ZERO-FIELD MASERS

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Summary

Solid state three-level masers operating with zero magnetic field are shown to be feasible and to have advantages over magnetic field masers in many applications. The requirements of the working substance are discussed and it is found that compounds of Cr^{2+} , Fe^{3+} , Ni^{2+} , and Gd^{3+} should be suitable. Diagrams and tables of maser properties of selected compounds are given ; on the basis of present knowledge a number of amplifying frequencies between 120 and 75,000 Mc/s should be available. The range of suitable compounds which has been studied is very small, and should be extended.

I. INTRODUCTION

A primary requirement of the three-level maser, which was stated by Bloembergen (1956) in his original proposal of the device, is that non-zero magnetic-dipole transition probabilities should exist between all three of the participating levels. This requirement is not fulfilled when the quantization of angular momentum is pure, since the selection rule $\Delta M = \pm 1$ applies. As a means of breaking down this selection rule, Bloembergen proposed that a paramagnetic salt possessing a Stark splitting due to its internal electric field should be subjected to a magnetic field inclined at an angle to the axis of the crystalline electric field. If the resulting Zeeman splittings are made comparable to the Stark splittings the quantization is very mixed and transitions may in general take place between all levels.

Use has been made of this principle, which one may call magnetic-field mixing, in a number of successful maser oscillators and amplifiers (for example, Scovil, Feher, and Seidel 1957; McWhorter and Meyer 1958).

In view of the great interest which has been aroused by the three-level maser it is surprising that no attention seems to have been paid to the possibility of realizing the device without using a magnetic field. It will be shown below that, among the paramagnetic substances already studied, there are several which provide the necessary transitions, between three levels, in zero magnetic field.

Such zero-field masers will not be tunable beyond the line width of the magnetic resonances involved, and so will hardly compete with magnetic-field masers where the profile of a naturally occurring radiation, such as the hydrogen line of radio astronomy, is to be studied. Nevertheless, zero-field masers possess some considerable advantages which may prove paramount in applications

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such as radar, communications, and high-sensitivity paramagnetic resonance experiments, where frequency, as such, is not important. The advantages are:

(1) The necessity for a magnet, which in magnetic-field masers has to fulfil exacting requirements of homogeneity, stability, and working space, is avoided.

(2) The orientation of the crystal loses its primary importance as an energydetermining factor. Thus large monocrystals of paramagnetic material will not be required; indeed powders could be used, so that unit filling factor could be achieved without difficulty.

(3) As a corollary of (2) it is possible to utilize differently oriented but otherwise equivalent paramagnetic centres in the crystal, whereas in a magneticfield maser only one type would, in general, be correctly oriented with respect to the field.

(4) Line broadening caused by inhomogeneity of the magnetic field, or of orientation of the crystal axes, is absent.

(5) A superconductor may be employed for the construction of the microwave circuits since no magnetic field is employed.

(6) Complicated or extended microwave structures, limited only by the requirement that they enter a Dewar vessel of reasonable size, may be used.

These advantages lead to great freedom in the design of masers. An attractive example is a travelling-wave maser consisting of a superconducting coaxial line filled with powdered paramagnetic and wound into a coil to permit convenient cooling of a considerable length.

In view of the advantages of zero-field masers we present a compilation of transition probabilities and frequencies calculated for a number of materials which, on the basis of present-day knowledge, are promising as working substances. The grounds for selection will also be given, and this will necessitate a consideration of maser and paramagnetic resonance theory.

II. THE THREE-LEVEL MASER

We refer at this point to Bloembergen's (1956) paper. Bloembergen considers a system with three energy levels $E_3 > E_2 > E_1$, to which is applied a strong microwave magnetic field at the frequency $v_{31} = (E_3 - E_1)/h$ and a weak field at the frequency $v_{32} = (E_3 - E_2)/h$. He gives an expression for the difference in population between levels for the case when all energy level differences are much less than kT. Preserving only terms of order $h\nu/kT$, we may ignore the distinction between w_{ii} and w_{ii} , thus obtaining

$$n_1 - n_2 = n_3 - n_2 = \frac{1}{3} \cdot \frac{hN}{kT} \cdot \frac{w_{21}v_{21} - w_{32}v_{32}}{w_{21} + w_{32} + W_{32}}.$$
 (1)

The notation is Bloembergen's: N is the number of paramagnetic centres, the w's are the thermally induced (relaxation) transition probabilities, W_{32} is the transition probability between the levels E_3 and E_2 due to the microwave field $H(v_{32})$, and T is the absolute temperature. Without loss of generality one may suppose that $w_{21}v_{21} > w_{32}v_{32}$, for, if not, the labels 1 and 3 can simply be reversed. Then $n_3 > n_2$, and stimulated emission occurs at the frequency v_{32} . The power emitted is

$$P_{\text{magn}} = \frac{Nh^2 v_{32} (w_{21} v_{21} - w_{32} v_{32}) W_{32}}{3kT (w_{21} + w_{32} + W_{32})}.$$
 (2)

We now wish to express W_{32} in terms of the exciting field $H(v_{32})$, the matrix element $\langle 2 | H.S | 3 \rangle$, and the width of the magnetic resonance line. At this point we depart from the nomenclature of Bloembergen and use the half-width at half-intensity Δv instead of the relaxation time T_2 . $(\Delta v = 1/(2\pi T_2).)$ Then the transition probability takes the form

$$W_{32} = \pi g^2 \beta^2 |\langle 3 | H.S | 2 \rangle|^2 / h^2 \Delta \nu = \pi g^2 \beta^2 H(\nu_{32})^2 |\langle 3 | S_H | 2 \rangle|^2 / h^2 \Delta \nu,$$
(3)

where g is the spectroscopic splitting factor, β the Bohr magneton, and S_H the projection of the spin operator in the direction of $H(v_{32})$.

