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Proposal for a New Type Solid State Maser*

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The Overhauser effect may be used in the spin multiplet of certain paramagnetic ions to obtain a negative absorption or stimulated emission at microwave frequencies. The use of nickel fluosilicate or gadolinium ethyl sulfate at liquid helium temperature is suggested to obtain a low noise microwave amplifier or frequency converter. The operation of a solid state maser based on this principle is discussed.

TOWNES and co-workers[1,2] have shown that microwave amplification can be obtained by stimulated emission of radiation from systems in which a higher energy level is more densely populated than a lower one. In paramagnetic systems an inversion of the population of the spin levels may be obtained in a variety of ways. The "180° pulse" and the "adiabatic rapid passage" have been extensively applied in nuclear magnetic resonance. Combrisson and Honig[2] applied the fast passage technique to the two electron spin levels of a *P* donor in silicon, and obtained a noticeable power amplification.

Attention is called to the usefulness of power saturation of one transition in a multiple energy level system to obtain a change of sign of the population difference between another pair of levels. A variation in level populations obtained in this manner has been demonstrated by Pound.[3] Such effects have since acquired wide recognition through the work of Overhauser.[4]

Consider for example a system with three unequally spaced energy levels, $E_3>E_2>E_1$. Introduce the notation,

$$h\nu_{31}=E_3-E_1 \quad h\nu_{32}=E_3-E_2 \quad h\nu_{21}=E_2-E_1.$$

Denote the transition probabilities between these spin levels under the influence of the thermal motion of the heat reservoir (lattice) by

$$w_{12}=w_{21}\exp(-h\nu_{21}/kT), \quad w_{13}=w_{31}\exp(-h\nu_{31}/kT), \quad w_{23}=w_{32}\exp(-h\nu_{32}/kT).$$

The *w's* correspond to the inverse of spin lattice relaxation times. Denote the transition probability caused by a large saturating field $H(\nu_{3i})$ of frequency

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[1] Gordon, Zeiger, and Townes, Phys. Rev. **99,** 1264 (1955).
[2] Combrisson, Honig, and Townes, Compt. rend. 242, 2451 (1956).
[3] R. V. Pound, Phys. Rev. 79, 685 (1950).
[4] A. W. Overhauser, Phys. Rev. 92, 411 (1953).

ν_{31} by W_{13}. Let a relatively small signal of frequency ν_{32} cause transitions between levels two and three at a rate W_{32}. The numbers of spins occupying the three levels n_1, n_2, and n_3, satisfy the conservation law

$$n_1+n_2+n_3=N.$$

For $h\nu_{32}/kT \ll 1$ the populations obey the equations[5]:

$$\begin{aligned}
\frac{dn_3}{dt}&=w_{13}\left(n_1-n_3-\frac{N}{3}\frac{h\nu_{31}}{kT}\right)+w_{23}\left(n_2-n_3-\frac{N}{3}\frac{h\nu_{32}}{kT}\right)\\
&\quad+W_{31}(n_1-n_3)+W_{32}(n_2-n_3),\\
\frac{dn_2}{dt}&=w_{23}\left(n_3-n_2+\frac{N}{3}\frac{h\nu_{32}}{kT}\right)+w_{21}\left(n_1-n_2-\frac{N}{3}\frac{h\nu_{21}}{kT}\right)\\
&\quad+W_{32}(n_3-n_2),\\
\frac{dn_1}{dt}&=w_{13}\left(n_3-n_1+\frac{N}{3}\frac{h\nu_{31}}{kT}\right)+w_{21}\left(n_2-n_1+\frac{N}{3}\frac{h\nu_{21}}{kT}\right)\\
&\quad-W_{31}(n_1-n_3).
\end{aligned} \tag{1}$$

