PHYSICAL REVIEW VOLUME 121, NUMBER 4 FEBRUARY 15, 1961

Cross Relaxation and Concentration Effects in Ruby

ROY W. ROBERTS
Melabs, Palo Alto, California

AND

JAMES H. BURGESS
Stanford University, Palo Alto, California

AND

HAROLD D. TENNEY
Melabs, Palo Alto, California

(Received October 13, 1960)

Cross relaxation effects in ruby maser crystals are treated by introduction of a cross relaxation probability in the rate equations. Detailed solutions have been obtained for several specific processes and compared to recent experiments. It is shown that cross relaxation can improve maser performance even in the absence of impurity doping. Pulse experiments at 0.06 and 0.14% chromium ion concentrations in a ruby traveling wave maser are interpreted in terms of a five-spin process in addition to a four-spin process.

I. INTRODUCTION

THE term "cross relaxation" refers generally to the communication of energy between magnetic ions in the crystal. As used in this paper, it refers to the simultaneous transition of two or more ions among their Zeeman energy levels induced by the dipole-dipole interaction. The transition probability then depends on the concentration of paramagnetic ions. Unbalance of Zeeman energy is compensated by a rearrangement of spins in the dipolar system. Since a large change of Zeeman energy requires the relatively improbable cooperation of a large number of ions, the transition probability falls off rapidly around zero unbalance. Thus, at low concentrations, Zeeman energy must be conserved to within a few times the paramagnetic resonance linewidth for a particular cross relaxation process to be important. With increasing concentration this bandwidth broadens until so many processes are allowed that temperature differences within the spin system become impossible. However, there is a region of low concentrations in which individual cross relaxation processes can be observed through their effects on (1) the energy level populations, (2) the effective cw relaxation times, and (3) the transient relaxation times of the paramagnetic system.

Since Bloembergen[1] first pointed out the importance of cross relaxation, many investigators[2–5] have reported experiments in which cross relaxation played an appreciable role, particularly in solid-state maser applications. It has not been generally recognized, however, that cross relaxation may improve maser performance even in cases not involving impurity doping. In the first part of this paper, we discuss several such processes involving three-, four-, and five-spin transitions which correspond to operating conditions in recent maser experiments. Calculated inversion ratios are compared with the experimental results. In the last part of the paper, we describe transient experiments with a ruby traveling-wave maser in which it appears that both a four-spin and a five-spin process are important.

II. CALCULATION OF CROSS RELAXATION EFFECTS

As has been discussed by Bloembergen and Shapiro,[3] cross relaxation may be incorporated into the framework of the rate equations for the energy level populations. The major condition on the use of the rate equation approach is that the transverse relaxation time T_2 be short enough to prevent large phase coherence effects.[6,7] The form of the cross relaxation term depends on the specific process involved but is based on the assumption of independent occupation probabilities. Thus, in case (a) below, the net rate of increase of population in level 1 is proportional to $n_2^2n_4-n_1n_3^2$. The proportionality constant is taken to be $W'(4/N)^2$, which defines the cross relaxation probability W'. The rate equations for levels 1 and 2 become then

$$\dot{n}_1=-(w_{12}+w_{13}+w_{14})n_1+w_{21}n_2+w_{31}n_3+w_{41}n_4+W'(4/N)^2(n_2^2n_4-n_1n_3^2), \quad (1a)$$

$$\dot{n}_2=w_{12}n_1-(w_{21}+w_{23}+w_{24})n_2+w_{32}n_3+w_{42}n_4+V_{23}(n_3-n_2)-2W'(4/N)^2(n_2^2n_4-n_1n_3^2), \quad (1b)$$

where V_{23} is the transition probability per unit time induced by radiation applied at frequency f_{23}. A factor of 2 multiplies the cross relaxation term in the second equation because each transition changes n_2 by two spins. The cross relaxation term is linearized in the high-temperature approximation by keeping only terms

[1] N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).
[2] C. H. Townes in *Quantum Electronics* (Columbia University Press, New York, 1960).
[3] S. Shapiro and N. Bloembergen, Phys. Rev. **116**, 1453 (1959).
[4] W. B. Mims and J. D. McGee, Phys. Rev. **119**, 1233 (1960).
[5] F. Arams, Proc. I.R.E. **48**, 108 (1960).
[6] A. M. Clogston, J. Phys. Chem. Solids **4**, 27 (1958).
[7] J. H. Burgess, J. phys. radium **19**, 845 (1958).