Provided that the field $H(v_{32})$ is small, so that $W_{32} \ll w_{21} + w_{32}$, equation (2) shows that the power emitted is proportional to $H(v_{32})^2$. One may then define a magnetic quality factor Q_M by the equation

$$\frac{-1}{Q_M} = \frac{\text{power emitted per unit volume}}{2\pi v_{32} \times (\text{stored energy per unit volume})}.$$

This definition differs from that of Bloembergen in that unit volume of the paramagnetic is here considered, so that dependence on the volume of any conducting enclosure is avoided. We believe that this definition has the merit of embodying only properties characteristic of the paramagnetic material. Let the further stipulation be made that N shall be the number of paramagnetic centres per unit volume, so that equations (1) and (2) now refer to unit volume. Then

$$-\frac{1}{Q_{M}} = \frac{4\pi}{3kT} \cdot \frac{Ng^{2}\beta^{2} |\langle 3 | S_{H} | 2 \rangle|^{2}}{\Delta \nu} \cdot \frac{w_{21}\nu_{21} - w_{32}\nu_{32}}{w_{21} + w_{32}} \dots (4)$$

The concept of magnetic Q is of central importance in any discussion of circuit properties of practical maser amplifiers. In the case of the cavity maser, for example, McWhorter and Meyer (1958) have shown that, under reasonable practical circumstances,

$$G^{\frac{1}{2}}B \doteq 2\nu_{32} / |Q_{M}|, \qquad \dots \qquad (5)$$

where G is the power gain, and B is the bandwidth.

As a very different example we shall take a travelling wave coaxial-line structure operating in the principal (TEM) mode. The gain per unit length attributable to the magnetic material is

where Z_0 is the intrinsic impedance of the magnetic material, Z is the wave impedance of the filled coaxial line, and v is the group velocity of the wave in the filled coaxial line.

In both cases it is evident that the larger $1/|Q_M|$ the better the performance, and we shall therefore use it as a figure of merit of paramagnetic materials.

III. EXTENSION OF THE MASER EQUATION TO FOUR LEVELS AND EXTRAPOLATION TO MORE THAN FOUR LEVELS

The number of paramagnetics with precisely three levels is limited, and in fact the successful masers so far operated have used four or eight levels. In spite of this the equations of a multilevel maser do not appear to have been published. However, some estimate of the influence of extra levels is needed for the assessment of suitability of working substances.

For a four-level maser, we find that, with a natural extension of Bloembergen's notation, the equation analogous to equation (1) is

$$n_{3}-n_{2}=\frac{1}{4} \cdot \frac{hN}{kT} \cdot \frac{w_{4}(w_{21}\nu_{21}-w_{32}\nu_{32})+w_{24}(w_{14}\nu_{21}-w_{34}\nu_{32})}{w_{4}(w_{21}+w_{32})+w_{24}(w_{14}+w_{34})}, \dots (7)$$

where $w_4 \equiv w_{14} + w_{24} + w_{34}$.

If no relaxation transitions exist between the fourth level and the other three, i.e. $w_{14}=w_{24}=w_{34}=0$, the population difference n_3-n_2 turns out to be three-quarters of that given by equation (1), which accords with expectation since in this case only $\frac{3}{4}N$ centres are participating in the maser process. The same result is produced in quite a variety of circumstances: (i) if $w_{24}=0$; (ii) if $w_{14}=w_{34}=0$; (iii) if $w_{14}/w_{21}=w_{34}/w_{32}$; (iv) if all the w's are equal.

It may also be seen that the position of the fourth energy level is of no account. However, equation (7), like equation (1), rests on the assumption that all energy differences are small compared to kT.

Very little is at present known about the values of the relaxation frequencies w. We shall assume here that the effect of extra levels is simply to reduce the working population, so that for an x-level maser,

$$n_3 - n_2 = \frac{1}{x} \cdot \frac{hN}{kT} \cdot \frac{w_{21}v_{21} - w_{32}v_{32}}{w_{21} + w_{32}}.$$
 (8)

The figure of merit then takes the form (cf. equation (4))

$$-\frac{1}{Q_{M}} \doteq \frac{4\pi}{xkT} \cdot \frac{Ng^{2}\beta^{2} |\langle 3 | S_{H} | 2 \rangle|^{2}}{\Delta \nu} \cdot \frac{w_{21}\nu_{21} - w_{32}\nu_{32}}{w_{21} + w_{32}} \dots (9)$$

IV. REQUIREMENTS OF THE SPIN AND HAMILTONIAN FOR ZERO-FIELD MASERS

In this section we shall discuss what values of spin are required to give three or more energy levels in zero field, and what components must be present in the spin Hamiltonian to provide transitions between the levels. It will be assumed that the nuclear spin is zero; its influence when it is not zero will be discussed in Section VII.

Paramagnetic resonance results are customarily presented in terms of the spin Hamiltonian formalism of Pryce (1950). The ground states of the paramagnetic centres are described in terms of a spin S, and the spin Hamiltonian is a function of spin operators with semi-empirical parameters. Once these are known all paramagnetic properties may be calculated, including those relevant to masers. A particularly useful compilation of spin Hamiltonian parameters

has been given in the review article on paramagnetic resonance by Bowers and Owen (1955).

The number of independent states of an ion with spin S is 2S+1; but, by virtue of Kramers' theorem (1930), the number of distinct energy levels cannot exceed $S+\frac{1}{2}$ for integer-plus-a-half spins. For integer spin the number of levels may be 2S+1. In either case the full multiplicity allowed by Kramers' theorem may not be realized in crystal fields of high symmetry. Assuming low enough symmetry, the multiplicity is tabulated below as a function of spin:

Spin	••	1/2	1	3/2	2	5/2	3	7/2
Number of levels	• •	1	3	2	5	3	7	4
Example		Cu ²⁺	Ni^{2+}	$\mathbf{Cr^{3+}}$	Cr^{2+}	Fe^{3+}		Gd ³⁺

A spin higher than 7/2 is not expected to occur and no examples of spin 3 are known. It is seen that all values of spin except 1/2 and 3/2 are suitable for zero-field masers.

We come next to the required properties of the spin Hamiltonian. By far the commonest form of zero-field Hamiltonian, for $S > \frac{1}{2}$, is

$$\mathscr{H} = D\{S_z^2 - \frac{1}{3}S(S+1)\},$$
 (10)

where z is an axis of symmetry of the crystalline field. A zero-field maser is out of the question with this Hamiltonian. Since \mathscr{H} commutes with S_z the eigenstates of the energy are simultaneous eigenstates of S_z . The eigenvalues of the Hamiltonian are

where M is the eigenvalue of S_z . This gives a series of levels, in the order $M=0, M=\pm 1, M=\pm 2, \ldots$ for ions with integer spin and in the order $M=\pm 1/2, M=\pm 3/2, M=\pm 5/2, \ldots$ for those with integer-plus-a-half spin. The pumping transition for a maser, which must always be a leap-frog transition, that is, one spanning two energy intervals, would here require $\Delta M=\pm 2$. But this is forbidden since the states are pure eigenstates of S_z and the normal selection rule, $\Delta M=\pm 1$, applies.