In the steady state the left-hand sides are zero. If the saturating field at frequency ν_{31} is very large, $W_{31} \gg W_{32}$ and w's, the solution is obtained

$$n_1-n_2=n_3-n_2=-\frac{1}{3}\frac{hN}{kT}\frac{-w_{23}\nu_{32}+w_{21}\nu_{21}}{w_{23}+w_{12}+W_{32}}. \tag{2}$$

This population difference will be positive, corresponding to negative absorption or stimulated emission at the frequency ν_{32}, if

$$w_{21}\nu_{21} > w_{32}\nu_{32}. \tag{3}$$

If the opposite is true, stimulated emission will occur at the frequency ν_{21}. The following discussion could easily be adapted to this situation. The power emitted by the magnetic specimen is

$$P_{\text{magn}}=\frac{N\hbar^2\nu_{32}}{3kT}\frac{(w_{21}\nu_{21}-w_{32}\nu_{32})W_{32}}{w_{23}+w_{12}+W_{32}}. \tag{4}$$

For a magnetic resonance line with a normalized response curve $g(\nu)$ and $g(\nu_{max})=T_2$, the transition probability at resonance is given by

$$W_{32}=\hbar^{-2}|(2|M_x|3)|^2 H_s^2(\nu_{32})T_2. \tag{5}$$

For simplicity it has been assumed that the signal field $H(\nu_{32})$ is uniform in the x direction over the volume of the sample. A similar expression holds for W_{31}.

For the moment we shall restrict ourselves to the important case that the signal excitation at frequency ν_{32} is small, $W_{32} \ll w_{23}+w_{31}$. No saturation effects at this transition occur and a magnetic quality factor can be defined by

$$-1/Q_{\text{magn}}=\frac{4P_{\text{magn}}}{\nu_{23}\langle H^2(\nu_{32})\rangle_{Av}V_c}. \tag{6}$$

Q_{magn} is negative for stimulated emission, $P_{\text{magn}}>0$. V_c is the volume of the cavity, and $(H^2)_{Av}$ represents a volume average over the cavity. The losses in the cavity, exclusive of the magnetic losses or gains in the sample, are described by the unloaded quality factor Q_0. The external losses from the coupling to a wave guide or coaxial line are described by Q_e. Introduce the voltage standing wave ratio β for the cavity tuned to resonance,

$$\beta=(Q_e/Q_0)+(Q_e/Q_{\text{magn}}).$$

The ratio of reflected to incident power is

$$\frac{P_r}{P_i}=\frac{(1-\beta)^2}{(1+\beta)^2}.$$

There is a power gain or amplification, when β is negative or, $-Q_{\text{magn}}^{-1} > Q_0^{-1}$. Oscillation will occur when

$$-Q_{\text{magn}}^{-1} > Q_0^{-1}+Q_e^{-1}=Q_L^{-1},$$

where Q_L is the "loaded Q." The amplitude of the oscillation will be limited by the saturation effect, embodied by the W_{32} in the denominator of Eq. (4). The absolute value of $1/Q_{magn}$ decreases as the power level increases. In the oscillating region the device will act as a microwave frequency converter. Power input is at the frequency ν_{13}, a smaller power output at the frequency ν_{23}. The balance of power is dissipated in the form of heat through the spin-lattice relaxation and through conduction losses in the cavity walls. For $-Q_{\text{magn}}=Q_L$, $\beta=-1$, and the amplification factor would be infinite. The device will act as a stable c.w. amplifier at frequency ν_{23}, if

$$Q_0^{-1}+Q_e^{-1} > -Q_{\text{magn}}^{-1} > Q_0^{-1}. \tag{7}$$

The choice of paramagnetic substance is largely dependent on the existance of suitable energy levels and the existence of matrix elements of the magnet moment operator between the various spin levels. The absorption and stimulated emission process depend directly on this operator, but the relaxation terms (w) also depend on the spin angular momentum operator via spin-orbit coupling terms. It is essential that all off-diagonal elements between the three spin levels under consideration be nonvanishing. This can be achieved by putting a paramagnetic salt with a crystalline field splitting δ in a magnetic field, which makes an angle with the crystalline field axis. The magnitude of the field is such that the Zeeman energy is comparable to the crystalline field splitting. In this case the states with magnetic quantum numbers m_s are all scrambled. This situation is usually avoided to unravel paramagnetic resonance spectra, but occasionally "forbidden lines" have been observed, indicating mixing of the m_s states. For our