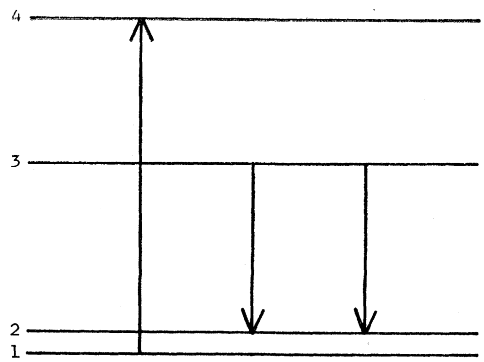

FIG. 1. Energy level diagram for chromium-doped sapphire. $\theta=90°$, $H_{dc}=1675$ oe. Three-spin cross relaxation process indicated by arrows.

involving the first power of $\Delta n_{ij}=n_i-n_j$. The rate equations can then be solved in the usual manner to give the steady-state inversion ratio

$$R_{ij}=-\Delta n_{ij}(V_{ij})/\Delta n_{ij}(0) \tag{2}$$

and the spin temperature

$$T^s{}_{ij}=-T_L/R_{ij}, \tag{3}$$

where T_L is the lattice temperature.

(a) The energy level diagram shown in Fig. 1 corresponds to ruby with a static magnetic field of 1675 oe applied normal to the C axis ($\theta=90°$). Since the relation $2f_{23}=f_{14}$ is satisfied, the indicated three-spin cross relaxation process conserves Zeeman energy. Transition 2-3 is pumped while the signal is taken at 1-3. In this case $f_s>f_p$. Following the method outlined above and assuming equal spin lattice relaxation times, the inversion ratio is found to be

$$R_{31}=\left[\left(\frac{3f_p}{2f_s}-1\right)\frac{W'}{w}+2-\frac{f_p}{f_s}\right]\Big/(-2+W'/w), \tag{4}$$

which indicates inversion can be obtained provided $W'/w>2$ even with the signal frequency greater than the pump frequency. These conditions correspond to those in the experiment of F. Arams[5] at Airborne Instruments Laboratory in which such inversion was observed.

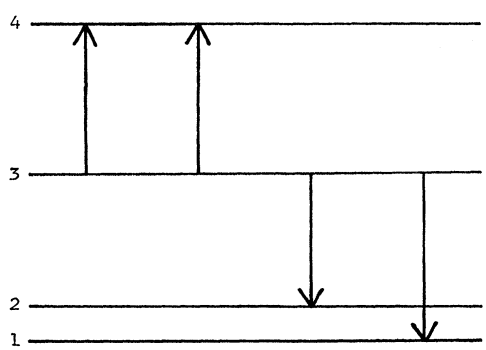

FIG. 2. Energy level diagram for chromium-doped sapphire. $\theta=90°$, $H_{dc}=2750$ oe. Four-spin cross relaxation process indicated by arrows.

(b) The energy level diagram showing a four-spin cross relaxation process is shown in Fig. 2. The 1-3 transition is pumped and the 1-2 transition is used for the signal. The energy levels satisfy the following relationship: $2f_{34}=f_{13}+f_{23}$. It can be seen that the cross relaxation transition probability will be proportional to $(n_3{}^4-n_1n_2n_4{}^2)$. For convenience the proportionality constant will be chosen to be $W'(4/N)^3$. By making the usual high-temperature approximation and assuming all w's equal, the steady-state inversion ratio R is obtained

$$R_{21}=\frac{f_p}{f_s}\,\frac{4+22W'/w}{8+19W'/w}-1. \tag{5}$$

If the cross relaxation term W'/w is zero, this expression predicts an inversion ratio of 1.48 for a pump frequency of 13.4 kMc and signal frequency of 2.6 kMc. However, experiments performed in this laboratory on a traveling wave maser gave a measured inversion ratio of 4.1. Substituting this value in Eq. (5) gives a value of W'/w of 1.68. These experiments were performed on 0.1% ruby.[8] If cross relaxation effects were not included, this measured inversion ratio would indicate essentially zero idler relaxation time, an unlikely possibility for a homogeneous material.