Fortunately for the zero-field maser, the term in S_z^2 , equation (10), is quite frequently accompanied by other terms, though generally it remains predominant. The additional terms fall into two classes : those with axial symmetry, viz. S_z^4 and S_z^6 ; and those with lower symmetry. The axially symmetric terms make no improvement in the situation, for the Hamiltonian after their inclusion still commutes with S_z .

It is to the terms with lower symmetry—rhombic, trigonal, tetragonal, and hexagonal—that one must look in order to realize a zero-field maser. These terms are conventionally expressed as operator functions which transform under rotation in the same way as the spherical harmonics. Most of the terms met with in paramagnetic resonance are given in full in Bleaney and Stevens' (1953) review article (pp. 132, 137, and 150); it is invariably the case that a term with m-fold symmetry contains the operators S_{+}^{m} and S_{-}^{m} , where These terms do not commute with S_z , and therefore the eigenstates of the Hamiltonian are not pure eigenstates of S_z , and normal selection rules no longer apply.

In general one may say that any paramagnetic with spin other than 1/2 or 3/2, which has a spin Hamiltonian of rhombic, trigonal, tetragonal, or hexagonal symmetry, is a candidate for a zero-field maser.

There is one exception to the rule. This is the case of perfect cubic symmetry, which has the Hamiltonian (Bleaney and Stevens 1953, p. 137)

$$\mathscr{H}_{\text{cubic}} = \frac{1}{6}a\{S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2+3S-1)\}, \quad \dots \quad (\mathbf{13})$$

where a is a numerical coefficient. For all spins less than 3 this Hamiltonian gives fewer than three levels, and for S=3 and 7/2 the number of levels is three but the leap-frog transition probability turns out to be zero. It should be emphasized that this is true only of perfect cubic symmetry; $\mathscr{H}_{\text{cubic}}$ in conjunction with other operators has rhombic, trigonal, or tetragonal symmetry and the rule then applies.

V. LINE WIDTH AND ULTIMATE PERFORMANCE

The figure of merit, equation (9), depends on the line width $\Delta \nu$. In a zero-field maser three agencies can contribute to this : (1) the random magnetic fields of the nuclei of the diamagnetic neighbours of the paramagnetic centres; (2) a spread in the values of the spin Hamiltonian coefficients; (3) the fields of the paramagnetic centres themselves. In principle, (1) and (2) can be made small compared to (3) by choosing a host material in which the diamagnetic atoms have small nuclear moments and by obtaining a sufficiently perfect crystal structure. Then performance would depend only on the line width due to paramagnetic spin-spin interaction (3).

Kittel and Abrahams (1953) have calculated the line width for a dilute paramagnetic with a cubic lattice. With some adaptation of their result one obtains

$$\Delta \nu = 6g^2 \beta^2 N \sqrt{\{S(S+1)\}/h}. \quad \dots \quad (14)$$

We shall take this to be a fair indication of line width for any lattice, not merely cubic. Then the figure of merit becomes, using (9) and (14),

$$-\frac{1}{Q_M} \doteq \frac{2h(w_{21}v_{21}-w_{32}v_{32})|\langle 3|S_H|2\rangle|^2}{kkT(w_{21}+w_{32})\sqrt{\{S(S+1)\}}}.$$
 (15)

The value of $|\langle 3 | S_H | 2 \rangle|^2$ will be typically of the order of $(\frac{1}{4})S^2$; the number of distinct energy levels, x, is $S + \frac{1}{2}$ and 2S + 1 for integer-plus-a-half and integer spins respectively; thus to a rough approximation (15) is independent of spin. Making now the simplifying assumption that $w_{21} \sim w_{32}$, and $v_{21} \gg v_{32}$, one obtains for the figure of merit

$$-\frac{1}{Q_M} \sim h v_{21} / 4kT \qquad (16)$$

for integer-plus-a-half spin (Kramers degenerate ions). For integer spin the figure of merit is roughly halved.

It is interesting to compare (16), which should be valid for a magnetic-field maser as well as for a zero-field maser, with the results of McWhorter and Meyer (1958). In their experiment, $v_{21} \sim 6 \times 10^9$ c/s, T = 1.25 °K, and S = 3/2. After adjustment for the doubling of multiplicity brought about by the presence of the magnetic field our theory predicts $-1/Q_M \sim h v_{21}/8kT$ or 1/35. In fact the experimentally measured figure, derived from the quoted gain-bandwidth product, by the use of equation (5), was 1/3300, or about 100 times worse than the ultimate predicted. The factor of 100 is made up in the following way. (a) The filling factor of the sample in the cavity was only 10 per cent., which contributes a factor 10. (b) The line width (derived from the quoted value of 5×10^{-9} sec for T_2) was 30 Mc/s, whereas that attributable to paramagnetic spin-spin interaction in the working population of 10^{19} per cm³ was, according to equation (14), only 6 Mc/s. This contributes a factor 5. (c) The approximation made in deriving equation (18), namely, that $v_{21} \gg v_{32}$, is not justified; in fact $v_{32} \neq \frac{1}{2}v_{21}$, which contributes a factor 2. The product of these factors is 100. The closeness of this agreement is only accidental, considering the approximations made in deriving equation (16).

The significant conclusion from the above comparison is that it is desirable to increase the paramagnetic concentration, or reduce other sources of line width, until the paramagnetic spin-spin width is dominant. The former courseincreasing concentration—cannot necessarily be followed with impunity. For example, in their experiments with a 1400 Mc/s maser using dilute potassium chromicyanide, Autler and McAvoy (1958) found that, whereas $\frac{1}{2}$ per cent. crystals $(N \sim 10^{19})$ functioned successfully, 1 per cent. crystals did not. This fact may be understood in terms of the theory of Giordmaine et al. (1958). According to this theory, the phonon frequencies near the spin resonances are considerably broadened by interaction with the spins. The phonon width Δv_{L} is proportional to $N^{\frac{1}{9}}$, and, for a typical case, $\Delta \nu_L \sim 400$ Mc/s at $N = 10^{19}$. It follows that if the resonance at v_{31} is saturated, as in pumping a maser, the temperature of all phonons in the range $v_{a1} \pm \Delta v_L$ is raised and these will saturate in turn any other spin resonances which they overlap. It is clear that in this model maser action would not occur if $\Delta v_L > v_{32}$, for then the saturation of v_{31} would spread to v_{21} with the result that $n_1 = n_2 = n_3$. The same failure can occur even if $\Delta v_L < v_{32}$ because the lattice modes are not expected to show a sharp cut-off at $\nu \pm \Delta \nu_I$.