[5] In case $h\nu_{31} \sim kT$, the Boltzmann exponential factors cannot be approximated by the linear terms. The algebra becomes more involved without changing the character of the effect.

purposes the mixing up of the spin states by Zeeman and crystalline field interactions of comparable magnitude is essential. The energy levels and matrix elements of the spin angular momentum operator can be obtained by a numerical solution of the determinantal problem of the spin Hamiltonian.[6] The number of electron spin levels may be larger than three. One may choose the three levels between which the operation will take place. The analysis will be similar, but algebraically more complicated. One has a considerable amount of freedom by the choice of the external dc magnetic field, to adjust the frequencies ν_{23} and ν_{13} and to vary the values of the inverse relaxation times w. It is advisable—although perhaps not absolutely necessary—to operate at liquid helium temperature. This will give relatively long relaxation times (between 10^{-2} and 10^{-4} sec), and thus keep the power requirements for saturation down. The factor T in the denominator of Eq. (4) will also increase the emission at low temperature. Although the order of magnitude of the $w's$ is known through the work of Leiden school,[7] there is only one instance where w's have been measured for some individual transitions.[8] Van Vleck's[9] theory of paramagnetic relaxation should be extended to the geometries envisioned in this paper. If a Debye spectrum of the lattice vibrations is assumed, the relaxation times will increase with decreasing frequency at liquid helium temperature, where Raman processes are negligible. This implies that the condition (3) should be easily realizable when $\nu_{32} < \nu_{21}$.

Important applications as a microwave amplifier could, e.g., be obtained for ν_{32}=1420 Mc/sec, corresponding to the interstellar hydrogen line, or to another relatively low microwave frequency used in radar systems. The frequency ν_{31} could be chosen in the X band, $\nu_{31}=10^{10}$ cps. To obtain well scrambled states with these frequency splittings one should have crystalline field splittings between 0.03 cm^{-1} and 0.3 cm^{-1}. Paramagnetic crystals which are suggested by these considerations are nickel fluosilicate[10] and gadolinium ethyl sulfate.[11] These crystals have the additional advantage that all magnetic ions have the same crystalline field and nuclear hyperfine splitting is absent, thus keeping the total number of possible transitions down. The use of magnetically dilute salts is indicated to reduce the line width, increase the value of T_2 in Eq. (5) and to separate the individual resonance transitions.

A single crystal 5% Ni 95% Zn Si F_6 . $6H_20$ has a line width of 50 oersted (T_2= $1.2X10^{-9}$ sec) and an average crystalline field splitting δ=0.12 cm^{-1} for the Ni++ ions. With an effective spin value S=1 there are indeed three energy levels of importance. The spin lattice relaxation time is about 10^{-4} sec at 2 °K as measured in a saturation experiment by Meyer.[12] Further dilution does not decrease the line width, as there is a distribution of crystalline fields in the diluted salt.

A single crystal of 1% Gd 99% La $(C_2H_5SO_4)_3.9H_20$ has an effective spin S= 7/2. In zero field there are four doublets separated respectively by δ=0.113 cm^{-1}, 0.083 cm^{-1}, and 0.046 cm^{-1} as measured at 20°K. These splittings are practically independent of temperature. The line width is 7 oersteds due to the distribution of local fields arising from the proton magnetic moments. This width could be reduced by a factor three by using the deuterated salt. The relaxation time is not known, but should be about the same as in other Gd salts,[7] which give $T_1 \sim 10^{-2}$ sec at 2°K.