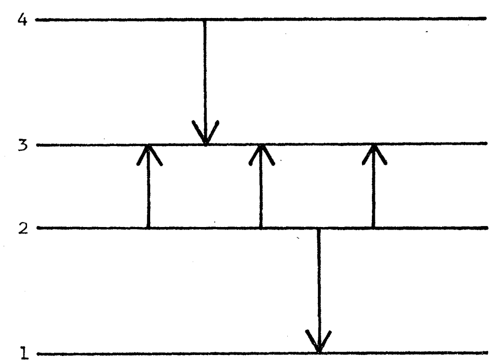

FIG. 3. Energy level diagram for chromium-doped sapphire. $\theta=54°\,44'$, $H_{dc}=3800$ oe. Five-spin cross relaxation process indicated by arrows.

Examination of the energy level diagram shows that the energy unbalance expressed in megacycles, $\Delta f=2f_{34}-(f_{13}+f_{23})$, is within five linewidths for signal frequencies from 2.6 kMc/sec to 6.0 kMc/sec and goes to zero at approximately 2.65 kMc/sec and 5.95 kMc/sec. These two frequencies correspond to those used in the Melabs traveling wave maser[9] and the Bell Telephone Laboratories[10] traveling wave maser, respectively.

[8] Nominal starting composition. This corresponds to approximately 0.05% chromium ion concentration. The ruby was obtained from Linde Company.

[9] R. Roberts and H. Tenney, unpublished report (1960).

[10] R. DeGrasse, E. O. Schulz-Dubois, and H. E. D. Scovil, Bell System Tech. J. 38, 2 (1959).

(c) The third example of cross relaxation to be considered involves a five-spin process. The energy level diagram shown in Fig. 3 corresponds to the "push-pull" angle for ruby with $\theta = 54° 44'$ and $H_{dc} = 3800$ oe. The energy level separations satisfy the following relationship: $3f_{23} = 2f_{12} = 2f_{34}$. The 1-3 and 2-4 transitions are pumped and the signal is equal to the 2-3 transition. The cross relaxation-induced transitions for the process shown in Fig. 3 are proportional to $W'(4/N)^4(n_2^4 n_4 - n_1 n_3^4)$. Because of the degeneracy of the push-pull operating point, two additional five-spin processes occur with the same probability W'. They lead to terms proportional to $W'(4/N)^4(n_4^2 n_2^3 - n_3^5)$ and $W'(4/N)^4(n_2^5 - n_3^3 n_1^2)$ in the rate equations. Under the assumed pumping conditions, these two terms and the previous term each reduce to $W'(4/N)^4(n_2^5 - n_1^5)$. The effect is to increase the total cross relaxation probability to $3W'$. The inversion ratio, assuming equal w_{ij}'s, is given by[9]

$$R_{32} = \frac{-1 + f_p/f_s}{1 + 45W'/w}. \tag{6}$$

For this process it is seen that cross relaxation decreases the inversion ratio. By assuming the values $f_p/f_s = 23/10$ and $W'/w = 1$ for a ruby at 4.2°K, an inversion ratio of 0.03 (negative spin temperature $= 150$°K) is obtained, which means, in practice, poor maser performance. If, however, the temperature is raised from 4.2° to 77°K, the spin lattice relaxation times[11] decrease by a factor of 100 and W'/w becomes 0.01. The inversion ratio at 77°K then becomes 0.9 (negative spin temperature $= 85$°K), which will give a useful maser gain.

These inversion ratios correspond closely to those obtained by T. Maiman[12] at Hughes Aircraft Laboratories for a 0.2% ruby and suggest that this process may be more important than the proposed pump-idler coupling which entails an energy unbalance greater than 5 kMc.

III. CONCENTRATION EFFECTS

To check the effects of concentration of chromium ions, a 0.3% ruby[13] was used in a pulsed traveling wave maser at 4.2°K at the operating point of Fig. 2. It was expected that the larger concentration would increase the cross relaxation probability and further enhance the inversion ratio. This did not turn out to be the case. The amount of electronic gain obtained was less than that obtained with the 0.1% crystal. It is evident from this result that the assumption implicit in case (b), that only the four-spin cross relaxation process need be considered, is no longer valid for the 0.3% ruby.