Since it may not be possible to increase paramagnetic concentration it is probable that the other course, of reducing the width due to diamagnetic neighbours, is the more promising. In most hydrated salts the protons in the water molecules cause a half-width of 20 Mc/s; by substituting heavy water this may be reduced to about 6 Mc/s (Bleaney and Stevens 1953, p. 119). By growing crystals which do not contain water of crystallization even greater improvements may be expected; for example, the diamagnetic neighbour width in dilute $K_3Cr(CN)_6$ crystals is only 3 Mc/s (Bowers 1952).

The other source of width—variation of spin Hamiltonian parameters is more obscure. For example, it was found by Bleaney and Trenam (1954) that among the diluted ferric alums the ammonium, potassium, and thallium sulphates did not give narrow lines, whereas the rubidium and methylamine sulphates and potassium selenate did.

More experimental data are needed concerning causes of line width in paramagnetic compounds. However, it is reasonable to expect that ways will be found to utilize the full potential figure of merit given by equation (16).

To demonstrate the implications of this equation one may propose an example of a cavity maser with a Kramers degenerate working substance (S=5/2 or 7/2) in which $\nu_{21}\sim 20000$ and $\nu_{31}\sim 3000 \text{ Mc/s}$, $T\sim 2 \,^{\circ}\text{K}$, $G\sim 30 \,\text{dB}$. From equations (5) and (16) the bandwidth would be 25 Mc/s. By contrast, the bandwidth so far achieved in a magnetic field maser at the same power gain is only 60 kc/s (McWhorter and Meyer 1958). The example shows that the present view of the maser as essentially a narrow-band device should be revised.

VI. RELAXATION TIMES

The relaxation times for transitions between the three levels affect both the pumping power requirements and the figure of merit of the maser. We shall discuss first the pumping power.

The power absorbed at saturation, P_a , may be found by adapting the treatment of Eschenfelder and Weidner (1953), giving

$$P_{a} = \frac{N(h\nu)^{2}w}{3kT} = \frac{N(h\nu)^{2}}{6kT} \cdot \frac{1}{\tau}, \qquad (17)$$

where w is the thermally induced (relaxation) transition probability between the two levels saturated, and τ is the associated spin-lattice relaxation time, which is equal to 1/(2w) (see, for example, Andrew 1955, p. 15). The power absorbed in pumping a maser is not correctly given, however, by direct substitution of v_{31} for v and w_{31} for w in equation (17) because the direct relaxations from level 3 to 1 are supplemented by those passing from 3 to 2 and thence to 1. From the Bloembergen equations we have derived the following general expression valid for three levels

where $\tau_{ii} = 1/(2w_{ii})$.

We now consider the desirable limitations on the relaxation times. We shall use an effective time $\tau = \{1/\tau_{31} + 1/(\tau_{21} + \tau_{32})\}^{-1}$; the experimental results available do not warrant a closer examination of the separate times.

The use of liquid helium temperatures is likely to be general since the figure of merit, equation (16), is inversely proportional to the absolute temperature. As a typical case, then, one may take $T \sim 1$, $N \sim 10^{19}$, $\nu_{31} \sim 10^{10}$, and x=4, whence the power absorbed is about $1/10\tau \text{ mW/cm}^3$. The volume of working substance will be some tens of cubic centimetres, so that $P_a \sim 1/\tau \text{ mW}$. Postulating an upper limit of 1 W, which would evaporate about a litre of liquid helium per hour, one is led to the requirement that τ be a millisecond or longer.

Relaxation times of the order of milliseconds have indeed been measured at liquid helium temperatures (Gorter 1947; Benzie and Cook 1950; Eschenfelder and Weidner 1953; Giodmaine *et al.* 1958). It appears to be generally the case that, if a paramagnetic has a long enough relaxation time at room temperature to give observable resonance lines, then it has a relaxation time longer than 1 msec at liquid helium temperatures. We shall therefore assume that to be suitable for a maser a paramagnetic must give observable resonance lines at room temperature.

As Bloembergen (1956) has remarked, the w's may be expected to reflect the Debye (v^2) phonon spectrum: if so, the figure of merit would contain $(v_{21}^3 - v_{32}^3)/(v_{21} + v_{32})$. Accordingly we shall assume, for the purpose of this paper, that even if v_{21} is only a few tens per cent. greater than v_{32} the substance is a reasonable candidate for a zero-field maser.

VII. INFLUENCE OF HYPERFINE STRUCTURE

If the nucleus of a paramagnetic centre has odd mass number it will possess angular momentum and magnetic moment. A magnetic interaction will exist between the nucleus and the paramagnetic electrons, to account for which the term

$$\mathscr{H}_{N} = A_{x}S_{x}I_{x} + A_{y}S_{y}I_{y} + A_{z}S_{z}I_{z} \quad \dots \quad (19)$$

must be added to the Hamiltonian, I_x , I_y , and I_z being the components of nuclear spin. An electric quadrupole interaction may also exist but is unimportant for the discussion in hand.

The effect of \mathscr{H}_N is to increase considerably the number of levels. With electronic spin S and nuclear spin I the number of independent states is (2S+1)(2I+1) and, although not all need correspond to distinct energy levels (see, for example, Fig. 8 of the paper by Bleaney and Ingram 1951), the number of levels, that is, x in equation (9), is often nearly an order of magnitude greater than the three required for maser action. The figure of merit is correspondingly reduced. Furthermore, hyperfine-structure masers, with their more closely spaced levels, are more likely to encounter the phonon-width trouble referred to in Section V.

