 4 are:

$$\left\langle M_x \right\rangle_f = \left\langle M_z \right\rangle_o \frac{\frac{H_1}{2}(H_o-\omega/\gamma) + \frac{H_1}{2}\frac{H_L^2}{H_o}}{\frac{(H_1)^2}{2} + (H_o-\omega/\gamma)^2 + H_L^2} \approx \left\langle M_z \right\rangle_o \frac{\frac{H_1}{2}(H_o-\omega/\gamma)}{\frac{(H_1)^2}{2} + (H_o-\omega/\gamma)^2 + H_L^2}$$

$$\left\langle M_y \right\rangle_f = 0 \tag{5}$$

$$\left\langle M_z \right\rangle_f = \left\langle M_z \right\rangle_o \frac{(H_o-\omega/\gamma)^2 + (H_o-\omega/\gamma)\frac{H_L^2}{H_o}}{\frac{(H_1)^2}{2} + (H_o-\omega/\gamma)^2 + H_L^2} \approx \left\langle M_z \right\rangle_o \frac{(H_o-\omega/\gamma)^2}{\frac{(H_1)^2}{2} + (H_o-\omega/\gamma)^2 + H_L^2}$$

Here, H_L is the local field defined by $\text{tr}(V^2) = H_L^2 \, \text{tr}(M_z^2)$.

Acceptable approximations to Eqs. 4 must yield Eqs. 5 as the steady-state solutions. Bloch's equations (in the limit $T_1 \to \infty$) are unacceptable by this criterion, but they can be made acceptable simply by changing the damping term $\langle M_x \rangle / T_2$ to $\left[\langle M_x \rangle - \langle M_x \rangle_f\right] / T_2$. Finally, the effect of spin-lattice relaxation can be taken into account by adding damping terms proportional to $1/T_1$ to all three equations of Eq. 5. We then obtain the modified Bloch equations

$$\frac{d}{dt}\langle M_x \rangle = (\gamma H_o - \omega)\,\langle M_y \rangle - \langle M_x \rangle \left(\frac{1}{T_1} + \frac{1}{T_2}\right) + \frac{\langle M_x \rangle_f}{T_2}$$

$$\frac{d}{dt}\langle M_y \rangle = -(\gamma H_o - \omega)\,\langle M_x \rangle + \frac{\gamma H_1}{2}\langle M_z \rangle - \langle M_y \rangle \left(\frac{1}{T_1} + \frac{1}{T_2}\right) \tag{6}$$

$$\frac{d}{dt}\langle M_z \rangle = -\frac{\gamma H_1}{2}\,\langle M_y \rangle - \frac{\langle M_z \rangle}{T_1} + \frac{\langle M_z \rangle_o}{T_1}$$

Equation 6 becomes identical with the usual Bloch equation if we set $\langle M_x \rangle_f = 0$.

Assuming, for simplicity, that $T_1 \gg T_2$ so that $1/T_1 + 1/T_2 \approx 1/T_2$, and defining the susceptibilities χ', χ'' by

$$\langle M_X \rangle = \langle M_x \rangle \cos \omega t + \langle M_y \rangle \sin \omega t = H_1(\chi' \cos \omega t + \chi'' \sin \omega t)$$

we obtain, from Eq. 6,

$$\chi' = \frac{1}{2}\omega_o \chi_o T_2 \frac{(\gamma H_o - \omega)T_2 + \left[1 + \frac{(\gamma H_1)^2}{2}T_1 T_2\right]\dfrac{(\gamma H_o - \omega)T_2}{\frac{(\gamma H_1)^2}{2}T_2^2 + (\gamma H_o - \omega)^2 T_2^2 + \gamma^2 H_L^2 T_2^2}}{1 + \frac{(\gamma H_1)^2}{2}T_1 T_2 + (\gamma H_o - \omega)^2 T_2^2} \tag{7}$$

$$\chi'' = \frac{1}{2}\omega_o \chi_o T_2 \frac{1}{1 + \frac{(\gamma H_1)^2}{2}T_1 T_2 + (\gamma H_o - \omega)^2 T_2^2} \cdot \frac{\frac{(H_1)^2}{2} + H_L^2}{\frac{(H_1)^2}{2} + (H_o - \omega/\gamma)^2 + H_L^2}$$

where $\chi_o = \langle M_z \rangle_o / H_o$, and $\omega_o = \gamma H_o$.

In the limit of very weak rf power, we have

$$\chi'' = \frac{\frac{1}{2}\omega_o \chi_o T_2}{1 + (\gamma \delta H T_2)^2} \cdot \frac{1}{1 + \left(\frac{\delta H}{H_L}\right)^2} \tag{8}$$

where $\delta H = H_O - \omega/\gamma$

This line shape for χ'' has a finite second moment $\overline{(\delta H)^2}$ given by

$$\overline{(\delta H)^2} = H_L/\gamma T_2$$

The damping content T_2 has been introduced on a purely phenomenological basis. It may now be related to the fundamental parameters of the spin system by requiring that the value of the second moment equal the theoretical Van Vleck (4) value. In the absence of exchange interaction, the Van Vleck second moment $(\Delta H)^2$ is related (1) to H_L^2, so that $(\Delta H)^2/3 = H_L^2$.

With exchange interaction present, let $H_L^2 = k^2(\Delta H)^2/3$. Then our second-moment criterion requires that

$$(\Delta H)^2 = \frac{k\,\Delta H}{\sqrt{3}\cdot\gamma T_2}$$

or

$$\gamma T_2 = \frac{k}{\sqrt{3}\,\Delta H} = \frac{k^2}{3 H_L}$$

With this value of γT_2, the susceptibility χ'' for weak rf power becomes

$$\chi'' = \frac{1}{2}\chi_0 H_0\frac{k(\Delta H)^3}{\sqrt{3}}\cdot\frac{1}{3\frac{(\Delta H)^2}{k}+(\delta H)^2}\cdot\frac{1}{k^2\frac{(\Delta H)^2}{\sqrt{3}}+(\delta H)^2}$$

It can be seen that when strong exchange interaction is present, the resultant linewidth is smaller than the dipolar width (k=1).

In regard to the problem of inversion by adiabatic fast passage, our Eq. 6 leads to conclusions similar to those of Redfield (1).

B. V. Gokhale

References

1. A. G. Redfield, Phys. Rev. 98, 1787 (1955).
2. F. Bloch, Phys. Rev. 70, 460 (1946).
3. A. Abragam and W. F. Proctor, Phys. Rev. 109, 1441 (1958).
4. J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).