Figure 4(a) shows the power transmitted through the maser at the signal frequency f_{12} versus time. Initially, the dc field and the signal were tuned to resonance in the absence of pump power, resulting in absorption. Saturating power at the pump frequency f_{13} was then pulsed on and, as shown, transmission began to increase

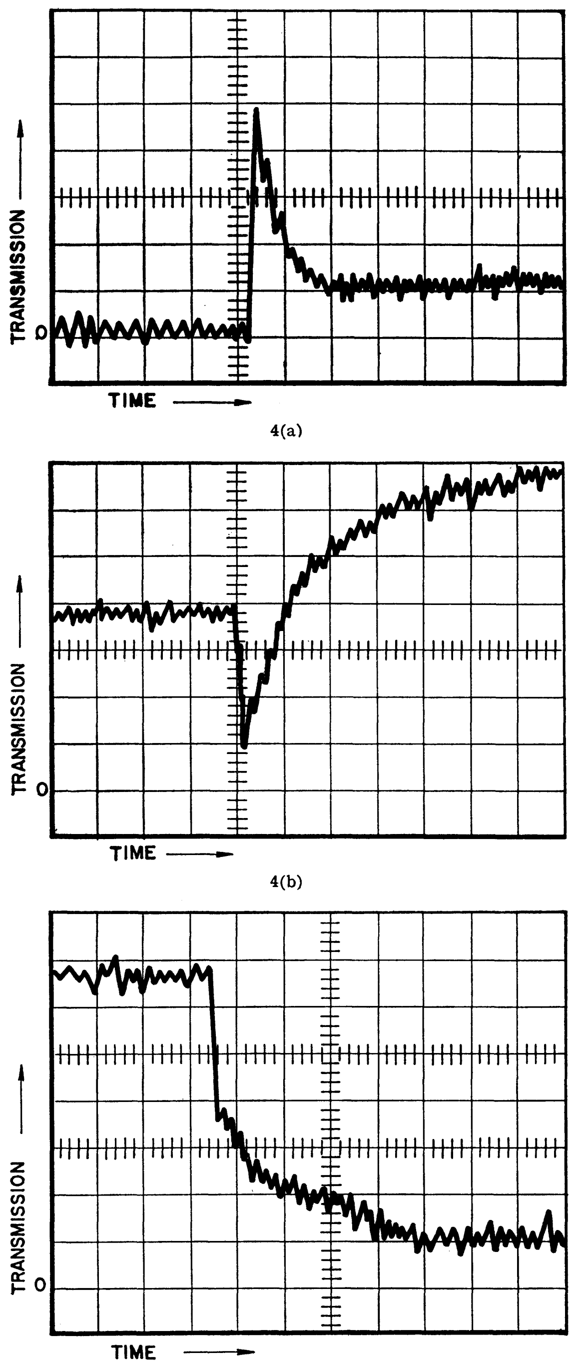

FIG. 4. Signal transmission through the traveling wave maser vs time. (a) 0.3% ruby, f_{13} pulsed on. (b) 0.3% ruby, f_{23} pulsed on. (c) 0.1% ruby, f_{23} pulsed on.

[11] J. C. Gill in *Quantum Electronics* (Columbia University Press, New York, 1960), p. 333.

[12] T. Maiman in *Quantum Electronics* (Columbia University Press, New York, 1960), p. 324.

[13] Starting composition. This corresponds to approximately 0.14% chromium ion concentration.

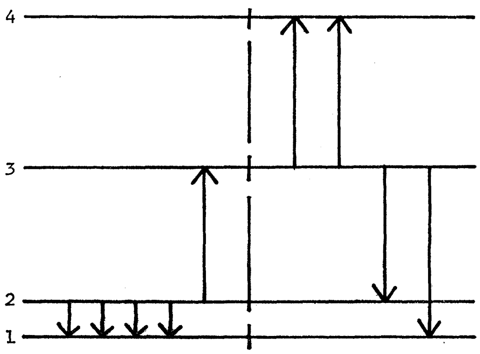

FIG. 5. Energy level diagram for chromium-doped sapphire. $\theta=90°$, $H_{dc}=2750$ oe. Four- and five-spin cross relaxation processes indicated by arrows.

at a very rapid rate, indicating the ruby was becoming emissive. However, before the maximum amount of gain could be realized, another competing mechanism dominated and caused the transmission to reduce to a low steady-state value. The conditions were the same initially in Fig. 4(b). Here saturating power at the idle frequency f_{23} was pulsed on. The transmission decreased sharply and then returned to a higher steady-state value. For comparison purposes, Fig. 4(c) shows the results of the same experiment, pulsing on f_{23}, for the 0.1% ruby. In this case, the transmission decreased considerably and remained at a very low steady-state value.