For these reasons we do not regard hyperfine-structure masers as likely to be as important as fine-structure masers (masers with electronic splittings only). Nevertheless, hyperfine-structure masers merit some consideration because they hold the promise of extending the frequency coverage of zero-field masers. The energy splittings caused by \mathscr{H}_N range from A to $(I+\frac{1}{2})A$; A is typically a few hundred Mc/s, and I may be as great as 7/2. Thus the band of frequencies covered is typically from 100 to 1000 Mc/s. We shall give one example of a hyperfine-structure maser in Section XI.

VIII. ELIGIBLE IONS

Since it is our aim to focus attention only on the most promising working substances for zero-field masers, we shall now apply rather liberally the disqualifications implied by the preceding sections.

Paramagnetism has been observed in compounds of the five transition groups, the iron, palladium, rare earth, platinum, and actinide groups, which are associated with unpaired electrons in the 3d, 4d, 4f, 5d, and 5f shells respectively. We shall consider these groups in turn. Most of the available paramagnetic resonance data are collected together in the review article by Bowers and Owen (1955), to which we refer as B & O.

The most thoroughly investigated group is the 3*d*. Most ions in the group give observable spectra at room temperature so that only a few need be disqualified by the relaxation-time criterion, leaving as eligible the ions VO^{2+} , V^{2+} , Cr^{2+} , Mn^{2+} (but not $[Mn(CN)_6]^{4+}$), Fe^{3+} (but not $[Fe(CN)_6]^{3+}$), Ni^{2+} , and Cu^{2+} . Next, the disqualification of ions which possess a large proportion of isotopes with hyperfine structure removes VO^{2+} , V^{2+} , Mn^{2+} , and Cu^{2+} . Those remaining which possess spin 1/2 or 3/2 must be disqualified for providing too few levels : Cr^{3+} , with S=3/2 is thus rejected, leaving Cr^{2+} (S=2), Fe^{3+} (S=5/2), and Ni^{2+} (S=1).

The next group, the 4d group, provides rather few investigated compounds because chemical stability appears to go hand-in-hand with diamagnetic bonding. Of the compounds investigated, none have spin other than 1/2 or 3/2, so that the entire group is disqualified. The same applies to the 5d group (B & O, p. 355).

In the 4f or rare earth group relaxation times are generally very short and liquid hydrogen or helium temperatures have had to be employed in order to observe the spectra. The only ions giving observable spectra at room temperature are the iso-electronic Eu²⁺ and Gd³⁺, which have S=7/2. Eu²⁺ is disqualified by its large proportion of isotopes with hyperfine structure (B & O, p. 363). Gd³⁺ has 30 per cent. isotopes with nuclear spin, but the associated hyperfine structure is so small that it eluded for years attempts to resolve it (Low 1956). The four electronic energy levels of Gd³⁺ are each thus effectively single and provide a good basis for a zero-field maser.

In the 5f series the behaviour appears to resemble that in the 4f series (Bleaney 1955; Hutchison *et al.* 1956), so that very short relaxation times are to be expected. Bleaney (1955) has pointed out that the ions Am^{2+} , Cm^{3+} , and Bk^{4+} are expected to behave analogously to Gd^{3+} and Eu^{2+} , with reasonably long relaxation times. However, the expense of these elements and the destruction of crystal structure which their radiations will cause, make it doubtful that they, or any other actinides, will be attractive candidates for zero-field masers and accordingly we shall not consider them further.

It is seen that the promising working substances for zero-field masers are the compounds of no more than four ions : Cr^{2+} , Fe^{3+} , Ni^{2+} , and Gd^{3+} . These will be discussed in detail in Section X.

IX. TRANSITION PROBABILITIES

The transition probability, equation (3), may be expressed in terms of an effective magneton number for the transition p analogous to that used in the description of magnetic susceptibilities. p is defined by

The figure of merit then takes the form (cf. equation (9))

$$\frac{-1}{Q_M} = \frac{4\pi N \beta^2 p^2}{x k T \Delta \nu} \cdot \frac{w_{21} \nu_{21} - w_{32} \nu_{32}}{w_{21} + w_{32}} \dots \dots \dots \dots \dots \dots (21)$$

If lmn are the direction cosines of H with respect to the axes xyz of the spin Hamiltonian,

$$p^{2} = l^{2} p_{x}^{2} + m^{2} p_{y}^{2} + n^{2} p_{z}^{2}, \ldots \ldots \ldots \ldots (22)$$

where $p_x^2 = g^2 |\langle i | S_x | j \rangle|^2$, and so on.

It is illuminating to notice that, for a free electron spin with oscillating field applied perpendicular to a steady field, $p^2 = g^2 |\langle -\frac{1}{2} | S_x | \frac{1}{2} \rangle|^2 = 1$ since $g = 2 \cdot 00$. Hence, in general, p^2 denotes the strength of a transition in terms of that for a free spin having the same line width : in other words, p^2 is the strength in free-spin units.

For powdered salts p^2 must be averaged over all directions of H, giving

$$p_{Av}^2 = \frac{1}{3}(p_x^2 + p_y^2 + p_z^2).$$
 (23)

If the spectroscopic splitting factor g were anisotropic, equations (20) and (21) would require generalization; but for compounds suitable for masers it turns out that g is always nearly isotropic.

X. MASER PROPERTIES OF SELECTED COMPOUNDS

We shall now consider the suitability of those compounds of Cr^{2+} , Ni^{2+} , Fe^{3+} , and Gd^{3+} which have been studied by paramagnetic resonance. In many cases results have been observed at room temperatures, and the properties deduced from them must be taken only as an indication of what will apply at liquid helium temperatures.

Energies and eigenstates have been calculated from the spin Hamiltonian by standard methods. The eigenstates have been then used to calculate transition probabilities which in the diagrams that follow will be labelled by the value of $p^2 = l^2 p_x^2 + m^2 p_y^2 + n^2 p_z^2$ appropriate to the transition. The information in the diagrams will allow prediction of maser performance in case it should be desired to obtain optimum transition probabilities by mounting crystals of the working substance in a definite orientation in the oscillating fields.

It should be noted, however, that, when there are several differently oriented paramagnetic ions per unit cell of the crystal structure, it is not in general possible to mount crystals so as to use the most favourable component of p^2 for all ions : the spatial average p_{Av}^2 is then a useful guide to performance. Furthermore, one of the characteristic features of zero-field masers is the possibility they provide of using powdered material, which allows structural freedom and good filling factor. Therefore, in the tables of maser properties of specific compounds we shall quote the spatial average.