Ill the absence of detailed calculations for the relaxation mechanism, we shall take $w_{12}=w_{13}=w_{32}=10^4$ sec^{-1} for the nickel salt and equal to 10^2 sec^{-1} for the gadolinium salt. The matrix elements $(2|M_x|3)$, etc., can be calculated exactly by solving the spin determinant. For the purpose of judging the operation of the maser using these salts, we shall take the off-diagonal elements of magnetic moment operator simply equal to $g\beta_0$, where $g=2$ is the Lande spin factor and β_0 is the Bohr magneton. For the higher spin value of the Gd^{+++} some elements will be larger but this effect is offset by the distribution of the ions over eight rather than three spin levels. Take $T=2°K$ and $Qo=10^4$, which is readily obtained in a cavity of pure metal at this temperature. A coaxial cavity may be used which has a fundamental mode resonating at the frequency ν_{32}=$1.42X10^9$ cps and a higher mode resonating at ν_{31}—10^{10} cps. Take the volume of the cavity V=60 cm^3 and $H_3^2=6(H^2)_{Av}$. If these values are substituted in Eqs. (4)-(6), the condition (7) for amplification is satisfied if $N>3X\ 10^{18}$ for nickel fluosilicate and $N>3X10^{17}$ for gadolinium ethyl sulfate ($N>10^{17}$ for the deuterated salt). The minimum required number of Ni++ ions are contained in 0.02 cm^3 of the diluted nickel salt. The gadolinium salt, diluted to 1% Gd, contains the required number in about the same volume. The critical volume is only 0.006 cm^3 for the deuterated salt. Crystals of appreciably larger size can still be fitted conveniently in the cavity. A c.w. amplifier or frequency converter should therefore be realizable with these substances. A larger amount of power can be handled by these crystals than by the P impurities in silicon which have a very long relaxation time, and require an intermittant operation, and where it is harder to get the required number of spins in the cavity.

So far we have assumed that the width corresponds to the inverse of a true transverse relaxation time T_2.

[6] See, e.g., Bleaney and K. H. W. Stevens, Repts. Progr. in Phys. **16,** 108 (1953).
[7] See, e.g., C. J. Gorter, *Paramagnetic Relaxation* (Elsevier Publishing Company, Amsterdam, 1948).
[8] A. H. Eschenfelder and R. T. Weidner 92, 869 (1953).
[9] J. H. Van Vleck, Phys. Rev. 57, 426 (1940).
[10] R. P. Penrose and K. H. W. Stevens, Proc. Phys. Soc. (London) **A63**, 29 (1949).
[11] Bleaney, Scovil, and Trenam, Proc. Roy. Soc. (London) **A223,** 15 (1954).
[2] J. W. Meyer, Lincoln Laboratory Report 1955 (unpublished).

Actually the width $1/T_2^*$ is due to an internal inhomogeneity broadening with normalized distribution $h(\nu)$ and $h(\nu_{max}) \approx T_2^*$ in both cases. The response curve for a single magnetic ion is probably very narrow indeed, $g(\nu_{max}) = T_2 \approx T_1$, and $T_1 = 10^{-4}$ should be used in Eq. (5) rather than $T_2^* = 1.2 \times 10^{-9}$ sec. The response to a weak threshold signal at ν_{32} now originates, however, from a small fraction of the magnetic ions. If $\gamma H(\nu_{32}) < 1/T_1 \approx 10^4$ cps, then only T_2^*/T_1 of the ions contribute to the stimulated emission and the net result is the same as calculated above. In most applications the incoming signal will be so weak that this situation will apply, even with a power amplification of 30 or 40 db.