Inspection of the energy level diagrams corresponding to the point of operation revealed a degeneracy for a five-spin cross relaxation process in addition to the four-spin process already considered. The energy levels satisfy the relationship $4f_{12}=f_{23}$. To determine if this degeneracy would account for the results described above, the rate equations were solved taking into account both cross relaxation mechanisms. The combined processes are shown in Fig. 5. The cross relaxation induced transitions caused by the four-spin process are given by $W_4'(4/N)^3(n_3^4-n_1n_2n_4^2)$ while those resulting from the five-spin process are given by $W_5'(4/N)^4(n_2^5-n_1^4n_3)$. The normal maser case in which the 1-3 transition is saturated will be considered first. The cross relaxation terms are linearized as before. By making the usual high-temperature approximation, and assuming all w's equal, the steady-state inversion ratio is

$$R_{21}=\left[\frac{f_p}{2f_s}-1+\frac{W_4'}{w}\left(\frac{22f_p}{8f_s}-\frac{19}{8}\right)\right]\Bigg/\left[1+\frac{19W_4'}{8w}+\frac{25W_5'}{8w}\left(3+4\frac{W_4'}{w}\right)\right]. \quad (7)$$

This expression reduces to the normal inversion ratio in the absence of any cross relaxation, $R=-1+f_p/2f_s$ and agrees with Eq. (5) when $W_5'=0$. Since the W_5' term appears in the denominator, it is seen that the five-spin process tends to decrease the inversion ratio in agreement with the experimental results shown in Fig. 4(a).

A similar analysis was carried out for the case in which the idle frequency f_{23} was pulsed on. Proper substitutions and approximations result in the following expression for the inversion ratio,

$$R_{21}=\left[\frac{f_p}{2f_s}+\frac{1}{2}-\frac{W_4'}{w}\left(\frac{3}{8}-\frac{22}{8}\frac{f_p}{f_s}\right)\right]\Bigg/\left[\frac{20W_5'}{8w}\left(3+\frac{4W_4'}{w}\right)+1-\frac{W_4'}{8w}\right], \quad (8)$$

where f_p is still defined as f_{13} and f_s as f_{12}. In the case of no cross relaxation,

$$R_{21}=-[(f_p/2f_s)+\tfrac{1}{2}]. \quad (9)$$

The inversion ratio and the resultant gain are negative. In the case of $f_p=13.4$ kMc/sec and $f_s=2.7$ kMc/sec, which corresponds to the operating point under consideration, $R=-3$, so that the absorption is expected to triple when saturating power is applied. However, the experimental measurements made on the 0.1% crystal gave an inversion ratio of -5 in this frequency range, indicating that W_4' is not negligible.

From Eq. (8) it can be seen that, as W_5' increases, the inversion ratio approaches zero. Since a five-spin process should depend more strongly on concentration than a four-spin process, W_5' should become important at higher concentrations. This was borne out by measurements made on the 0.3% crystal, which gave smaller negative inversion ratios of from -0.4 to -0.6.

IV. SUMMARY AND CONCLUSIONS

It appears that at low chromium ion concentrations, cross relaxation effects in ruby can be described by specifying one or two specific cross relaxation processes. These effects can be taken into account by adding suitable terms to the rate equations. Solution of the linearized rate equations then allows one to predict qualitatively the effects of the cross relaxation processes on maser performance and the behavior with varying concentration. The optimum concentration for maser action will depend on the particular operating point and the lowest order cross relaxation mechanism for which energy conservation is nearly satisfied. However, as the concentration is increased, so many higher order processes become important that it is impossible to maintain temperature differences in the spin system. This establishes a maximum allowable concentration above which maser amplification is not possible.

V. ACKNOWLEDGMENTS

We would like to thank Dr. J. C. Cromack for many helpful discussions pertaining to this subject. This work was supported in part by the Air Force Cambridge Research Center.