The ions Cr^{2+} and Ni^{2+} will be treated first. They both lack Kramers degeneracy and have larger splittings and probably shorter relaxation times than Fe^{3+} and Gd^{3+} which are Kramers degenerate.

$$Cr^{2+}: S = 2.$$

Only one compound, $CrSO_4.5H_2O$, has been studied (Ono *et al.* 1954). The results were obtained with undiluted crystals. There are two differently oriented ions per unit cell, each with the Hamiltonian

$$\mathscr{H} = D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2)$$
. (24)

The g-value is nearly isotropic and equal to $2 \cdot 0$. The energy levels are (B & O, p. 336): $E_1 = -2(D^2 + 3E^2)^{\frac{1}{2}}, E_2 = -D - 3E, E_3 = -D + 3E, E_4 = 2D$, and $E_5 = 2(D^2 + 3E^2)^{\frac{1}{2}}$. The transition probabilities are given in Figure 1.



Fig. 1.—Transition probabilities for Cr^{2+} in free-spin units with oscillating field in the direction (*lmn*). The numerical values of the energy for $CrSO_4.5H_2O$ at room temperature are given; g^2 is taken as 4. For meaning of D and E, see equation (24).

The frequencies and spatially averaged transition probabilities are given in Table 1.

From Table 1 it is evident that a very promising possibility exists for a maser amplifying at about 18,000 Mc/s. The higher modes, b and c, may become practicable in the future.

Salt	Temper- ature of Measure- ment (°K)	Pumping Frequency (Mc/s)	Pumping Probability for Powdered Salt (free-spin units)	Amplifying Frequency (Mc/s)	Amplifying Probability for Powdered Salt (free-spin units)	Difference Frequency (Mc/s)
$CrSO_4.5H_2O$	290	$\begin{array}{ccc} (a) & 77,000 \\ (b) & 270,000 \\ (c) & 270,000 \end{array}$	4 0.01 0.01	18,000 77,000 59,000	$1 \cdot 3$ 4 4	59,000 190,000 210,000
$\begin{array}{lll} K_2Ni(SO_4)_2.6H_2O & . \\ (NH_4)_2Ni(SO_4)_2.6H_2O \\ Tl_2Ni(SO_4)_2.6H_2O & . \\ (NH_4)_2Ni(S\Theta O_4)_2.6H_2O \\ NiSO_4.7H_2O & . \\ \end{array}$	290 90 290 90 290	115,000 75,000 80,000 76,000 150,000	$ \begin{array}{c} 1 \cdot 7 \\ 1 \cdot 7 \end{array} $	30,000 29,000 6,000 27,000 60,000	$ \begin{array}{r} 1 \cdot 7 \\ 1 \cdot 7 \\ $	85,000 46,000 74,000 49,000 90,000

TABLE 1 MASER PROPERTIES OF Cr²⁺ and Ni²⁺ salts

 $Ni^{2+}: S = 1.$

A number of nickel salts has been studied, and it has been found that where the crystalline environment has trigonal or higher symmetry the spin Hamiltonian provides only two distinct levels (Bleaney and Stevens 1953, p. 144) and so is useless for a zero-field maser. The majority of salts, however, are suitable, exhibiting rhombic symmetry with the same Hamiltonian as that of $CrSO_4.5H_2O$ given above. The *g*-value is nearly isotropic and equal to $2 \cdot 25$. The energies and transition probabilities are given in Figure 2.

Table 1 gives maser properties of suitable nickel salts (B & O, p. 350). The data refer to undiluted salts; dilution may alter the frequencies by 20 per cent. In the Tutton salts there are two, and in $NiSO_4.6H_2O$ four differently oriented ions per unit cell.



Fig. 2.—Energies and transition probabilities for Ni²⁺ assuming $g^2=5$. The transition probabilities are given in free-spin units and the oscillating field has the direction (lmn). For D and E, see equation (24).

It can be seen that a variety of amplifying frequencies is likely to be provided at liquid helium temperatures by nickel salts. The transition probabilities are substantial, being greater than the free-electron probability even for powdered salt.

That paramagnetic resonance has been observed in so few nickel salts is probably because the zero-field splittings for most salts are even greater than those in Table 1. These will constitute a reserve of maser materials for the future as the millimetre wave region develops.

$$Fe^{3+}: S = 5/2.$$

The behaviour of ferric salts hitherto studied is described by the spin Hamiltonian of Bleaney and Trenam (1954) which in zero field takes the form

where the coordinate system $\xi \eta \zeta$ refers to three mutually perpendicular axes with respect to which the z-axis is the (111) direction. Such a Hamiltonian is to be expected when the environment of the ion is predominantly cubic with cubic axes $\xi \eta \zeta$, with a superposed distortion along the (111) or z-direction such that the resulting symmetry is only trigonal with z as axis. The term in Fis usually of small influence. The term in a, or cubic term, has off-diagonal elements when expressed in the S_z -representation, as may be seen in the matrix given by Meijer (1951). These provide the leap-frog transitions which are necessary for zero-field maser action.

General formulae for the zero-field levels and eigenstates of the Hamiltonian (25) have been given by Bleaney and Trenam (1954). The energy levels are doublets at

$$E_{1,2} = \frac{1}{3}D - \frac{1}{2}(a-F) \pm \frac{1}{6} \{ (18D + a-F)^2 + 80a^2 \}^{\frac{1}{2}}, \\ E_3 = -\frac{2}{3}D + a-F, \}$$
 (26)

and the eigenstates involve trigonometric functions of an angle α defined by

$$\tan \alpha = a \sqrt{20} / \{9D + \frac{1}{2}(a - F)\}.$$
 (27)

From these eigenstates transition probabilities may be calculated, which we present for the general case in Figure 3. The g-value is isotropic and equal to $2 \cdot 00$.



Fig. 3.—Transition probabilities for Fe³⁺ in free-spin units with oscillating field in the direction (*lmn*), assuming $g^2=4$. The order of levels is appropriate to *D* positive and predominant. For $E_{1,2,3}$, α , and *D*, see equations (25), (26), and (27).