For use as an oscillator or high level amplifier with a field $H(\nu_{32})$ in the cavity larger than $1/\gamma T_1$, one has essentially complete saturation ($W_{32} \gg w_{23} + w_{13}$) in Eq. (4) for those magnetic ions lying in a width $2\pi\Delta\nu = \gamma H(\nu_{32})$ in the distribution $h(\nu)$. One has then for the power emitted instead of Eqs. (4) and (5)

$$P_{\text{magn}} = \frac{h^2 \nu_{32}}{3kT} N(-w_{32}\nu_{32} + w_{21}\nu_{21}) \gamma H(\nu_{31}) T_2^*. \quad (8)$$

The power is proportional to the amplitude of the radio frequency field rather than its square. This effect has been discussed in more detail by Portis.[13] It will limit the oscillation or amplification to an amplitude which can be calculated by using Eq. (8) in conjunction with Eqs. (6) and (7).

The driving field $H(\nu_{31})$ will necessarily have to satisfy the condition $\gamma H(\nu_{31}) > w_{31} = T_1^{-1}$ to obtain saturation between levels 1 and 3. The power absorbed in the crystal will be proportional to the amplitude $H(\nu_{31})$, and is in order of magnitude given by

$$P_{\text{abs}} \sim N \frac{h^2 \nu_{13}^2}{3kT} w_{13} \gamma H(\nu_{31}) T_2^*. \quad (9)$$

This equation looses its validity if $\gamma H(\nu_{31}) > T_2^{*-1}$. In this case the whole line would be saturated, but such excessive power levels will not be used. For $T_1^{-1} < \gamma H(\nu_{31}) < T_2^{*-1}$, the effective band width of the amplifier is determined by $H(\nu_{31})$. It is about 0.5 Mc/sec for $H(\nu_{31}) = 0.2$ oersted. The power dissipated in a specimen of fluosilicate ten times the critical size is 0.5 milliwatt under these circumstances. For the gadolinium salt, also ten times the critical size, either deuterated or not, the dissipation is only 0.005 milliwatt. There should be no difficulty in carrying this amount out of the paramagnetic crystal without excessive heating. The power dissipation in the walls under these conditions will be 5 milliwatts. Liquid helium will boil off at the rate of only 0.01 cc/min due to heating in the cavity. Since helium is superfluid at 2°K, troublesome vapor bubbles in the cavity are eliminated.

The noise power generated in this type of amplifier should be very low. The cavity with the paramagnetic salt can be represented by two resonant coupled circuits as discussed by Bloembergen and Pound.[14] Noise generators are associated with the losses in the cavity walls, kept at 2°K, and with the paramagnetic spin abosrption which is described by an effective spin temperature, associated with the distribution of the spin population. The absolute value of this effective temperature also has the order of magnitude of 1°K. The input is from an antenna, which sees essentailly the radiation temperature of interstellar space. Reflected power is channeled by a circulating nonreciprocal element[15] into a heterodyne receiver, or, if necessary, into a second stage Maser cavity. The circulator makes the connection: antenna→maser cavity→heterodyne receiver→dummy load→antenna. If the antenna is not well matched, the dummy load may be a matched termination kept at liquid helium temperature to prevent extra power from entering the cavity. The input arm of the cavity at frequency ν_{31} will be beyond cutoff for the frequency ν_{32}. The coaxial line passing the signal at ν_{32} between cavity and circulator will contain a rejection filter at frequency ν_{31} to prevent overloading and noise mixing at the mixer crystal of the super heterodyne receiver.

It may be concluded that the realization of a low-noise c.w. microwave amplifier by saturation of a spin level system at a higher frequency seems promising. The device should be particularly suited for detection of weak signals at relatively long wavelength, e.g., the 21-cm interstellar hydrogen radiation. It may also be operated as a microwave frequency converter, capable of handling milliwatt power. More detailed calculations and design of the cavity are in progress.

[13] A. M. Portis, Phys. Rev. **91**, 1071 (1953).

[14] N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).

[15] C. L. Hogan, Bell System Tech. J. **31**, 1 (1952).