Although paramagnetic resonance has been observed in a wide variety of undiluted compounds (B & O, p. 342), the only compounds in which the spectrum of Fe³⁺ has been observed in diluted form (i.e. with high resolution) appear to be the alums (B & O, p. 342), the acetylacetonate (Jarrett 1957), MgO (Low 1957), and Al₂O₃ (sapphire) (Kornienko and Prokhorov 1957; Bogle and Symmons, paper in preparation).

Apart from MgO, where the Hamiltonian is purely cubic and need not be considered for a zero-field maser (Section IV), two classes of compounds may be distinguished.

The first class comprises the alums, except methylamine alum, and is characterized by comparable values of D and a, each being a few hundred Mc/s. This class is easy to pump and provides amplifying frequencies from 100 to 1000 Mc/s. The second class comprises methylamine alum, the acetylacetonate, and sapphire; in these compounds D is some thousands of Mc/s while aremains a few hundred. The pumping transition probability reduces to $(20/9)(a^2/D^2)\{n^2+\frac{1}{4}(l^2+m^2)\}$ for $a \ll D$, which shows that this class is difficult to pump. It provides amplifying frequencies of the order of 10,000 Mc/s.

The maser properties of the above-mentioned compounds are given in Table 2. The methylamine alum is omitted because the pumping probability turns out to be only 0.003 free-spin unit. The acetylacetonate is included in spite of there being no data on the size of a, because the presence of off-diagonal terms is indicated by the failure of the Hamiltonian $D\{S_z^2 - \frac{1}{3}S(S+1)\}$ to fit the measurements (Jarrett 1957).

The alums have four differently oriented ions per unit cell, the acetylacetonate two, and sapphire two.

MASER PROPERTIES OF DILUTE Fe ⁵⁺ AND GG ⁵⁺ COMPOUNDS								
Ion	Diluent	Temper- ature of Measure- ment (°K)	Pumping Frequency (Mc/s)	Pumping Probability for Powdered Material (free-spin units)	Amplifying Frequency (Mc/s)	Amplifying Probability for Powdered Material (free-spin units)	Dif- ference Fre- quency (Mc/s)	
Fe ³⁺ Fe ³⁺ Fe ³⁺ Gd ³⁺	$\begin{array}{rll} \mathrm{KAl}(\mathrm{SeO}_4)_2.12\mathrm{H}_2\mathrm{O}\\ \mathrm{Sapphire} & . & .\\ \mathrm{Cobalt} & \mathrm{acetyl-}\\ \mathrm{acetonate} & . & .\\ \mathrm{Sm}_2(\mathrm{SO}_4)_3.8\mathrm{H}_2\mathrm{O} \end{array}$	20 4 290 290	2,475 $31,300$ $17,000$ (a) 14,760 (b) 25,040 (c) 17,670	$ \begin{array}{c} 0.95 \\ 0.02 \\ \\ 2.4 \\ 0.04 \\ 0.04 \end{array} $	1,020 12,030 6,000 7,370 10,280 7,390	3·4 5·3 5 17 5 8	1,455 19,270 11,000 7,390 14,760 10,280	
			(0) 17,070	0.04	1,590	0	10,280	

Table 2 maser properties of dilute Fe^{3+} and Gd^{3+} compounds

$Gd^{3+}: S = 7/2.$

The general form of the spin Hamiltonian for gadolinium salts is given by B & O, p. 364. Recasting the Hamiltonian in terms of the *b*-coefficients, which are normally used to express experimental results, one obtains

The operators P_6^0 and P_6^0 are rather complicated functions of S_z which are given explicitly by Elliott and Stevens (1953). The only case known not to be described by equation (28) is Gd³⁺ in CaF₂, which has been studied by Ryter (1957). Here the Hamiltonian has cubic symmetry and so does not provide a basis for a zero-field maser (see Section IV).

The dominant term in the Hamiltonian, except for cubic symmetry, is always the first, just as in the case of most iron group compounds. (D of

equation (10) has the same meaning as b_2^0 of (28).) The energy levels are thus approximately those of $b_2^0(S_z^2 - \frac{1}{3}S(S+1))$ acting alone, that is, $-5b_2^0$, $-3b_2^0$, b_2^0 , and $7b_2^0$, so that the possible maser amplifier frequencies are about $2b_2^0$ and $4b_2^0$.

The Hamiltonian of equation (28) presents a generality not found in nature : in compounds so far studied it possesses either hexagonal symmetry, in which case $b_2^2=0$, or else rhombic symmetry, in which case $b_6^6=0$. Nevertheless, no misunderstanding need arise if the energy levels are written down as if all terms in (28) were simultaneously present. With the assumption that b_2^0 is the dominant term, the levels are given by the following equations, which are correct to the second degree in b_2^2 and b_6^6 :

$$E(\pm 7/2) = 7b_2^0 + 7b_4^0 + b_6^0 + (7/30)(b_2^2)^2/b_2^0 + (2/21)(b_6^6)^2/b_2^0),$$

$$E(\pm 5/2) = b_2^0 - 13b_4^0 - 5b_6^0 + (5/6)(b_2^2)^2/b_2^0 - (2/21)(b_6^6)^2/b_2^0,$$

$$E(\pm 3/2) = -3b_2^0 - 3b_4^0 + 9b_6^0 + (31/10)(b_2^2)^2/b_2^0,$$

$$E(\pm 1/2) = -5b_2^0 + 9b_4^0 - 5b_6^0 - (25/6)(b_2^2)^2/b_2^0.$$
(29)

The above expressions, except for the term in $(b_6^6)^2$, have in effect been given by B & O, pp. 365 and 368. Although the term in $(b_6^6)^2$ is unimportant for compounds studied hitherto we have included it for the sake of compounds which may be studied in the future.

When one comes to consider transition probabilities it proves desirable, for clarity, to present separate diagrams for the hexagonal and rhombic classes. This is done in Figures 4 and 5 respectively.

Class I. Gd³⁺ with hexagonal Hamiltonian

The only diluted compounds in this class which appear to have been studied in detail are the ethyl sulphate and double nitrate (B & O, p. 367) and the anhydrous chloride (Hutchison, Judd, and Pope 1957). In these salts the pumping transition probabilities are very small, namely, 3×10^{-6} , 6×10^{-5} , and 4×10^{-5} that of a free spin respectively. It is doubtful whether they will ever find application in a zero-field maser and we shall not consider them further.

Class II. Gd³⁺ with rhombic Hamiltonian

The only representative of this class for which data are available appears to be the sulphate octohydrate, which has been studied at room temperature with the corresponding samarium salt as diluent (B & O, p. 367). In this salt $r \equiv b_2^2/b_2^0 \equiv 0.60$, which is by no means small compared to unity. Consequently the energies and the transition probabilities are not given with sufficient accuracy by equation (29) and Figure 4. We have solved the problem numerically in order to obtain the results shown in Figure 6.

Table 2 shows that several possible pumping and amplifying frequencies exist, with substantial transition probabilities. To demonstrate this variety, which is a feature of Gd^{3+} in a rhombic environment, is the main purpose of the entry; no great credence is to be attached to the actual magnitudes since (1) on cooling to liquid helium temperatures b_2^0 may be expected, by analogy with the ethylsulphate (Bleaney *et al.* 1951), to change by about 10 per cent., with the other *b*'s not necessarily changing in proportion; and (2) the diluent will have to be changed from paramagnetic samarium to diamagnetic yttrium. Lanthanum sulphate does not crystallize isomorphously with the gadolinium salt; yttrium sulphate does so, and the Gd^{3+} spectrum has been qualitatively observed in this diluent (Bogle, unpublished data).



Fig. 4.—Transition probabilities in free-spin units for Gd^{2+} with a hexagonal Hamiltonian and with oscillating field in the direction (lmn). g^2 is taken as equal to 4. For b_6^6 and b_2^0 , see equation (28). The order of levels is appropriate to b_2^0 positive and dominant.



Fig. 5.—Transition probabilities in free-spin units for Gd^{3+} with a rhombic Hamiltonian and with oscillating field in the direction (lmn). g^2 is taken as equal to 4. $r=b_2^2/b_2^0$; for b_2^2 and b_2^0 , see equation (28). The order of levels is appropriate to b_2^0 positive and dominant.

The conclusion to be drawn from the foregoing discussion is that gadolinium compounds with low symmetry are the most promising for zero-field masers. These have been neglected in the past, probably because both the presence of off-diagonal elements in the Hamiltonian and the frequent occurrence of several directionally inequivalent ions per unit cell have rendered analysis difficult. Some information is already available about the nitrate (Bleaney *et al.* 1951) and the chloride hexahydrate (Dieke and Leopold 1957) which suggests that they will be suitable working substances, with frequencies of similar order to those of the sulphate octohydrate. It can hardly be doubted that a wealth of gadolinium compounds of low symmetry awaits investigation.



Fig. 6.—Energies and transition probabilities for Gd^{3+} in $Sm_2(SO_4)_3.8H_2O$ at 290 °K. The transition probabilities are averages for a powdered sample and are expressed in free-spin units.

XI. AN EXAMPLE OF A HYPERFINE-STRUCTURE MASER

Ions satisfying the relaxation-time criterion (Section VI) and possessing a large proportion of isotopes with nuclear spin are (B & O, pp. 334, 363) V²⁺, Mn^{2+} , Cu^{2+} , and Eu^{3+} . We choose for our example $(NH_4)_2Mn(SO_4)_2.6H_2O$ diluted with the corresponding zinc salt, which has been thoroughly investigated at 20 °K by Bleaney and Ingram (1951).

Manganese consists entirely of isotope 55 with nuclear spin equal to 5/2; the hyperfine-structure coupling is practically isotropic so that in zero field the Hamiltonian is (neglecting a small cubic term)

$$\mathscr{H} = D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) + AS.I.$$
 (30)

The electronic spin S is 5/2. The values of the parameters are : D=830, E=150, and A=-280 Mc/s. Because the parameters are all of comparable magnitude the quantization is very mixed and the calculation of the energy levels and eigenstates can only be effected by numerical methods. The energy levels are given numerically by Bleaney and Ingram (Fig. 8 of their paper); it may be seen that they extend in a series from 0 to 8500 Mc/s with gaps averaging 400 Mc/s and nowhere exceeding 900 Mc/s.

Expressing transition probabilities in free-spin units as before, one may say that a series of pumping frequencies exists between 4500 and 8500 Mc/s with probabilities of order $(E/D)^2$ or 0.03, and amplifying frequencies between 60 Mc/s and 2000 Mc/s with probabilities of order unity. If a non-resonant microwave structure were used, the salt would provide amplification at 2220, 2160, 2040, 1980, 1920, 1440, 1200, 720, 600, 480, 180, 120 Mc/s, the pumping frequency being required to vary only from 8500 to 7000 Mc/s.

ZERO-FIELD MASERS

XII. CONCLUSION

The important fact which has emerged from the search for zero-field maser materials is that even with the few compounds of the eligible ions Cr^{2+} , Fe^{3+} , Ni^{2+} , and Gd^{3+} which have been studied a wide range of frequencies should be available. That the number of known suitable compounds is not greater is simply a consequence of the fact that attention in the past has been concentrated on compounds with properties either inessential or detrimental to zero-field maser action : namely, compounds easily obtainable as large crystals ; likely to lead to the discovery of nuclear spins ; possessing few inequivalent ions ; or characterized by a simple spin Hamiltonian.

There is need for systematic research into that great majority of compounds of the ions named which is as yet untouched. Much of the work may be best pioneered by the classical cavity-resonator technique (fixed frequency and variable magnetic field). The loss of sensitivity occasioned by the necessity, where it exists, to use small crystals should be offset by application of the modern technique of high-frequency field modulation which has proved so simple and sensitive (see, for example, Buckmaster and Scovil 1956; Llewellyn 1957). At the same time direct measurements at zero-field will be needed, since the work of Bleaney, Scovil, and Trenam (1954), one of the few examples of zero-field measurements, has shown that the spin Hamiltonian which fits measurements at fixed frequency and variable field may not correctly predict the zero-field levels. In the case of dilute gadolinium ethyl sulphate the discrepancy amounted to 7 per cent. or 100 Mc/s. The theoretical basis of this anomaly is not yet understood and more experimental data on zero-field splittings are desirable for the solution of this problem as well as for maser design.

When data become available for a large proportion of the stable compounds of suitable ions, it is possible that zero-field masers will be able to supersede magnetic-field masers in the majority of applications.

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